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Anion – anion interactions: their nature, energy and role in crystal formation

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Abstract. Theoretical and experimental data array confirming the possibility of occurrence of bonding interactions in a crystal between like-charged species, namely anions, that contribute significantly to the crystal packing formation is analyzed. The main types of anion – anion interactions, their strength and contribution to the stabilization of ionic crystals are systematically analyzed for a wide range of organic and inorganic salts. The potential of various theoretical and experimental methods of investigations aimed at detection of anion – anion interactions and estimation of their energy is discussed. The bibliography includes 142 references.

I. Introduction

According to classical concepts of theoretical chemistry, the ionic crystals are built owing to bonding cation – anion (CA) interactions only, and any contacts between like-charged species [cation – cation (CC) or anion – anion (AA)] in a crystal are either absent or repulsive. The proximity of anions (for instance, in highly symmetric crystals of alkali halides) can be explained by the formation of close packing, *i.e.*, small cations force large anions to come in contact with each other.[1] However, in the case of the salts with bulky ions, even on the basis of the geometrical criteria of detecting bonding interactions (shortened contacts, definite orientation of anions in respect of each other[2]) alone, one can suggest the presence of AA association in the condensed state. These associates not only possess the same geometrical characteristics[2] as the CA pairs, but also have similar spectral properties[3] (for instance, luminescence[3,4]). Furthermore, 'self-assembly' of monoanions of dicarboxylic acids through hydrogen bonds is regarded as the widespread phenomenon, and analogous interactions in the case of aqueous systems of inorganic acids play an important role in biological objects.[5] Nevertheless, most investigators consider these interactions between anions exclusively repulsive and explain the proximity of anions in a crystal by 'contracting effect' of the CA bonds. Such point of view is based on the results of theoretical investigations of isolated AA associates according to which the latter are unstable in the gas phase.[2] It is known, however, that quantum chemical calculations, especially those within the widely used density functional theory, poorly describe the dispersion interactions.[6–8] Furthermore, the quantum chemical investigations of the AA association in the absence of counterions may lead to *a priori* incorrect results, because both the polyanionic and polycationic clusters in the isolated state are not 'realistic' systems[9] due to the high uncompensated charge.

To date, there is only a small number of methods that allow detecting the formation of AA pairs in the condensed state. Thus the similarity of spectral properties of the CC or AA associates and those of the energetically stable ionic pairs makes it possible to use electronic absorption spectroscopy for their detection. This approach was successfully applied for distinguishing bonding CC interactions in various actinide salts containing AnO_2^+ and AnO_2^{2+} groups linked by the An···O bonds.[10] In all cases, such bonding manifested itself as a bathochromic shift in the electronic absorption spectra (EAS) of crystals relative to the spectra of solutions, and the value of this shift depended on the number of the CC interactions in the crystal as well as on the type of the resulting associate. Similarly, the presence of an additional charge transfer band in EAS of solutions containing the hexacyanoferrate anion together with a nucleophilic ion such as I^-, $S_2O_3^{2-}$, and the like[11] was indicative of the AA pairing. The possibility of occurrence of bonding interactions between like-charged species (atoms) was also confirmed by the IR[10] and NMR data.[12] All these methods, however, provide the information on the AA(CC) interactions only on the qualitative level. The proof of the possibility of their occurrence and the estima-

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tion of their strength is possible only on the basis of the topological analysis of the experimental electron density function $\rho(\mathbf{r})$ in a crystal within Bader's 'Atoms in Molecules' theory (AIM).[13] This approach allows one to unambiguously distinguish the bonding interactions from the whole body of contacts regardless of the nature of species involved in their formation as well as to estimate their energy (by means of the correlation scheme proposed by Espinosa *et al.*[14,15]) on the basis of the X-ray diffraction data. A series of this kind of studies that appeared in the recent years made it possibile to perform the systematic analysis of bonding interactions between the like-charged species, mainly between the anions, and to undertake an attempt to add the newer data on the AA association into the whole picture of interactions between species in crystals. In particular, the aim of the present review is to systematically analyze the data on the occurrence of the AA interactions in the crystals of a wide range of organic and inorganic salts, to estimate their strength and role in the stabilization of ionic systems, and to compare the peculiarities of the AA interactions found by means of the topological analysis of the experimental and/or theoretical electron density distribution function with the data for crystals and solutions obtained using various theoretical and experimental methods.

II. Investigations of interactions between like-charged ions: from a geometrical approach to the electron density analysis.

To date, there is no consensus in the literature on the existence of bonding interactions between the like-charged species. On the one hand, the AA interactions such as $O-H\cdots O^-$ in the salts of certain acids (for instance, $KHCO_3$ or KHC_2O_4) are regarded as strong hydrogen bonds, because they are directional and the corresponding distances between the proton donor and acceptor (for instance, O···O 2.522 Å in the crystal of KHC_2O_4) appeared to be even smaller than those for the classical hydrogen bonds.[2] From another point of view based on the idea that the interactions between the ions with the same sign of charge *a priori* destabilize the system, this association of anions is forced. At the same time, using a simple geometric approach (a comparison of interatomic distances with the corresponding van-der-Waals radii) one can locate in most cases the shortened contacts between the anions. Moreover, it was shown [16–20] that this type of contacts can play the key role in the formation of crystal structure, *i.e.*, cause the formation of a certain supramolecular architecture.

For example, in the crystals of a wide range of 2,5-diazabicyclo[2.2.2]octane-3,6-dione (DBO) and 3,7-diazabicyclo[3.1.1]nonane-2,6-dione (DBND) derivatives,[21] the molecules are assembled into H-bonded heterochiral zigzag tapes [N···O 2.533(4)–2.748(5) Å], which are nearly independent of the nature of the substituent. Such a supramolecular motif also persists in the case of ionic systems. Thus according to the results of X-ray diffraction of tetrahydrates of potassium (acid salt), strontium, calcium, and cobalt 3,6-dioxo-2,5-diazabicyclo[2.2.2]octane-1,4-dicarboxylates (DBOD),[22] the packing of the DBOD and DBND dianions remains unchanged. In the structures of the above-mentioned salts (Fig. 1), the dianions are also assembled into the H-bonded zigzag chains with the distance between the proton donor and acceptor [N···O 2.854(4)–3.042(5) Å] exceeding is only slightly that in the neutral DBO and DBND. The mutual arrangement of these associates also persists; the distance between the chains varies from 5.49 Å in potassium DBOD to 6.12 Å in the strontium salt. Furthermore, even the incorporation of a bulky cation such as Sr^{2+} does not lead to the breakdown of the H-bonded framework but rather to weakening of the $N-H\cdots O$ bonds between the dianions. Thus, the driving force of the supramolecular organization in the crystals of the examined salts is not the interactions between the oppositely charged species but the hydrogen bonds between the anions. The formation of such extremely stable supramolecular motifs can be the basis for the design of, for instance, liquid crystal materials using this class of compounds.[21,22]

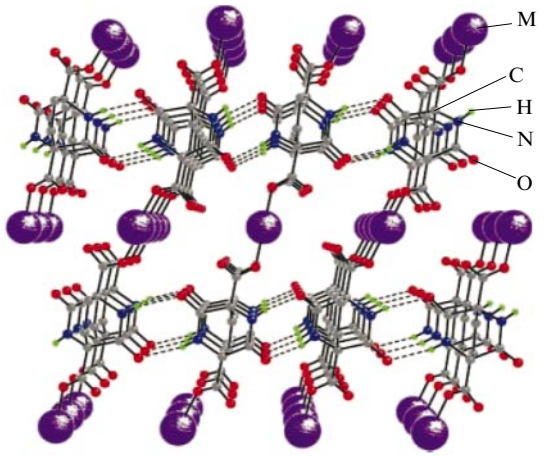
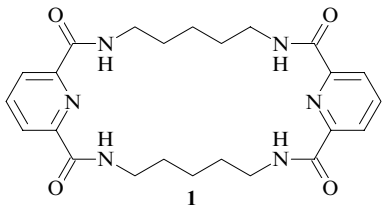


Figure 1. Zigzag chains in the crystals of H-bonded dianions of a series of tetrahydrates of DBOD salts.[22]
M is a metal ion.

Similarly, in the crystal of the complex of macrocyclic tetraamide receptor **1** with $PhCOO^-(NBu^n_4)^+$, the interactions between the anions lead to the formation of the supramolecular architecture,[23] which has earlier been observed only for the alkali metal complexes with crown ethers.[24]



1

This compound is the first example of the crystal structure in which the receptor molecules are packed in such a way that the channels filled with the benzoate anions are formed. The latter are assembled into chains in a 'head-to-tail' manner by means of a bifurcate bond $C-H\cdots A^-$ ($A^- = PhCOO^-$) between the hydrogen atom in the *para*-position of the benzene ring and both oxygen atoms of the carboxylate group of the adjacent anion (Fig. 2). The distances between the proton donor and acceptor (C···O) are 3.17 and 3.35 Å, and the hydrogen atom significantly deviates from the plane of the aromatic ring (~0.17 Å) in the direction of the atoms O(1) and O(2). Therefore, the conclusion has been made that this is the AA association that causes the formation of the channels by the receptor

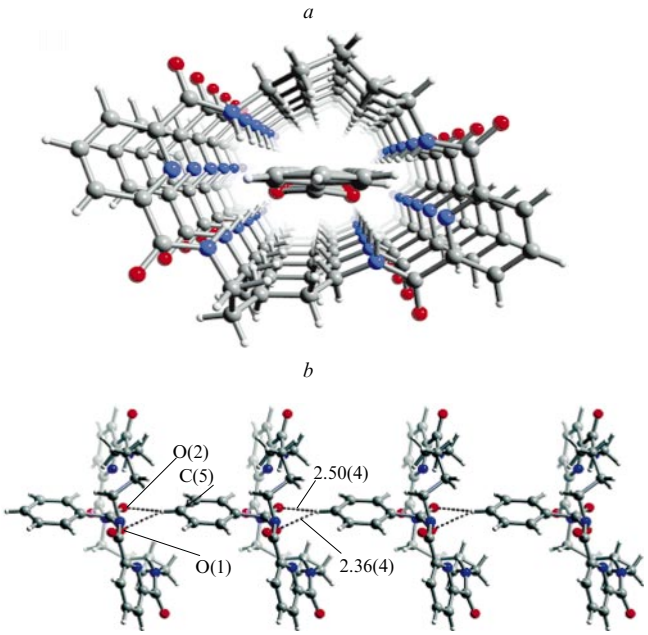


Figure 2. A fragment of the crystal packing of the complex of receptor **1** with $PhCOO^-(NBu^n_4)^+$ demonstrating the formation of channels filled with anions (*a*) and its view in the perpendicular projection (*b*).[23]

molecules and, as a result, can serve as a promising approach to the template synthesis in supramolecular chemistry of anions. Numerous investigators working in the field of crystal engineering, including targeted design of interlocked materials,[25] development of ion-electronic devices,[26] and anion recognition,[27] hold the same point of view.

At the same time, quantum chemical calculations using HF/6-31+G(2d,2p) and B3LYP/6-31+G(2d,2p) showed, by the example of potassium hydrogen oxalate, that the analogous hydrogen bonds $O-H\cdots O^-$ are not hydrogen bonds in the classical notion of this term.[2] Such 'pseudo-hydrogen' bonds were identified as tugboat interactions that do not stabilize a system, but only minimize the AA repulsion. In the crystal of the compound chosen as a model, the $HC_2O_4^-$ anions are assembled in chains (Fig. 3) with the distance O···O equal to 2.522 Å, and the crystal packing involves alternating corrugated layers formed by the K^+ ions and anionic chains. The calculation of the

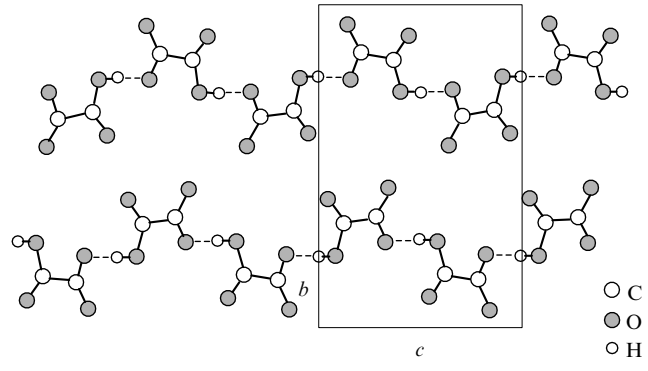


Figure 3. Hydrogen-bonded chains of the anions $HC_2O_4^-$ in the crystal of potassium hydrogen oxalate.[2]

interaction energy for two ions $HC_2O_4^-$ with retention of the experimental geometry suggests that the anions repel each other.[2] The stability of the AA chains in the crystal is attributed exclusively to the presence of the K^+ cations, which is confirmed by the results of the calculation of the species $K_2(HC_2O_4)_2$, which does not dissociate into separate ions. This shows that the CA interactions compensate for the electrostatic repulsion between the anions, and the chain structure present in the crystals, apparently, characterized by the least repulsion. On the basis of the data obtained it was concluded that the contacts $O-H\cdots O^-$ do not link the anions, but only organize them in space. At the same time, the importance of AA associates formed by means of such 'pseudo-hydrogen' bonds as supramolecular building blocks, for instance, for the synthesis of organic conductors and superconductors,[28] is not denied.

IR spectroscopy and electronic absorption spectroscopy are widely used to study weak contacts in molecular clusters.[29] The value of these methods for the investigation of interactions between the like-charged species was demonstrated by the example of crystalline actinide compounds where mutual coordination of cations AnO_2^+ or AnO_2^{2+} is observed through the bridged oxygen atom.[10,30] These CC contacts can easily be identified by the simple analysis of geometric parameters obtained from the X-ray diffraction data. The occurrence of interactions $AnO_2^+\cdots AnO_2^+$ also manifests itself in the corresponding IR spectra and EAS: in the case of direct interaction between the cations AnO_2^+, the maximum of the absorption band for the crystals is significantly shifted towards the long-wave region as compared with that for the solution by a value that depends on the character of the CC contacts. As noted in a review,[10] the occurrence of the CC interactions is common to crystals of Np^V, U^V and, probably, Pu^V and Am^V salts; such interactions often act as a factor determining the crystal structure. The occurrence of the CC interactions affects the behaviour of actinide salts upon dissolution and crystallization and also the rate of some of their redox reactions.[10] Such specific complex formation was also observed in the corresponding solutions.[11]

Moreover, the authors of one of the recent reports devoted to the investigation of interactions $UO_2^+\cdots UO_2^+$ in polynuclear uranyl complexes[31] succeeded, for the first time, to locate stable cationic associates in solution by means of NMR spectroscopy. The formation of these associates was also manifested in the presence of antiferromagnetic coupling between the uranium ions occurring as a superexchange through the oxo-bridges involved in the bonding. A similar situation was observed in the crystal of coordination polymer Cu_2(2,5-dmpz)Br_2 (dmpz is dimethylpyrazine).[32] In this case, however, the magnetic exchange coupling could be attributed to the through-space interaction between neighbouring polymer chains rather than to the through-bond interaction $-Cu-Br\cdots Br-Cu-$. The strength of this interaction, which is unusually high for this type of interactions, shows the potential of its use for construction of novel magnetic materials.[32]

The analysis of the EAS for solutions of salts with cobalt and iron octahedral low-spin complexes as the complex anions[11,33] also allowed detecting the formation of the AA associates. The existence of the latter, as it was shown by the example of the salt Li_3AlN_2, resulted from charge transfer that can occur between the like-charged species and is similar to that between a cation and an anion.[34] Similar charge transfer between cobalt and iron complex

anions [11,33] manifested itself as an additional broad band in the visible-IR and near-IR regions. In the framework of the electrostatic theory of interionic interactions, it was shown [11] that the association of the like-charged species is the most favourable in the case of bulky ions bearing small charge, polar solvents, and high ionic strength of the solution. Under these circumstances, the AA association is a particular case of ion association, and the main difference between these associates and CA pairs is that the former are less stable and can be observed only in the spectra of concentrated aqueous solutions of electrolytes. The possibility of existence of the AA associates was explained [11] by the presence of one or more cations around the interacting anions because of which the Coulomb interactions are no longer the determining factor and the ion size starts playing the key role.

Therefore, the electronic absorption spectroscopy and IR-spectroscopy allow not only detection the CC or AA interactions in a crystal or a solution, but also their analysis on a qualitative level, in particular determination of the character of the resulting supramolecular associate and, probably, comparison of the relative strength of these interactions. On the other hand, these methods do not provide the direct estimates of the energy of the CC or AA interactions, as the value of the shift is significantly affected by the type of aggregation. Another problem is that the spectra obtained for the liquid phase are to be compared with those for the solid phase and the results obtained are to be correlated with the structural data to additionally confirm the assumptions made. Information thus obtained seems to prove the possibility of occurrence of bonding interactions between the like-charged ions in real systems, although this conclusion is inconsistent with the 'chemical logic' and with the results of quantum chemical calculations of the isolated AA or CC associates. However, it is calculations that serve as a basis for some authors to state that the presence, in a solution or a crystal, of the CC or AA contacts that have the properties of chemical bonds (for instance, luminescence, *i.e.*, the shift of a band in EAS) does not necessarily result from the bonding character of the interactions between them.[35]

Thus it was shown [3,36] that these properties in the frozen solutions of $[Au(C(NHMe)_2)_2]^+$ and $TCNE^-$ (TCNE is tetracyanoethylene) result from the formation of energetically stable associates of the $(cation)_2(solvent)_m$ and $(anion)_2(solvent)_n$ types where the interactions of the solvate molecules with the corresponding ions cause the latter to approach each other and, as a consequence, lead to the non-zero overlap of their orbitals. In the case of the dimers $[Au(C(NHMe)_2)_2]^+$, the d_{z^2}-orbitals of the gold atoms overlap, this being considered by some authors as a manifestation of the aurophilic bonding interactions.[37–39] Moreover, similar in itself interactions between the cations were found in numerous crystalline alkaline earth and rare earth salts (see the review [40] and references cited therein).

It is believed [3,36] that such interactions are, however, forced in nature and the existence of the dimers $[Au(C(NHMe)_2)_2]^+ - [Au(C(NHMe)_2)_2]^+$ and $TCNE^- - TCNE^-$ in the corresponding ionic crystals results exclusively from the stabilization owing to the interactions with the counterions. The Hartree–Fock and MP2 calculations of the isolated dimers $[Au(C(NHMe)_2)_2]_2^{2+}$ and $(TCNE)_2^{2-}$ and the clusters of $(cation)_2(acetone)_m$ and $(anion)_2(dichloromethane)_n$ types demonstrated the 'destabilizing' character of the AA associates in the absence of a solvent molecule and the stability of the system in the case of m and n amounting to 4 and 6.[3,36] Similarly, on the basis of the results of the calculations of the isolated dimers $[TTF]_2^{2+}$ (TTF is tetrathiafulvalene),[41] and their clusters $[TTF]_2(anion)_2$ and $[TTF]_2(solvent)_2$, it was concluded that the formation of such CC associates is forced by the CA interactions. On the other hand, it is well known that, for instance, the radical anions $TCNE^-$ in the corresponding crystals form dimers with the distance C···C equal to 2.83–3.09 Å, which is nearly independent of the nature of the counterion. A recent investigation of the tetracyanoethylene salt $[MeNC_5H_5]_2[TCNE]_2$ in the crystalline state [42] also did not confirm the assumptions that the existence of the dianion $(TCNE)_2^{2-}$ is caused exclusively by the 'contracting' effect of the CA interactions. Moreover, the energy diagram of orbitals [3,36] (Fig. 4) for the formation of the AA pair in solution does not differ from that for the stable dimers the chemical bonding in which is unquestionable. This similarity causes the AA and CC dimers to have similar luminescence and some other properties.[3,4,42]

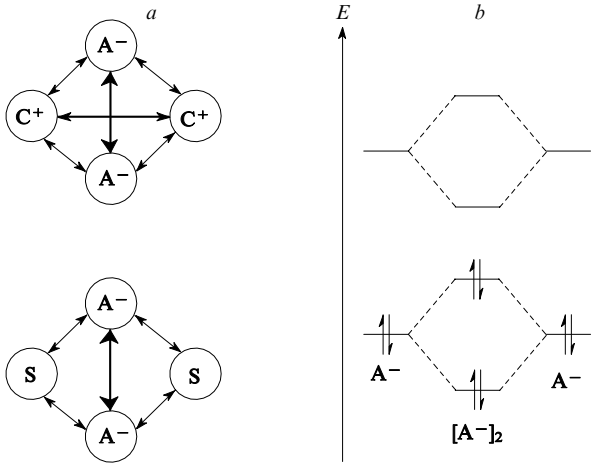


Figure 4. A schematic representation of the tetramers $(anion)_2(cation)_2$ and $(anion)_2(solvent)_2$ (*a*) and the diagram of HOMO and LUMO for $[A^-]_2$ (*b*).[3]
In the tetramers, thin double-ended arrows correspond to attraction, thick ones correspond to repulsion.

In spite of experimental evidence of the occurrence of the AA interactions, the results of quantum chemical calculations of isolated associates, which are hardy correct in the case of the CC or AA interactions, are thought to be more important than the peculiarities of EAS and IR spectra observed experimentally.[3,43] Moreover, the statement that there is no such a bonding is based only on the instability of a hypothetical CC or AA associate,[2–5,44,45] which has nothing to do with the reality.[3] The results of the calculation of such a cluster with an uncompensated charge that neglect totally the effect of counterions on the species under study will not agree, in general, with the differences observed in EAS and IR spectra of the compounds with the CC or AA bonds and of those without them.[10]

In addition to the investigation of the AA and CC bonding in salts with bulky ions, the occurrence of such interactions was also examined in the case of 'point' ions, for instance, of halide anions (X^-) in aqueous solutions of alkali halides. Two methods are described that are widely

used to investigate the $X^-\cdots X^-$ interactions, *viz.*, the neutron diffraction with isotopic substitution and the *ab initio* quantum chemical calculations. It is of interest that in both cases the results of investigations prove the possibility of the existence of stable aggregates X_2^{2-} in solutions of the salts MX (M is an alkali metal). Thus the AA pairs with the distance between the ions Cl^- equal to 4.2 Å were detected by neutron diffraction in a concentrated solution of lithium chloride.[46] Presumably, the stabilization of the Cl_2^{2-} pair is achieved owing to the presence of both water molecules that link the neighbouring anions and the Li^+ ions. At the same time, in the solution of nickel(II) chloride, a water shell around the Ni^{2+} ions does not allow them to stabilize the AA dimer and, as a result, no direct contacts between the chloride ions are found. In contrast, cations in a dilute solution of $CuCl_2$ are not so strongly bonded to water molecules, and the whole picture of bonding coincides with that for LiCl.[47] The results obtained agree well with the data from magnetic relaxation measurements for aqueous solutions of alkali halides showing the presence of long-lived $F^-\cdots F^-$ (see Ref. 48).

The possibility of formation of stable dimers from the X^- anions (X = F, Cl) where the distance between them is close to the sum of the corresponding van-der-Waals radii was also confirmed by the theoretical investigation of the clusters $X^-(H_2O)_nX^-$ (see Ref. 48). The authors of this study admitting the strong electrostatic repulsion between like-charged ions do not deny the presence of a bonding component in these interactions. According to their *ab initio* calculations of aqueous clusters (within the MP3 level of theory), such systems may exist in the gaseous phase only with at least three water molecules that interact so as to offset (minimize) the repulsion between the two ions. At the same time, the estimation of the contribution of polarization effects to the energy of cluster stabilization indicated their importance and allowed assuming that they are also responsible for the formation of the stable AA pairs in aqueous solutions. It was thus concluded[48] that the AA association in solutions of chloride salts is caused by both the influence of bonding interactions between the ions X^- and water molecules and the attraction between like-charged ions owing to polarization effects that overcome the corresponding Coulombic repulsion. Unfortunately, as it was noted, the quantitative description of the AA association is not possible within this approach.

Up to date, the only experimental method that allows both distinguishing bonding interactions and estimating their energy in the case of crystalline objects is the high-quality X-ray diffraction investigation followed by the topological analysis of the total electron density distribution function [$\rho(\mathbf{r})$] obtained analytically[49] within Bader's 'Atoms in Molecules' theory.[13] As any property of a many-electron system in a ground state can be expressed as a functional of $\rho(\mathbf{r})$,[50] the electron density distribution function contains all the necessary structural information including parameters of the CC or AA interactions. In this case, it is the topological analysis of the experimental electron density distribution function $\rho(\mathbf{r})$ in a crystal in terms of AIM theory that is the tool to obtain this information. The detailed summary of Bader's theory can be found in a series of papers, for instance, in a review;[51] here only some basic concepts are given essential for understanding how the conclusion on the presence and the strength of the interactions under study is reached.

First, within this theory, there is a clear definition of an atom as a region in the real space that is bounded by a flux surface in each point of which the gradient of the $\rho(\mathbf{r})$ function perpendicular to this surface vanishes.[13,52–54] As a result, the physical space can be divided into non-overlapping regions, *i.e.*, atomic basins, which are the atoms. An average value of an observable value for an atom (for instance, the atomic charge) can be obtained by integrating the corresponding function [for instance, $\rho(\mathbf{r})$] over the atomic basin. The properties are additive; for instance, the charge of a molecule or an ion can be obtained by summing up the charges of the constituent atoms.

Second, according to the AIM theory, the structure of a many-electron system (with a given configuration of nuclei)[13] is fully and uniquely defined by a set of critical points (CP) of the $\rho(\mathbf{r})$ function where $\nabla\rho(\mathbf{r}) = 0$. In the three-dimensional space, only four types of stable critical points can exist: CP (3, −3) or a maximum (nucleus), CP (3, +3) or a minimum (cage structure), and saddle points of a ring and of a bond, *i.e.*, CP (3, +1) and (3, −1). The latter is regarded special: two trajectories originating from it and belonging to the basins of two atoms define a line along which $\rho(\mathbf{r})$ is maximum in respect of any neighbouring lateral point; this is the so-called bond path. Bader showed[13] that the presence of the bond critical point and the bond path between the two atoms is a necessary and sufficient condition for a chemical bond (chemical bonding or bonding interatomic interaction) to exist. As a rule, the set of bond paths coincides with the set of bonds obtained in accordance with the 'chemical considerations', but sometimes, however, leads to the unexpected results (see, for instance, Ref. 55 and references cited therein).

Third, the use of this approach allows describing the indicated interactions on both the qualitative and quantitative levels.[56,57] Based on the sign of the Laplacian $\nabla^2\rho(\mathbf{r})$ and the electron energy density $h_e(\mathbf{r})$ at CP (3, −1) (Ref. 55), all the interactions can be divided into three categories: 1) shared interactions [$\nabla^2\rho(\mathbf{r}) < 0$, $h_e(\mathbf{r}) < 0$], which are characteristic of the covalent bonds; 2) intermediate interactions [$\nabla^2\rho(\mathbf{r}) > 0$, $h_e(\mathbf{r}) < 0$], which comprise polar bonds and a series of homopolar ones[58] as well as strong hydrogen bonds;[59–61] 3) closed-shell interactions [$\nabla^2\rho(\mathbf{r}) > 0$, $h_e(\mathbf{r}) > 0$], when the density is concentrated in the atomic basins. If the peculiarities of intermolecular bonding are analyzed, the latter are of interest, because this group comprises most of the non-covalent interactions.[56,57,61] In addition to the determination of the interaction type, this approach combined with the correlation scheme proposed by Espinosa *et al.*[14,15] allows estimating its energy with a high accuracy (E_{int}/kcal mol^{-1}):

$$E_{int} = -313.754\, v(\mathbf{r}), \quad (1)$$

where $v(\mathbf{r})$ is the potential energy density (in a.u.) at the corresponding CP (3, −1) that is obtained, in particular, from the X-ray diffraction data on the basis of the gradient expansion.[62] It is to be mentioned that the above relation is valid for weak interactions, such as H···H and C–H···O contacts,[63,64] as well as interactions Mg···C and Ca···C,[65,66] strong and medium-strength hydrogen bonds,[61,67] Au–PPh_3 and Gd–OH_2 bonds,[68,69] which correspond to the intermediate type of interatomic interactions.

Therefore, the topological analysis (within the AIM theory) of the total electron density distribution function

obtained in a high-quality X-ray diffraction experiment is the ideal approach to the investigation of the CC or AA interactions, which are impossible to detect or to quantitatively characterize using other methods.

It is to be mentioned that the concepts of the AIM theory, which were initially developed for molecular systems in the isolated state, were successfully transferred to ionic crystals.[70–72] In the most detailed description of the latter,[73] systematic investigation of $\rho(\mathbf{r})$ in alkali halides was carried out. The high symmetry of these crystals allows one to approximate an atomic basis by a polyhedron (Fig. 5) with CP $(3,+3)$ in its vertices, bond CP on its faces and ring CP on its edges. In this case, the atoms are considered to be bonded if the corresponding atomic polyhedra share a face. On this basis, Pendas *et al.*[73] developed a convenient approach to the search and description of interatomic interactions based on the quantum chemical periodic calculations [using the *ab initio* PI (*ai* PI) method [74]]. It is to be mentioned that this approach provided a solution to the problem of quantum chemical calculations, which is the need to use large clusters to obtain correct results, because the periodicity of a system allows performing a calculation of a small number of independent atoms only. The reliability of the data obtained was confirmed by the results of investigation of a series of simple ionic crystals [75,76] for which the calculated parameters, both the geometrical and energetical ones, reproduced the experimental parameters with a high accuracy (5%).

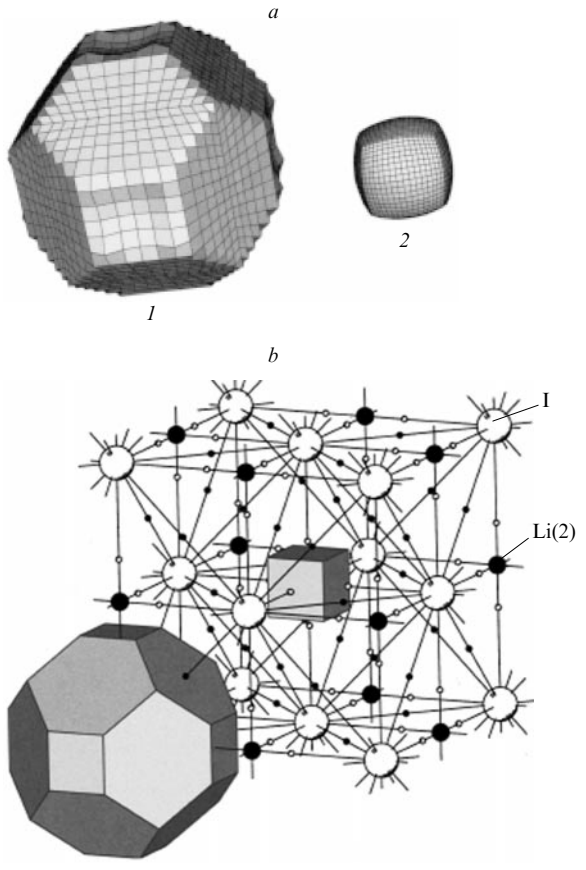


Figure 5. Atomic basins for iodide (*1*) and lithium (*2*) ions in the crystal of lithium iodide (*a*); the same basins approximated by the corresponding polyhedra (*b*).[73]

The quantum chemical calculation [73] (by means of the *ai* PI method) for the phase B1 of lithium iodide (see Fig. 5) showed that the iodide anions form a cubic close-packed structure in which octahedral holes are filled by smaller lithium cations. The shortened distance I···I (4.28 Å) and, at the same time, the presence of CP $(3,-1)$ suggest the bonding character of the AA contacts. The similar results, although for the CC interactions, were obtained in the quantum chemical periodic investigations of crystals of a series of the salts AlX_3 (X = F, Cl, OH).[77] The analysis of the electron density distribution in various crystalline phases of the chosen systems along the Al–Al line (3.3–3.6 Å) showed the corresponding CP $(3,-1)$. Based on the data obtained, a concept of 'anions in a metal matrix' was developed [77] according to which the geometry of the sublattice formed by aluminium cations and the electron density distribution within it regulate the peculiarities of crystal packing in total. In other words, the CC interactions are structure-forming ones and result in a metal matrix, which acts as a 'host' for the non-metal ions and determines the positions of the latter in a crystal.[77] The validity of such representation was confirmed by the example of metal binary compounds, *viz.*, oxides, halides, sulfides.[78,79]

In spite of good agreement between the results of the topological analysis in the case of common CA interactions and the 'chemical logic', some authors call into question the sufficiency of the condition of the presence of CP $(3,-1)$ for the bonding interaction between like-charged species to exist. Assuming that the AA interactions found, for instance, in crystals of lithium and sodium halides [80] cannot be bonding ones, Abramov performed the calculation of the lattice energy of LiF.[81] The energy of the crystal lattice (U) was considered as the sum of the energies of the electrostatic attraction/repulsion and non-Coulombic short-range repulsion of electronic clouds of the neighbouring atoms. The obtained values of U agreed rather well with the experimental data ($\Delta U \approx 7$ kJ mol^{-1}) indicating the stability of the structure; only the basic interactions Li–F contributed to the latter, while the secondary interactions Li···Li and F···F appeared to be repulsive. On the basis of these data, the author concluded that the appearance of the CP $(3,-1)$ between the neighbouring fluoride ions in the studied crystals does not indicate the occurrence of the bonding interaction, but is only the result of the close packing peculiarities.

The approximation used in this study [81] and based on the fact that the repulsion forces act on two anions 'bound' in such a way, was, however, subjected to criticism by Bader,[55,82] who showed its inadequacy using only the terms of quantum mechanics. The evidence he gave [55,82] was based on the well-known fact that the wave function and the electron density distribution function of any system in the ground state are such that its total energy is minimum.

As a result, the CP $(3,-1)$ appearing between two atoms causes the local decrease in the potential energy density. As the minimum on the energy surface corresponds to the state of the electrostatic equilibrium, the forces acting on nuclei when the system deviates from it restore the geometry of a system back to the equilibrium one; in other words, they are attractive forces. At the same time, every bond path in the function $\rho(\mathbf{r})$ is mirrored in the function $-v(\mathbf{r})$ by a line linking the same nuclei along which the potential energy density is maximally negative (*i.e.*, the most stabilizing) in respect of any neighbouring trajectory of the vector field

$-\nabla v(\mathbf{r})$. In turn, the function $v(\mathbf{r})$ is negative everywhere and, hence, there are no regions corresponding to repulsion in it. It is the homeomorphism of the functions $\rho(\mathbf{r})$ and $-v(\mathbf{r})$ that causes the decrease in the energy, which accompanies the formation of a bond path between atoms, in particular, between the anions X^- in the crystals of alkali halides. It was assumed [81] that the high value of the ratio of the ionic radius of an anion to that of a cation leads to the occurrence of the AA contacts as well as the corresponding CP $(3,-1)$ and bond paths. However, in the crystal of LiI (Ref. 82), the electron density value at CP $(3,-1)$ attributed to the interactions I···I is higher than in the case of the CA bonds, which are considered to be most stabilizing. In Bader's opinion,[55,82] the model that served as a basis for the conclusion about the 'repulsive' character of the AA interactions [81] is a very rough approximation and does not provide reliable determination of their nature. Thus a crystal was considered as consisting of spherical ions that does not allow taking into account the electrostatic contributions into the potential energy, which resulted from the deformation of spherically symmetric densities of atoms. Moreover, if one assumes that an additional repulsion force acts on the pair of fluoride anions in LiF in the absence of forces compensating for it (because the attractive forces appeared only when a system deviates from the equilibrium), the crystal would be unstable. On this basis, there is no reason to expect the presence of any 'repulsive' AA interactions in crystals.

Thus, the possibility of occurrence of bonding interactions between like-charged ions was demonstrated, which could not be reproduced by *ab initio* quantum chemical calculations of isolated associates, but was observed experimentally. It was shown that the presence of a CP $(3,-1)$ and a corresponding bond path can be regarded as the universal indicator of a bonding interaction, because it is the result of the electron density accumulation that is sufficient to compensate for the repulsive forces between two anions. Moreover, the use of this approach to describe a chemical bond sets it free from the limitations imposed by the Lewis electron pair model, which does not allow describing the bonding in metals and condensed phases formed by closed-shell atoms.

When the advantages and drawbacks of the above methods are carefully considered, the topological analysis within the AIM theory of the function $\rho(\mathbf{r})$ in a crystal, which is obtained experimentally or within the periodic calculations, appears to be the ideal approach to the qualitative and quantitative description of the CC and AA interactions in ionic systems. Its applications allowed confirming the occurrence of such contacts in the condensed state and stimulated analysis of the AA interactions (mostly of the X···X and O···O types) in highly symmetric crystals of inorganic salts owing to their availability and to the possibility to obtain a high-quality dataset of the X-ray diffraction data.

III. Anion – anion association involving halide anions in inorganic salts

As was mentioned above, in crystals of some alkali halides there are shortened AA contacts corresponding to bonding interactions. They are observed in the case of both the phase B1 (NaCl, space group *Fm*3*m*) and the phase B2 with a CsCl-like structure (space group *Pm*3*m*).[73] The main factor that determines the phase (B1 or B2) certain salt can crystallize [81] and the occurrence of interactions $X^-\cdots X^-$ (Ref. 83) is the ratio of the ionic sizes. On this basis, Pendas *et al.*[1] attempted to relate the topology of the electron density in crystals of these salts to the ionic radius (Fig. 6). Unfortunately, the use of the systems of ionic radii documented in the literature does not allow, for instance, establishing the stable phase (B1 or B2) for a half of the compounds MX,[84] because the corresponding radii are, as a rule, isotropic, although their pronounced anisotropy has been demonstrated in many investigations.[84,85] This problem was solved by defining the ionic radius as a distance between the nucleus and the boundary of atomic (ionic) basins. In this case, the 'bonding radius' (r) of an ion (depending on the direction) is a length of the vector originating from the corresponding CP $(3,-3)$ and ending in the CP $(3,-1)$. Depending on which atomic basin this particular atom contacts with in this point, one can define several such parameters for each ion. When the crystals MX (M is an alkali metal) were examined, primary attention was paid to the values r_a and r_c corresponding to the 'bonding radii' of an anion and of a cation along the line of a CA bond. It was shown [1] that in salts with similar r_a and r_c values, such as KF, KCl and RbBr, there are CA interactions only. In the case of the phase B1, if $r_a/r_c < 1.15$, there are also only the CA bonds in a crystal of the salt, but if $r_a/r_c > 1.15$ AA, association is also observed. For the phase B2, the reverse sequence was obtained: if $r_a/r_c > 1.15$, only the CA bonds are present and if $r_a/r_c < 1.15$, both the CA and AA bonds are present. The latter, for instance, is valid for LiI the AA bonds in the crystal of which were described above. On the other hand, if cations are larger than anions, the opposite situation is observed: the ions exchange the roles and the CC interactions appear.

Thus, the use of a simple geometrical parameter, though obtained on the basis of the results of the electron density

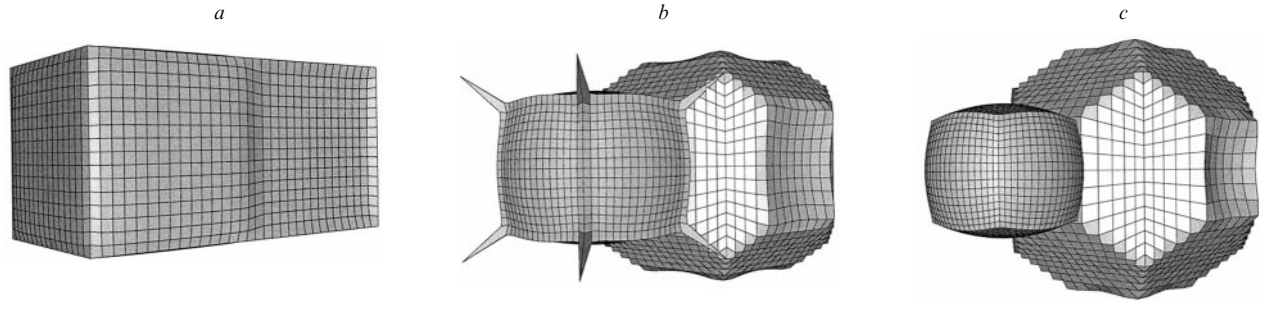


Figure 6. Atomic basins for KF (*a*), NaCl (*b*) and LiCl (*c*);[74] (*a*) without the AA interactions; (*b*) and (*c*) with the AA interactions.

investigations, allows indirectly assuming the presence of the AA bonds in crystals of alkali halides. In the case of other types of crystals, one can use the topological analysis of the function $\rho(\mathbf{r})$ as well and find the corresponding CP (3,−1). It should be mentioned, however, that the bonding radii of ions obtained [73] in the case of the crystalline salt LiI (0.9377 Å for lithium, 2.1448 and 2.1797 Å for iodine along the I···I and I−Li lines, respectively) agree rather well with those calculated by Shannon [86] (0.9 and 2.06 Å). One can assume that the relations between the ionic size and the topology of the electron density in a crystal, which were derived by Pendas *et al.*,[1] will be valid for the system of the Shannon radii as well.

The occurrence of bonding interactions between the ions X^- is not the feature of alkali halides only. A similar situation is also observed for the alkaline-earth metals. Thus the contacts of the $F^-\cdots F^-$ type that contribute greatly to the stabilization of a system in the crystalline state were found when analyzing structural and thermodynamic properties of the crystal of MgF_2 in a wide range of temperature and pressure.[87] According to the topological analysis of the function $\rho(\mathbf{r})$ obtained within the periodic calculations (using the *ai* PI method) in the absence of the external pressure ($P = 0$), the 'bonding radii' of the anion (along the CA and AA lines) vary from 1.078 to 1.632 Å, which suggests its high deformability. The cations are, in contrast, rather stiff; the values r for the bonds Mg−F are 0.866 and 0.879 Å. The occurrence of the AA interactions is apparently related to the difference in the size of the species: the value r_a/r_c, where r is an average 'bonding radius', reaches 1.45, which suggests the presence of a bonding interaction between anions in the case of the phase B1 MX. The increase in pressure is accompanied by the linear decrease in the ratio of the ionic radii (according to the results of the *ai* PI calculations) from 1.45 ($P = 0$) to 1.38 ($P = 100$ GPa). This additionally suggests that the ions F^- are more deformable than the ions Mg^{2+}. Thus, the results of the topological analysis of the electron density distribution function in the crystalline magnesium fluoride agree with the classical considerations: small cations that are difficult to polarize are surrounded by larger anions that are easy to deform.

It is to be mentioned that the AA interactions in this salt are difficult to explain only of the basis of the close packing of ions, because such interactions were also found in the isolated dimers and trimers of MgF_2. The investigation of various isomers of the latter showed [88] that in some cases the fluoride ions that are located as far as 2.496–2.600 Å from each other are involved in the formation of the AA bonds; the cations do not interact with each other. The analysis of the functions $\rho(\mathbf{r})$ obtained within the MP2 calculation confirms that dipole–dipole interactions between the fluoride anions in these systems stabilize the non-planar conformation of $(MgF_2)_3$. As a result, the trimer appears to be the first cluster of MgF_2 in which the isomer with the D_{2d} symmetry is more stable than the associate with the D_{3h} symmetry where no $F^-\cdots F^-$ bonds exist. Thus, the given data show that AA interactions between the anions in crystals of alkali and alkaline-earth halides not only contribute greatly to the stabilization energy, but can be to some extent considered 'structure-forming' ones.

A simple ratio of ionic radii determines the occurrence of the AA interactions in the crystals built from two types of ions. Meanwhile, it was shown [89,90] by the example of a series of cubic alkali perovskites that the geometrical approach to this problem in the case of more complex systems also appears to be rather informative. The analysis of the topology of the electron density calculated by means of the *ai* PI method for crystals of 120 perovskites (the salts QMX_3, Q is an alkali metal, M is an alkaline-earth metal, X is a halogen) allowed all the studied salts to be divided into three groups. The structures of the first type ($CsSrF_3$ and $CsBaF_3$) are characterized by the presence of the bonds Q−X, M−X and the interactions Q···Q; the formation of the latter resulted from the significant difference in sizes of the ions Q^+ and X^- and from high value of the parameter a owing to the presence of the bulky ions Q^+. In the crystals of the second group, there are only the bonds Q−X and M−X. In the structures of the third type, the additional contacts X···X appear. As in the case of alkali halides,[1] the ratio of ionic radii along the M−X and Q−X lines in the perovskites determines the presence or absence of the AA interactions.[90] Thus, for the third group of structures, in which the anions X^- interact with each other, the ratio $r(M)/r_1(X) < 0.82$, where $r(M)$ and $r_1(X)$ are the 'bonding radii' of the ions M^{2+} and X^- along the bond M−X. It is to be mentioned that in the case of the salts from the first and the second groups where the bonds $X^-\cdots X^-$ are absent, the basins of the cations M^{2+} have triangular and nearly two-dimensional 'wings' (Fig. 7) that pass between

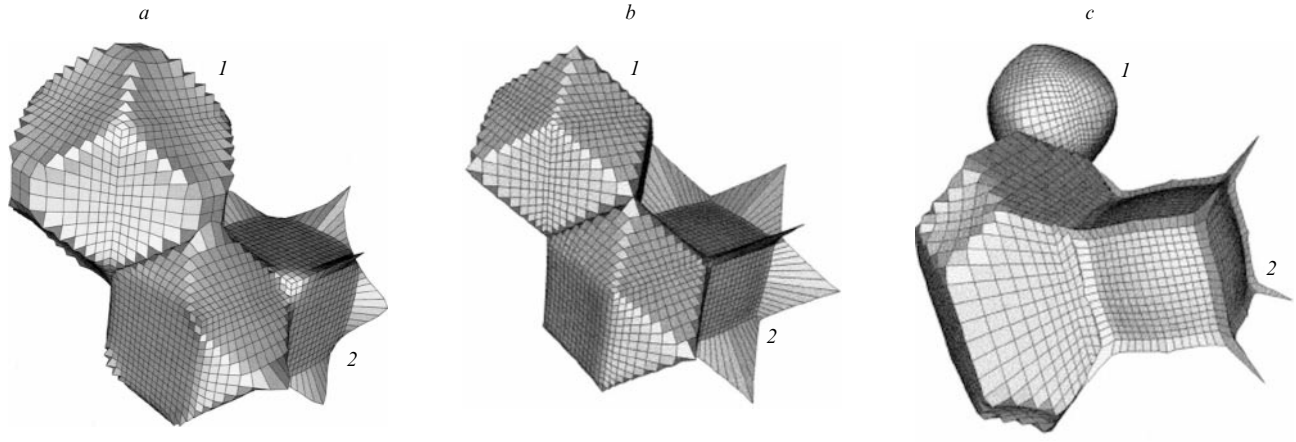
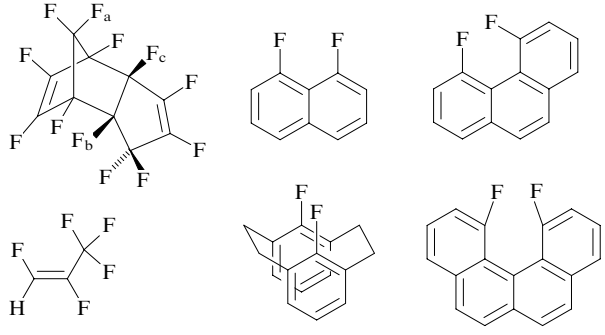


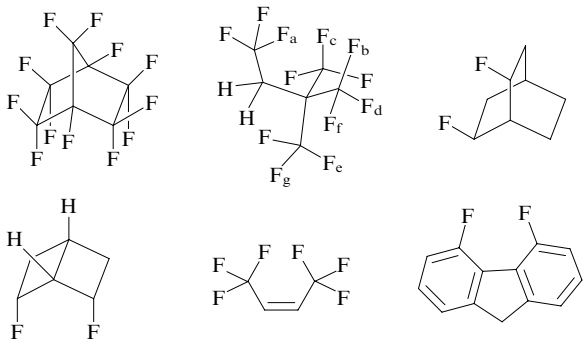
Figure 7. Atomic basins in the crystalline perovskites $CsSrF_3$ (*a*), $KCaF_3$ (*b*) and $LiZnCl_3$ (*c*). *1* and *2* are the basins of alkali and alkaline-earth metal cations, respectively.[90]

the neighbouring ions X^- preventing the occurrence of the AA interactions.

In addition to the development of the geometrical approach to the description of the structural peculiarities of perovskites, the estimation of the stability of their crystals was carried out.[90] On the one hand, it was found that electrostatic interactions govern the lattice energy; the bonds M–X characterized by the highest value of $\rho(\mathbf{r})$ at CP (3,−1), determine the properties of the salts to the greater extent than other contacts. On the other hand, the crystals without the interactions $X^-\cdots X^-$ and with the 'unusual' basins of the ions M^{2+} appear to be less stable. Therefore, the AA interactions in alkali perovskites play an important role in the stabilization of certain types of crystal structures.

The conclusion made on the importance of the bonds X···X are indirectly confirmed by the fact that the contacts Cl···Cl with the similar topology are responsible for the existence of the solid chlorine. In the crystal state, the molecules Cl_2 are organized into layers (the distance Cl···Cl is significantly smaller than the sum of their van-der-Waals radii and is equal to 3.82 Å), which suggests the occurrence of a specific directional interaction between them. The topological analysis of the electron density distribution function in the crystal of chlorine obtained from the X-ray diffraction data [70] showed that each chlorine atom interacts with 12 others including those that lead to the formation of the molecule Cl_2. All the intermolecular interactions correspond to the 'closed-shell' interactions and are characterized by the values of $\rho(\mathbf{r})$ and $\nabla^2\rho(\mathbf{r})$ of the same order of magnitude as those for the contacts X···X in the above halide and perovskites. Although such a consideration makes the interactions Cl···Cl in the crystal of chlorine similar to those between halide anions, the non-polarity of the molecule Cl_2 causes the electrostatic component not to make an additional destabilizing contribution to the repulsion between the like-charged species. The situation that is more similar to that considered above is observed in a series of fluorinated hydrocarbons.[91,92] Thus it was Hargittai who pointed out the possibility of such bonding F···F,[93] and later [92] the CP (3,−1) were located between the fluorine atoms of two CF_3 groups. An attempt was undertaken [12] to relate the results obtained to the data of any physicochemical method to additionally confirm the occurrence of bonding interactions between the like-charged fragments. The subjects of investigation chosen were several fluorine-containing hydrocarbon systems with known through-space scalar fluorine–fluorine spin–spin coupling constants (SSCC).





The theoretical investigations [12] of the compounds with intramolecular distances F···F in the range of 2.423–2.864 Å showed the presence of the CP (3,−1) in all systems for which large SSCC J_{FF} were experimentally observed. At the same time, in the case of a related compound in which the distance F···F in a molecule was 2.78 Å there was no CP (3,−1) along the corresponding line and the calculations performed [94] indicated the small value of SSCC J_{FF}. Such agreement between the results of the topological analysis of the function $\rho(\mathbf{r})$ and the NMR data serves an additional proof of the existence of bonding interactions between atoms (ions) bearing the partial charge of the same sign.

The results given above lead to the conclusion that neglecting such interactions, which in some cases [according to the value of the electron density in the CP (3,−1)] are comparable in strength with classical (for instance, CA) interactions, can result in incorrect estimates of the stability and the related physicochemical parameters of ionic crystals.

In addition to the theoretical studies devoted to the investigation of the chemical bonding between like-charged species, a series of investigations in which such interactions were observed experimentally is documented. Thus, Tsirelson *et al.*[95] performed the topological analysis of the electron density distribution function obtained from the X-ray diffraction data for the crystals of LiF, NaF, NaCl and MgO. Although the distribution function obtained in such a way 'suffers' from the experimental limitations, and the calculated function $\rho(\mathbf{r})$ depends to the great extent on the method and the basis set used, it was assumed that the number and the type of CP will be the same in both cases. Indeed, in the crystals of LiF in which according to the proposed classification [1] the AA interactions should occur, the set of the critical points including a CP (3,−1) between the fluoride anions in both functions coincides. Moreover, the topological characteristics at this CP are nearly identical. For instance, the values of $\rho(\mathbf{r})$ and $\nabla^2\rho(\mathbf{r})$ therein are, respectively, 0.08 e Å^{-3} and 1.00 e Å^{-5} for the experimental distribution and 0.08 e Å^{-3} and 1.02 e Å^{-5} for the theoretical electron density distribution. A similar situation is observed in the crystalline NaF.[95] In this case, however, two out of three values (λ_1 and λ_2) of the electron density curvature determining the type of a critical point are within the experimental error (−0.07 and −0.02 e Å^{-5}). The experimental functions $\rho(\mathbf{r})$ for NaCl and MgO differ from those for the studied fluorides as the CP (3,+1) was located in this position; some values λ_i therein also appeared to be close to zero. On the other hand, the topology of the function $\rho(\mathbf{r})$ calculated at the Hartree–Fock level for the three-dimensional crystal of MgO is similar to that in the crystals of LiF and NaF. The model electron densities for

the corresponding pro-crystals, *i.e.*, the systems formed by spherically symmetric atoms (ions), were additionally examined. The topological peculiarities found for the experimental function $\rho(\mathbf{r})$ of the salts persisted in the case of their atomic (ionic) pro-crystals. The exception was sodium chloride in which the type of the critical point along the line Cl···Cl changed from the ring CP in the crystal to the bond CP in the pro-crystal. It is to be mentioned that the latter agrees with the conclusions made earlier,[1] this crystal being identified as one with the AA interactions. Thus, although an attempt to unambiguously establish the type of the CP between the anions in the crystals of NaF, NaCl, and MgO failed,[95] information on the interactions $F^-\cdots F^-$ in LiF can be regarded reliable.

It is to be mentioned that until recently the electron density was considered not to be the only function the topological analysis of which was able to reveal bonding interactions. Thus in continuation of investigations,[95] Tsirelson *et al.*[96] examined on the qualitative level the electrostatic potential distribution in the crystals of LiF, NaF and MgO. Unfortunately, in all cases the authors failed to locate a bond CP along the line X···X. As a result, the authors noted that apparently the model used does not describe correctly the areas of the uniform distribution of the electrostatic potential.[96] However, it was shown later that the topological peculiarities of the electrostatic potential do not provide the information on the bonding.[97]

Thus, the topological analysis of the total electron density distribution function obtained from the X-ray diffraction data is more informative in the AA bonding aspect than other experimental methods. Moreover, this approach can be even more preferred than the classical methods of quantum chemistry, which have an important shortcoming, *viz.*, the strong dependence of the data obtained on the choice of the method and the basis set (see, for instance, Ref. 48). Although the *ai* PI calculations give physically sound results, the scope of their application is limited to the highly symmetric and highly ionic crystals, which is mainly the case of inorganic salts.

IV. Interactions between the chalcogenide anions in ionic crystals

The second type of the AA interactions in crystalline salts that is described rather well in literature is the contacts chalcogen – chalcogen. The key attention was paid to the inorganic oxides and silicates, although the investigations were also performed for a series of bulky anions involved in the formation of numerous hydrogen bonds. For instance, magnesium oxide was one of the subjects of investigation.[95] A comparison of the results obtained, mainly the set of CP in the electron density and the electrostatic potential, was also the aim of a separate investigation.[98] It was shown that in all cases a saddle point appeared along the line O···O, although its type as CP (3, −1) can unambiguously be established only for the theoretical function $\rho(\mathbf{r})$ calculated on the Hartree – Fock level. In the case of other functions, including the electron density distributions calculated for the atomic and ionic pro-crystals, the CP (3, 1) type was assigned to the CP between the anions, *i.e.*, the latter can be the bond CP (3, −1) and the ring CP (3, +1) as well owing to the low (close to zero) values of the curvature of the function $\rho(\mathbf{r})$ at this point. The function $\rho(\mathbf{r})$ for the pro-crystal, however, does not necessarily reflect the peculiarities of the chemical bonding in the real crystal,[95] because it does not correspond to the ground state.

At the same time, the similar contacts chalcogen – chalcogen in the case of the crystalline sulfides MS_n do correspond to bonding interactions.[99] In the solid state, these salts[100] are formed by polyhedra MS_n in such a way that some sulfur atoms bind not only to the metal cations, but also to sulfur atoms of the neighbouring polyhedron forming the dimers S_2 (the distance S···S ~3.5 Å). Thus, according to the results of the analysis[99] of various iron and copper sulfides, the octahedra FeS_6 in the disulfides FeS_2, pyrite and marcasite, are indeed linked together by S_2^{4-} dimers. In the crystal of smithite Fe_3S_4, the similar octahedra are assembled into layer, which are linked by the groups S_2 into the three-dimensional framework. The topological analysis of the calculated functions $\rho(\mathbf{r})$ performed for these structures showed the CP (3, −1) and the corresponding bond paths between the anions S^{2-}, which unambiguously indicates the occurrence of bonding interactions between them (Fig. 8). This interactions cannot be considered as weak, because the value of $\rho(\mathbf{r})$ at CP is comparable with that for the eight-membered rings S_8 found in the natural sulfur.[99] Moreover, it was found[101] that in the crystal of pyrite the interactions S···S are even stronger than CA bonds in accordance with the values of $\rho(\mathbf{r})$ equal to 0.89 and 0.55 e Å^{-3}, respectively. Therefore, it is the AA interactions that contribute the most to the formation of the crystal packing of pyrite rather than the most stabilizing (according to the electrostatic considerations) bonds Fe – S. In the case of the mineral smithite, the AA interactions are responsible for the formation of the layered crystal structure (see Fig. 8 *c*). Thus, the bonding interactions $S^{2-}\cdots S^{2-}$ govern the existence of rather complicated geometrical schemes in sulfides and apparently the non-stoichiometric ratio of components therein.

The interactions between the chalcogen atoms (oxygen atoms in this case) of more complex anions were identified

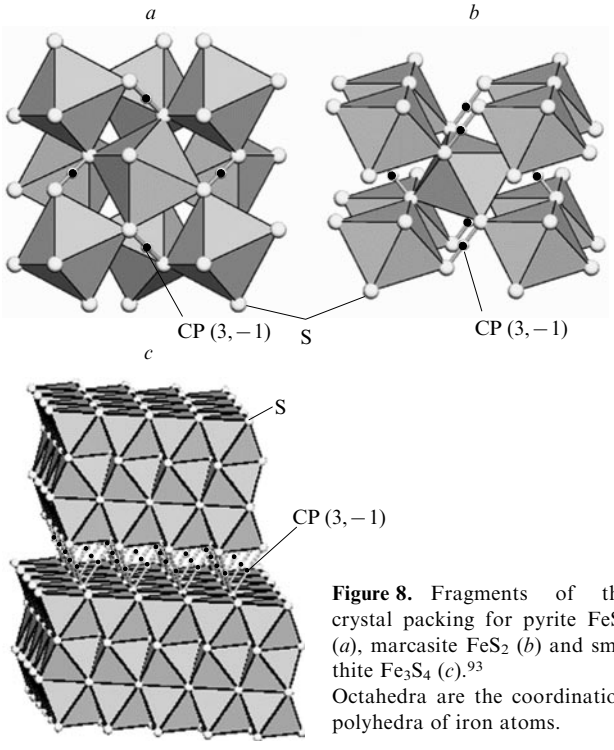


Figure 8. Fragments of the crystal packing for pyrite FeS_2 (*a*), marcasite FeS_2 (*b*) and smithite Fe_3S_4 (*c*).[93]
Octahedra are the coordination polyhedra of iron atoms.

in an early investigation of the absolute electron density distribution in the crystal of the natural magnesite $MgCO_3$.[102] A peak of the electron density, which was obtained from the X-ray diffraction data using the rather simple model,[102] was observed (0.24 e Å^{-3}) between the oxygen atoms of neighbouring carbonate anions that are located as far as 3.02 Å from each other. Such an accumulation of the electron density was explained by the slight overlap of lone electron pairs of the oxygen atoms. Based on the fact that the maximum of the distribution of $\rho(\mathbf{r})$ in the crystal of $MgCO_3$ is observed for the slightly longer contact in which the distance O···O is equal to 2.93 Å, it was concluded, however, that it has the 'repulsive' character. It is evident that the latter assumption contradicts Bader's conclusion[55,82] according to which any interactions in an equilibrium system are stabilizing. Thus, in this case one can also expect the interaction between the anions to be bonding.

The occurrence of the AA interactions involving oxygen atoms is also common for the crystals of the polymorphs of As_2O_3 (according to the SVWN/6-311G** calculation).[103] In addition to the expected bonds As–O therein, there are rather strong interactions As···As and O···O. For instance, the values of $\rho(\mathbf{r})$ at CP (3,−1) of the bonds As···As (3.728 Å) and O···O (3.361 Å) in the crystal of claudetite I are equal to 0.056 and 0.045 e Å^{-3}, while those for the interactions As–O (3.038–3.429 Å) reach 0.093 e Å^{-3}. In the case of the mineral arsenolite, the value of $\rho(\mathbf{r})$ for the intermolecular interaction O···O (3.022 Å, 0.073 e Å^{-3}) appears to be lower that that for the bonds As–O (3.050 Å, 0.085 e Å^{-3}) by ∼15% only. Moreover, in the crystal of arsenolamprite (ε-As) consisting of the layers of three-coordinated arsenic atoms, the layers are held together only owing to the interactions As···As (3.873–4.013 Å) similar to those in the claudetite I. The similar intermolecular bonding O···O (2.972–3.217 Å) with parameters [$\rho(\mathbf{r})$ = 0.030–0.052 e Å^{-3}] close to those for the interactions O···O in the arsenolamprite contribute 90% of the crystal structure stabilization energy for the binuclear carbonyl complex $Mn_2(CO)_{10}$.[104]

The anion–anion association of the chalcogen–chalcogen type is also common for the crystals of silicates and SiO_2. A detailed investigation of both the experimental and theoretical electron density distributions for a wide range of the corresponding minerals was carried out.[105] In the studied crystals, the polyhedra SiO_n (n = 4, 6) as the main building blocks were linked to each other in a certain manner. Although the smallest distance O···O (for instance, 2.29 Å for the mineral stishovite) is found between the atoms of the same face of the polyhedron, the corresponding CP (3,−1) could not be located. At the same time, the main features of the interactions between the fragments SiO_n were reproduced well[106] by both the periodic calculations and the analysis of the experimental distribution of $\rho(\mathbf{r})$. On the other hand, the results of the theoretical investigation[107] of yet another form of SiO_2, coesite, allowed localizing the CP (3,−1) attributed to the interactions O···O (the interatomic distance is 2.6–3.6 Å) between the fragments SiO_n. In the next report from this research group,[108] a conclusion was made that the presence or the absence of the interactions O···O is significantly affected by the electron density distribution of the silicon atom. Thus in spite of the shortened distance O···O in the polyhedron SiO_4, the corresponding bond path is absent as a result of the 'destructive' influence of the central silicon atom. On the other hand, the electron density distribution of the silicon atoms of the two tetrahedra joint together can cause the additional electron density accumulation along the line O···O and appearance or strengthening of the bond O···O. The topological parameters of the interactions between the oxygen anions in the coesite are comparable with those for weak interactions O···O found in some fragments of nucleic acids where they play an important role in stabilizing the structure.[109]

It is to be mentioned that in all the above silicates and polymorphs of SiO_2 the interactions O···O corresponded to the 'closed-shell' interactions. The exception is the pyrite-like modification of silica, *viz*., silicon oxide III, which is the high-pressure form of silica. According to the X-ray diffraction data for the latter (271 GPa, 300 K),[110] the contact O···O in the crystal (2.06 Å) is the shortest of all the contacts found to date for silicates and SiO_2 forms. As this value is significantly higher than that in the molecule O_2 (1.21 Å), it was concluded[110] that these two oxygen atoms are not bound to each other. The topological analysis of the electron density distribution function calculated for the crystal of silicon oxide III, however, showed[110] that there is a CP (3,−1) along the line O···O. The values of $\rho(\mathbf{r})$ and $\nabla^2\rho(\mathbf{r})$ at this point (0.45 e Å^{-3} and 8.42 e Å^{-5}) are similar to those for the dimers S_2 in the crystal of pyrite. The negative value of the local electron energy density $h_e(\mathbf{r})$ (−0.0035 a.u.) at the CP (3,−1) suggests the intermediate character of this interaction. As a result, the type of the latter makes it similar to the bonds M–O.[111]

The natural mineral danburite, a borosilicate $CaB_2Si_2O_8$, is of special interest for studies of the interactions O···O in silicates with the interatomic distance varying in a wide range, as the corresponding interatomic distances O···O are 2.3–3.5 Å.[85] The peculiarities of the chemical bonding in the crystal were examined[112] by means of the periodic quantum chemical calculations. The analysis of the topology of the theoretical function $\rho(\mathbf{r})$ allowed locating eleven CP (3,−1) attributed to various types of contacts between the oxygen atoms located as far as 2.3–3.36 Å from each other. It was concluded that their occurrence is caused by the geometry of ionic basins. The latter was demonstrated by the example of the different behaviour of the coordination polyhedra SiO_4^{4-} and BO_4^{5-}. The main difference between them was that the oxygen atoms in the tetrahedra BO_4^{5-} are bound to each other, while those in SiO_4^{4-} do not. Assuming that both fragments are regular tetrahedra and the oxygen anions are hard spheres, the occurrence of the AA interactions along the edges of the fragments could be expected if $r_c/r_a \leqslant 0.707$. In this case, $r_B/r_O = 0.489$ and $r_{Si}/r_O = 0.727$, which explains the absence of a CP (3,−1) between the neighbouring oxygen atoms in the silicates studied by Tsirelson *et al*.[105] Similarly, according to the theoretical data obtained for the crystalline oxides MgO and CaO, the different ratio of sizes of the cation and of the anion governs the presence of the AA interactions in the former and their absence in the latter. The authors also contributed to the debates on the bonding nature of interactions between the anions. They noted that ionic basins in a crystal cannot be approximated by spheres or point charges, as Abramov did,[81] and that the significant interactions of the multipole–multipole types occur between them. The latter conclusion agrees, for instance, with the results of other investigations[113,114].

Thus, the data given above indicate that in a series of crystals the AA interactions exist, which correspond to the

closed-shell interactions (in terms of the AIM theory) and display the modest values of $\rho(\mathbf{r})$ in the corresponding CP. In certain cases, some facts were given indicating the important role they play in the stabilization of particular types of crystal packing and the influence they have on the physicochemical properties of ionic materials. Unfortunately, the investigations cited above were limited to the examination of the interactions $X^-\cdots X^-$ and $O^{2-}\cdots O^{2-}$ on the qualitative level, *i.e.*, to the analysis of the sections of the deformation (or other) electron density distribution and of a small number of topological parameters at CP $(3,-1)$. This serious flaw was corrected in subsequent studies.[115] A detailed analysis of the functions $\rho(\mathbf{r})$ obtained from the X-ray diffraction experiment and the *ab initio* periodic calculation of yet another silicate, diopside ($CaMgSi_2O_6$), was carried out. The analysis allowed locating the CP $(3,-1)$ and the bond paths between four and two pairs of silicon tetrahedra in the experimental and the theoretical electron density distributions, respectively. Presumably, the occurrence of the above CP is caused by both the shortened distances between the oxygen atoms and the overlap of their lone electron pairs. The main topological characteristics of the interactions O···O observed are comparable with those for most of the above structures. Their strength was estimated by means of Espinosa s correlation [see Eqn (1)].[14,15] The average values of the energy of these interactions appear to be equal to 3.0 kcal mol^{-1} according to the experimental data and to 2.8 kcal mol^{-1} according to the results of the calculation; they are comparable with the similar values for weak hydrogen bonds.[116] Thus, the AA interactions contribute to the stabilization of a structure to the same extent as the classical intermolecular interactions the existence of which is not called into question.

In all the above investigations, the subjects of investigations was highly symmetric crystals of inorganic salts and oxides in which the occurrence of interactions between like-charged species was mainly attributed to the close packing effects. In the case of the lower-symmetry crystals in which both ions participate in the formation of numerous hydrogen bonds this assumption is, however, *a priori* incorrect. The occurrence of the intramolecular (intraionic) AA interactions in a series of organic salts in the crystal state was confirmed in the study of biguanidinium dinitramide and bis(dinitramide) ((BIGH)(DN) and $(BIGH_2)(DN)_2$).[117] The investigation of the experimental electron density distribution showed that in both cases the oxygen atoms O(1) and O(4) of the dinitramide anion (Fig. 9) located nearly as far as the sum of the van-der-Waals radii and bearing the negative charge interact with each other. The critical points $(3,-1)$ and the corresponding bond paths were located in both the $\rho(\mathbf{r})$ and the $-v(\mathbf{r})$ functions, which is an unambiguous indicator of the bonding interaction O···O. The similar distribution was obtained by the quantum chemical calculation of the anion DN. Note that the oxygen atoms of the same nitro group are not bound to each other, although the corresponding distance O···O is significantly smaller than that between the atoms O(1) and O(4). This phenomenon was rationalized[112] by carrying out the calculation (on the Hartree–Fock level) of the trinitromethanide ion $C(NO_2)_3^-$. In this case, the smallest distance O···O, equal to 2.084 Å, was observed for the oxygen atoms of the same NO_2 group. Nevertheless, the bond path between them could not be located. The simple visual inspection of the gradient field $\nabla\rho(\mathbf{r})$ in the plane of the anion (Fig. 10) showed that the basins of the nitrogen atoms act as a barrier between the oxygen atoms preventing the formation of the bond path. There are no such limitations for the oxygen atoms of the neighbouring nitro groups, and even the larger distance O···O (2.453 Å) does not prevent the interaction between them.

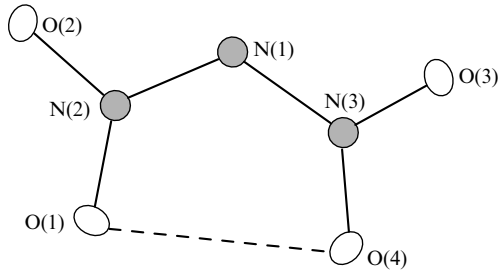


Figure 9. A general view of the dinitramide anions from the X-ray diffraction data.[117]

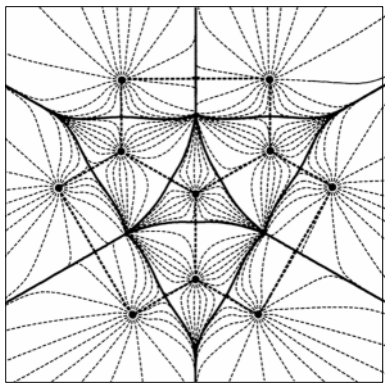


Figure 10. The gradient field $\nabla\rho(\mathbf{r})$ in the plane of the anion $C(NO_2)_3^-$ [according to the HF/TZV + (1d) calculation].[112]

Interactions between atoms bearing the partial negative charge within a structural unit are not the feature of ionic crystals only. The interactions with the similar geometry and topology were also observed in the case of molecular systems. For instance, it was found[118] that the occurrence of the intramolecular interactions O···O is common for some of the conformers of the enol forms of *cis*-β-diketones. Since the estimation of the role of these interactions in the stabilization of a certain conformation when numerous other contacts are present is a very difficult task, the authors chose the isolated molecules of naphthalene-1,8-diol (**2**) and naphthalene-1,5-diol (**3**) in which the formation of the interaction O···O to be found is possible only in the first case (Fig. 11). According to the results of the B3LYP and MP2 quantum chemical calculations, molecule **2** with the intramolecular interaction O···O [the CP $(3,-1)$ and the bond path were located] appears to be less stable than molecule **3** by 5.29 (B3LYP) and 5.97 (MP2) kcal mol^{-1}. The values of the atomic energies obtained by integrating the function $h_e(\mathbf{r})$ over the basins of the equivalent oxygen atoms show, however, the reverse trend: the atoms that are involved in the interaction O···O (in molecule **2**) make a greater contribution to the stabilization of the system than those that are not (in molecule **3**); the difference in the energies of these oxygen atoms reaches 5.47 (B3LYP) and

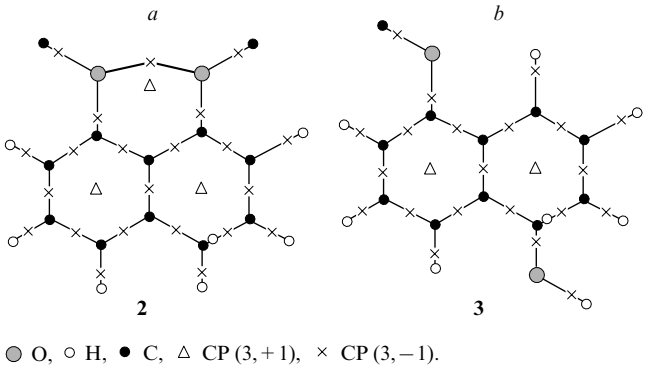


Figure 11. The molecular graphs for the naphthalene-1,8-diol (*a*) and naphthalene-1,5-diol (*b*) obtained[118] by the B3LYP and MP2 calculations using the 6-311++G** basis set.

8.15 (MP2) kcal mol^{-1}. In other words, the bonding interaction between the oxygen atoms makes locally 'contributes' ~11 (B3LYP) and ~16 (MP2) kcal mol^{-1}. Presumably, the lower stability of molecule **2** as compared with that of molecule **3** resulted from the difference in energy inputs of carbon atoms of the backbone. These results once again demonstrate that interactions between like-charged species are important for a deeper understanding of the reasons for the stability of a certain conformation.

The authors of report[118] approach most closely the quantitative description of interactions between two atoms bearing a partial negative charge in the case of organic compounds. However, the use of 'energy of the local stabilization', which was obtained from the absolute values of the atomic energies is, first of all, hardly correct, because their difference is, apparently, caused by not only the intramolecular interaction O···O; second, it requires comparison of several conformers to be made. In the case of the real crystals, the situation becomes even worse. It is impossible to find two compounds with the identical packing of molecules (ions) and the only difference between them being the presence of an interaction O···O while all other contacts are the same. As a result, an estimate for the strength of such a bond is needed in terms of its energy provided, for instance, by the Eqn (1). This was given by Zhurova *et al.*[119] for pentaerythritol tetranitrate the crystal of which contains intermolecular contacts formed by the oxygen atoms of the NO_3 fragments. The corresponding CP (3, −1) were located in the experimental function $\rho(\mathbf{r})$. Since the bond paths were located in both the functions [$\rho(\mathbf{r})$ and $-v(\mathbf{r})$], it was concluded that the interaction O···O has the bonding character. The main advantage of this investigation was, however, not the localization and the description of these interactions using the values of $\rho(\mathbf{r})$ and $\nabla^2\rho(\mathbf{r})$ at CP, but the quantitative estimation of their energy. The values obtained fell in the range from 1.3 to 3.0 kcal mol^{-1} depending on the interatomic distance, which in some cases is larger than the similar parameters for the van-der-Waals complexes.[120] Moreover, in spite of the rather low strength of these interactions, their disruption is thought to significantly destabilize the crystal and initiate the process leading to the explosion.

V. Anion–anion interactions: from detection to the estimation of energy and role in stabilization of crystal structure

Up to date, in spite of the development of the approach to the examination of the AA association, which is based on the analysis of the function $\rho(\mathbf{r})$, the corresponding investigations mainly concerned the crystals of simple salts (halides, silicates, *etc.*) or oxides. In the mentioned systems, the occurrence of the AA interactions was explained exclusively by the presence of small cations that cause bulky anions to come in contact with each other. On the other hand, it has recently been shown that bonding AA interaction can also occur in the systems for which this condition does not hold.[121] This was demonstrated by the example of the crystal of hydroxylammonium chloride $[NH_3OH]^+Cl^-$ in which the bulky cation forms numerous hydrogen bonds and the minimum distance $Cl^-\cdots Cl^-$ [3.8053(5) Å] appears to be smaller than that in sodium chloride (3.981 Å). According to the results of the statistical analysis of the Cambridge Crystallographic Data Centre (CCDC) carried by the authors,[121] the distance $Cl^-\cdots Cl^-$ in 134 structures of organic chlorides varies in the range of 3.6–3.9 Å; in 76 compounds, this value is smaller than the sum of the van-der-Waals radii of the chlorine atom (3.8 Å), which suggest the possible tendency towards the AA association. The topological analysis of the function $\rho(\mathbf{r})$ in the crystal of hydroxylammonium chloride allowed locating the CP (3, −1) and the corresponding bond path along the line connecting two nearest chloride anions (Fig. 12). Although

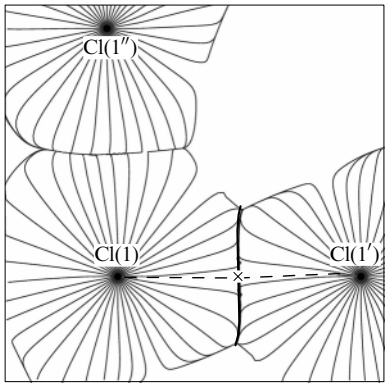


Figure 12. The molecular graph in the section of the $Cl^-\cdots Cl^-$ contact in the crystal of $[NH_3OH]Cl$.
The interatomic surface is specified by a bold line, the bond path is specified by a dashed line; the cross marks the CP (3, −1).[121]

the values of $\rho(\mathbf{r})$ and $\nabla^2\rho(\mathbf{r})$ in the located CP are close to those in NaF (Ref. 95) and NaCl (Ref. 1), the values of the curvature of the electron density function (λ_i) significantly deviated from zero, which allowed authors to unambiguously establish the type of this critical point as CP (3, −1).[121] In spite of the formally 'repulsive' character of the AA contacts, the mechanism of the formation of this interaction $Cl^-\cdots Cl^-$ is the same as for all the intermolecular interactions: the 'transfer' of the electron density from the areas of its accumulation to those of its depletion (Fig. 13). It was shown that the AA interactions in the hydroxylammonium chloride are dispersive in nature and are extremely weak. Their energy (E_{int}) estimated from the

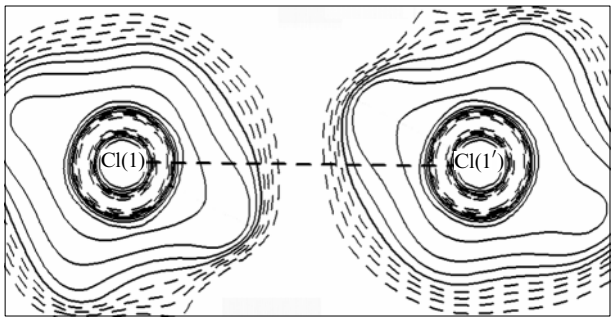
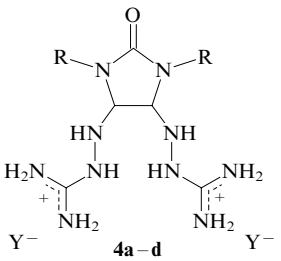


Figure 13. The distribution of the electron localization function in the area of the AA interaction in the crystal of $[NH_3OH]Cl$.[121]

X-ray diffraction data using the Eqn (1) was not more than 1 kcal mol^{-1} (E_{int} = 0.7 kcal mol^{-1}). The distribution of charges makes these interactions $Cl^-\cdots Cl^-$ similar to halogen bonds of the type C–Cl(2)···Cl(1),[122] because the charge of the chlorine atom (−0.28 *e*) in $[NH_3OH]Cl$ owing to the formation of several strong hydrogen CA bonds (with the total energy of 23.4 kcal mol^{-1}) appears to be significantly lower than the formal one, which is −1 *e*. This diminishes the electrostatic repulsion between the anions, apparently, allowing for the occurrence of the AA interactions. On the other hand, the negative charge of the anion that is still significant causes their considerable weakening in comparison with the halogen bonds the energy of which is from 1.2 to 43.0 kcal mol^{-1} in the extreme case.[122] As a result, a conclusion was made that the formation of such AA associates contribute (although slightly) to the crystal stabilization, and the exchange of the cation (and, hence, the variation of CA interactions) may cause the increase in this input. Therefore, the AA interactions can be of considerable interest for the 'crystal engineering'.

The solution of this problem requires information concerning the possibility of appearance of bonding AA interactions in a wide range of ionic crystals, both organic and inorganic, as well as their energy, their role in the crystal packing formation and their influence on the physicochemical characteristics of ionic materials. In this context, systematic investigations devoted to the analysis of various manifestations of the AA association in crystals have recently started to appear.

The influence of weak interactions $NO_3^-\cdots NO_3^-$ on the physicochemical properties of crystals were demonstrated by the example of 1,3-dialkyl-4,5-bis(3-aminoguanidinium)imidazolidin-2-one nitrates and chlorides (**4a**–**d**);[123] for one of them, namely, compound **4a**, the spontaneous resolution into enantiomers (space group $P6_1$) was observed upon crystallization.[124]



4a–**d**

Compound **4**	R	Y
a	Me	Cl
b	Me	NO_3
c	Et	Cl
d	Et	NO_3

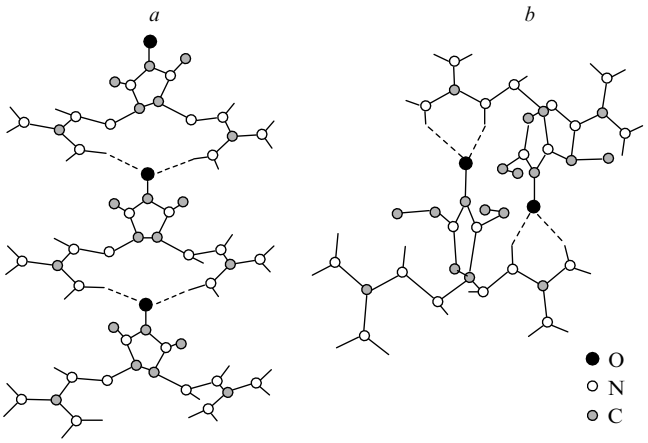


Figure 14. Schematic representation of a translational chain formed by the interactions N–H···O in the crystals of salts **4a**,**b**,**d** (*a*) and that of a dimer formed by the bonds N–H···O in the crystal of compound **4c** (*b*).[123]

Three other salts crystallized in racemic (centrosymmetric) space groups. The spontaneous resolution of salt **4a** can be explained by the presence in a crystal of a chiral associate (a translational chain) formed by the dications linked by strong hydrogen bonds (Fig. 14 *a*), which is thought to be the sufficient condition for the formation of a conglomerate.[125] Indeed, it was shown[123] that the cations in the crystal of **4c** are linked by strong hydrogen bonds (E_{int} = 9.8 kcal mol^{-1} according to the B3LYP/6–31G** calculation) into the centrosymmetric dimers (Fig. 14 *b*), which apparently causes this compound to crystallize as a racemate. However, the crystals of both nitrates were found to contain chains formed by the hydrogen bonds nearly identical to those in the crystals of salt **4a**, although no spontaneous resolution occurred. At a first glance, such a difference may be attributed to the CA interactions providing the additional bonding between the neighbouring dications of a chain in the crystal of salt **4a** (Fig. 15 *a*). The similar stabilization is however observed only for one of the nitrates (compound **4d**) (Fig. 15 *b*), while in the crystal of compound **4b** the nitrate anions do not act as the 'elements holding together the links of a chain' (Fig. 15 *c*). As a result, it was suggested that the racemic packing of the nitrates is related to the formation of the centrosymmetric dimer $NO_3^-\cdots NO_3^-$ (Fig. 16), which is rather common for this type of the anions. Indeed, in the case of the methyl and ethyl derivatives (**4b**, **4d**), the nitrate anions appeared to be bound to each other by the contacts O···π (or π···π) (see Fig. 16) with the shortened distance O···N [2.763(2)–3.180(2) Å]. Thus, the data obtained[123] showed that the role of strong hydrogen bonds is, in general, exaggerated. Weak interactions of the type $NO_3^-\cdots NO_3^-$ can also play the determining role in the stabilization of a certain crystal packing and can indirectly have significant influence on the physicochemical properties of crystals.

As the quality of the crystals of both nitrates was not high enough to derive the function $\rho(\mathbf{r})$ from the experimental data, the strength of the interactions $NO_3^-\cdots NO_3^-$ was estimated later[126] in the study of a model compound, urea nitrate, in the crystal of which similar AA dimers [O···O 2.9688(4) Å, N···O 3.0583(4) Å] are present. In this case, the contacts $NO_3^-\cdots NO_3^-$, which correspond to the bonding interactions based on the presence of the CP

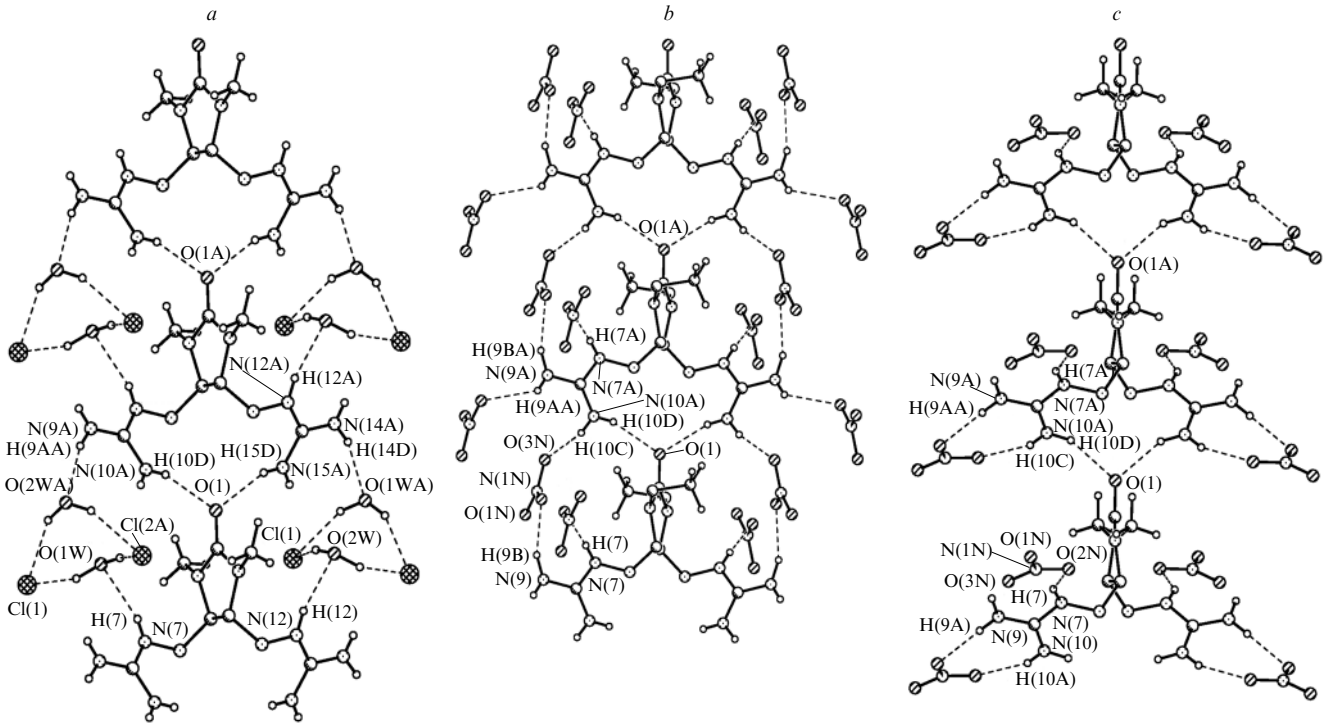


Figure 15. Hydrogen-bonded translational chains in the crystals of salts **4a** (*a*), **4d** (*b*) and **4b** (*c*).[123]

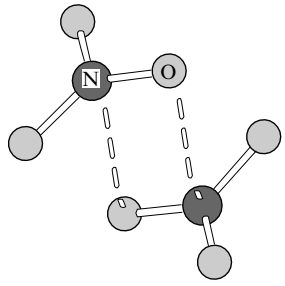


Figure 16. A general view of the dimers $(NO_3)_2^{2-}$ in the crystals of salts **4b**,**d**.[123]

(3,−1) and the corresponding bond path, together with the CA interactions of the type nitrate···π-system of the cation [C···O 3.0201(4) Å] assembled the hydrogen-bonded layers forming the 'pseudo-tetramer' (Fig. 17). Although the anions in the crystal of urea nitrate are slightly shifted relative to each other as compared with the crystals of salts **4b**,**d**,[124] this AA interaction was described as the π···π type owing to the delocalization of the electron density over the anion, while the CA bonding in the 'pseudo-tetramer' corresponded to the interaction between the oxygen atom of the anion and the cation π-system. Taking into account the similarity of the geometrical parameters of these interactions, one can expect their energies to be of the same order of magnitude. Indeed, the values of the energy obtained were 1.4 and 1.3 kcal mol^{-1}, which, according to the geometrical parameters, can be considered the realistic estimate for the AA interactions in nitrates **4b**,**d**. This value appeared to be significantly higher than that for the AA association in the crystal of hydroxylammonium chloride.[121] The assumption was made that, although the charge of the nitrate anion (−0.47 *e*) in the urea nitrate is higher than that of the ion Cl^- in hydroxylammonium chloride (−0.28 *e*), the higher accumulation of the charge density on the oxygen atoms (−1.18 *e*) of the ion NO_3^- leads to the

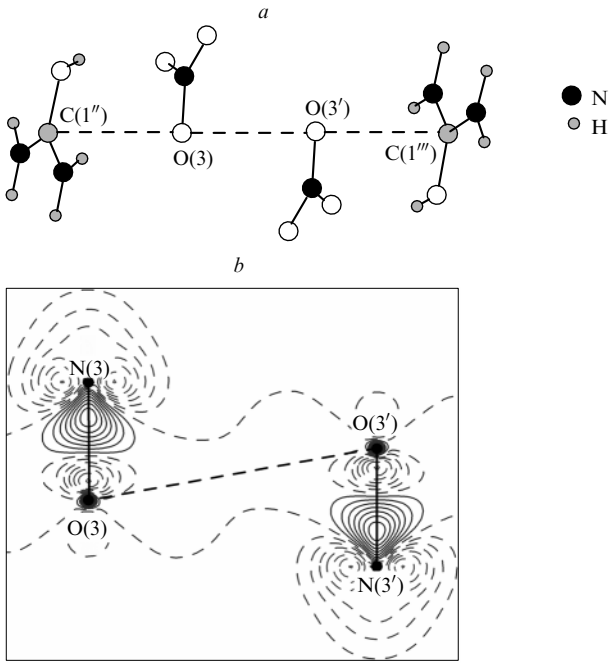


Figure 17. A general view of the 'pseudo-tetramer' formed through the contacts $NO_3^-\cdots NO_3^-$ and $NO_3^-\cdots$π-system of the cation in the crystal of urea nitrate (*a*) and the deformation electron density distribution in the area of the AA interaction (*b*).[126]

more effective overlap of electronic shells of the interacting atoms and, hence, to the strengthening of the AA interaction in urea nitrate.[126]

It is to be mentioned that, based on the results of the analysis of CCDC data carried out in the study,[123] certain mutual disposition of nitrate anions is characteristic of the

crystals of organic nitrates, and, hence, the analogous AA bonding can also be observed in many other crystalline nitrates. The presence of a multi-charged cation in a salt is most likely to cause the increase in the input of the AA association into the stabilization of the crystals of nitrates. Such effect was observed in the crystal of neopentanetetrayltetrammonium nitrate (**5**)[127] in which four different nitrate anions form multiple contacts $NO_3^- \cdots NO_3^-$ (Fig. 18).

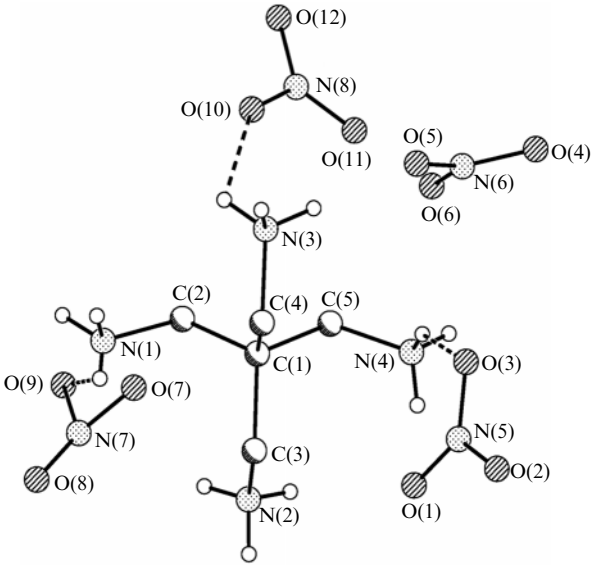


Figure 18. A general view of a formula unit in the crystal of neopentanetetrayltetrammonium nitrate (**5**).[127]

According to the results of the topological analysis of the function $\rho(\mathbf{r})$, the energy of these AA interactions was up to 3.2 kcal mol^{-1} and in total reached 10.9% (for comparison, in the case of the urea nitrate this value[126] was not more than 5%) of the energy of all the bonding interactions per formula unit of compound **5**. Moreover, the detailed analysis of interionic interactions in this crystal showed that the strength of the CA hydrogen bonds formed by each nitrate anion does not correlate with the charges of the corresponding anions. As the additional CA interactions of the types C–H···O and N···O contribute in total only 2 kcal mol^{-1} into the stabilization of the system, the conclusion was made that the absence of such a correlation was caused by the AA association. Indeed, the nitrate anions not only 'donate' the electron density to the cations through the system of the CA hydrogen bonds, but also act as its acceptors in the formation of the AA interactions (Fig. 19). This causes the redistribution of the charge over the anionic sublattice, which, in turn, affects the strength of the hydrogen bonds with the cation. Thus, although these are the hydrogen bonds that make the main contribution into the stabilization of the crystal lattice of compound **5**, the interactions between the nitrate anions can also be considered structure-forming ones.

The presence of the AA interactions in the condensed state can also be confirmed independently, for instance, using the electronic absorption spectroscopy. This was accomplished in the study of disodium pentacyanonitrosoferrate dihydrate (sodium nitroprusside).[128] In its crystal, the shortened [2.6423(5) Å] contacts O···O (Fig. 20) were found between the neighbouring anions, which is common

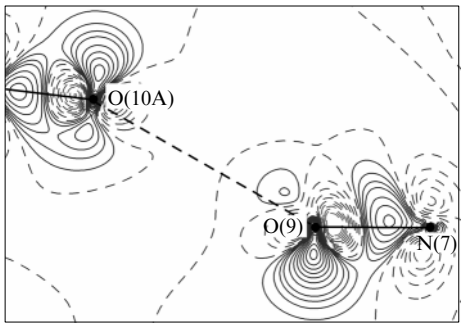


Figure 19. The deformation electron density distribution in the area of the AA dimer in the crystal of neopentanetetrayltetrammonium nitrate (**5**).[127]

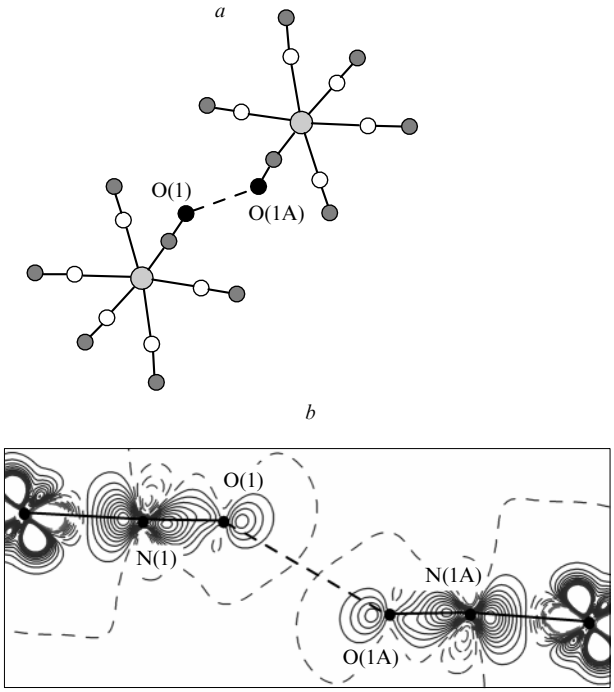


Figure 20. A fragment of the crystal packing for sodium nitroprusside illustrating the formation of the contact O···O (*a*) and the corresponding deformation electron density distribution (*b*).[128]

for the most of the nitroso-containing compounds (137 ordered structures were found in CCDC with the distance O···O in the range of 2.5–3.1 Å). As it has been shown earlier by the EAS analysis,[11] the AA association involving the nitroso group of the nitroprusside moiety is common for the systems $[FeNO(CN)_5]^{2-}$–X (X is an anion acting as a reducing agent) in solution.[129,130] The possibility of the anions to approach each other in the crystal was also proven by the potentiometric data[128] indicating that the CA bonding involve only the interactions with the cyano groups. The latter is apparently caused by the electrostatic reasons, *i.e.*, by the pronounced concentration of the charge density on the CN fragments the charge of which varied from -0.64 to -0.30 *e* in the crystal. The nitroso group also appeared to be negatively charged (-0.34 *e*), which contradicts the commonly assumed positive value of its charge.[131] The published vibrational frequency in $[FeNO(CN)_5]^{2-}$ [ν(N–O) = 1900 cm^{-1}][131] is, however, close to that for

the neutral molecule NO (1876 cm^{-1}),[131] which cannot be considered as a proof of the positive charge on the nitroso group of the ion $[FeNO(CN)_5]^{2-}$. The negative charge on the group NO also agrees with the results of the experimental and theoretical investigations of the nitroprusside anion.[132, 133] The total charge of the anion in the crystal of sodium nitroprusside appeared to be -1.75 *e*. On the one hand, the high negative charge should cause the strong electrostatic repulsion between the species and the significant weakening of the bonding AA interactions, the occurrence of which in sodium nitroprusside followed from the presence of the corresponding CP (3, −1) along the line O···O.[128] On the other hand, the obtained value of the charge transfer from the anion (0.25 *e*) indicated the relative weakness of the CA bonds. Indeed, the energy of the CA bonds and the interactions of the cation with water molecules in the crystal were estimated to be less than 3.9 kcal mol^{-1}, while for the AA association this value approached 3.0 kcal mol^{-1}. The strengthening of the interactions O···O in the crystal of sodium nitroprusside[128] as compared with those in urea nitrate[126] was explained by the decrease in the interatomic distance while the charge on the oxygen atoms is practically the same (-0.32 *e* in sodium nitroprusside[128] and -0.33 *e* on average in urea nitrate[126]), which provides more effective overlap of valence shells of the oxygen atoms. The contribution of the AA association in the crystal of sodium nitroprusside is 17% of the total interaction energy; this is probably sufficient for it to persist in solution.

The electrostatic component of all the above AA interactions destabilized the system, as they involved like-charged ions and, moreover, the atoms directly bound were the atoms bearing the charge of the same sign. It is evident that the contribution of this component should be lower than that in the case of the salts containing the anions that are able to bind in a 'plus-to-minus' manner. One of such 'building blocks' was the chloride anion the geometry of which (a trigonal pyramid) allows the oxygen atoms of the neighbouring fragment ClO_3^- to easily approach the chlorine atom. The statistical analysis of the crystal structures of chlorates[134] showed that the anions are located in the similar way in most chlorates [from the Inorganic Crystal Structure Database (ISCD)], where short (2.868–3.064 Å) and directional contacts Cl···O complete the formation of the coordination sphere of the chlorine atom. This was also observed for two of ten known structures with bulky cations (according to the analysis of CSD). Their energy was estimated by the topological analysis of the function $\rho(\mathbf{r})$ performed for the crystal of sodium chlorate.[134] In this case, the CA interactions are the bonds Na−O, which, according to the results of the investigation of sodium nitroprusside[128] (E_{int} < 3.7 kcal mol^{-1}), are rather weak. Thus, the value of the charge transfer in the crystal of sodium chlorate (0.09 *e*) indicated the high competivity of the interactions Cl···O (Fig. 21) present therein. This allowed expecting that the AA association was the dominant one in the crystal of sodium chlorate. The interaction energy Cl···O was, however, 2.0 kcal mol^{-1} only, although the total contribution of three AA bonds (the coordination number of the chlorine atom is 6) approached 23% of the energy of all the interactions in the crystal. On the other hand, the nature of the interactions Cl···O makes them similar to bonds $AnO_2^+\cdots AnO_2^+$ (Refs 10 and 30) the presence of which in some crystalline salts and

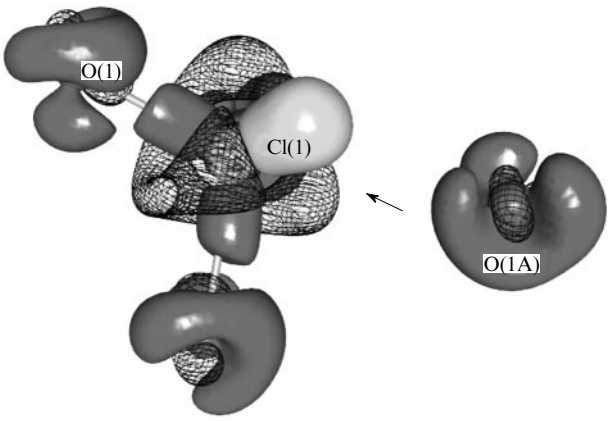


Figure 21. The three-dimensional deformation electron density distribution in the area of the Cl(1)···O in the crystal of sodium chlorate.[134] An arrow indicates the direction of the charge transfer, namely, from the lone electron pair of the oxygen atom O(1A) to the antibonding orbital of the bond Cl(1)−O(1).

solutions manifested in the IR spectra and EAS as well as in some physicochemical properties.

It is evident that the most effective bonding is ensured where the anions are bound by hydrogen bonds, which are among the strongest interactions.[5] This assumption was confirmed experimentally by the example of potassium hydrogen phthalate[135] the crystal structure of which is formed by the AA hydrogen [O···O 2.5357(4) Å, ∠OHO 171(2)°] and CA coordination [K···O 2.6266(2)–3.5120(3) Å] bonds only (Fig. 22). The energy of the CA interactions in the crystal of potassium hydrogen phthalate appeared to be rather low (0.4–4.8 kcal mol^{-1}) and comparable with that for the additional interactions C−H···O and C−H···C (0.5–1.6 kcal mol^{-1}), which agrees with the rather small value of the charge transfer (0.05 *e*). The hydrogen bond between the anions is, in

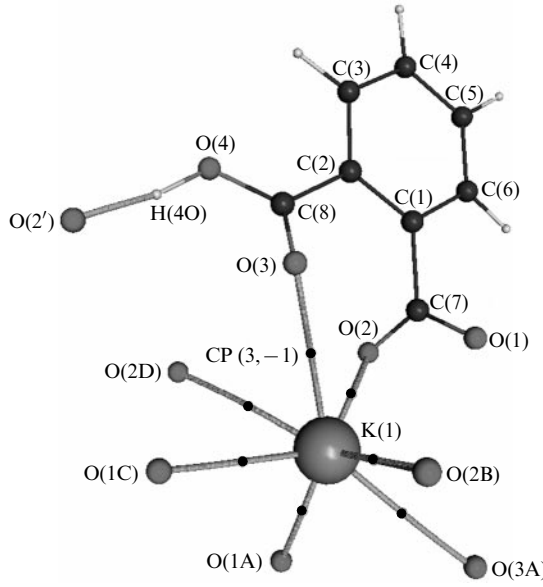


Figure 22. The CP (3, −1) and the bond paths for the coordination interactions K−O and the hydrogen bond in the crystal of potassium hydrogen phthalate.[135]

contrast, rather strong (43.3 kcal mol^{-1}), and its energy is 2.5 times greater than the total energy of the CA interactions (17.8 kcal mol^{-1}). As a result, the conclusion was made that the driving force for the supramolecular organization in the crystal of potassium hydrogen phthalate is the 'self-assembly' of anions and the subsequent formation of the coordination bonds K$-$O.[135]

The similar situation apparently takes place in the case of alkali metal acid salts of dicarboxylic acids. Some investigators[2] still assume that the hydrogen AA bonds in crystals of these salts should be considered exclusively as secondary ones, caused by the approach of anions owing to the CA bonds. Moreover, the results of their investigations based on the calculations of the isolated AA associates that are not refer to the real systems are included as a classical example into the textbooks of supramolecular chemistry.[136] At the same time, the data obtained to date unambiguously suggest that the strength of the AA interactions may be not only comparable with, but even significantly greater than, that of CA bonds. To demonstrate that the hydrogen bonds between the anions do not differ in principle from the classical ones, the detailed investigation was performed for pyridiniosuccinate (**6**), which exists as a zwitterion in the crystal (Fig. 23).[137] The corresponding interactions COOH$\cdots$COO$^-$ are intermediate between the classical (neutral species are involved) and anion$-$anion (negatively charged fragments are directly bound) hydrogen bonds. In contrast to the AA interactions, the bonding character of such 'pseudo-anion' bonds is however not being called into question. On the other hand, analysis of the hydrogen bonds between zwitterions can be done by the quantum chemical methods as well as by the experimental approach on the basis of Bader's 'Atoms in Molecules' theory. To compare this type of bonding with that between neutral and charged species, a quantum chemical investigation was also carried out for compound **6**, its analogue, acid **7a** and its anion **7b** as well as their hydrogen-bonded dimers in the gas phase (Fig. 23, 24).[137]

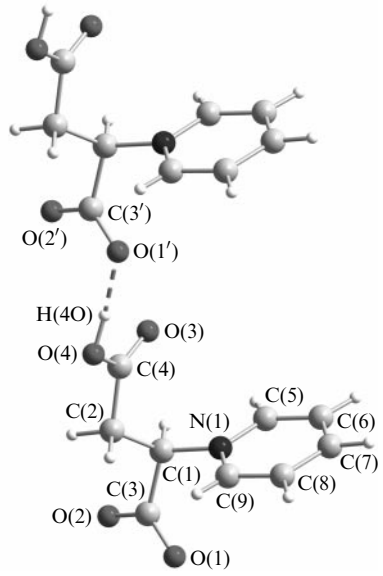


Figure 23. A fragment of the packing of pyridiniosuccinate (**6**) illustrating the formation of the hydrogen bond COOH$\cdots$COO$^-$ (Ref. 137).

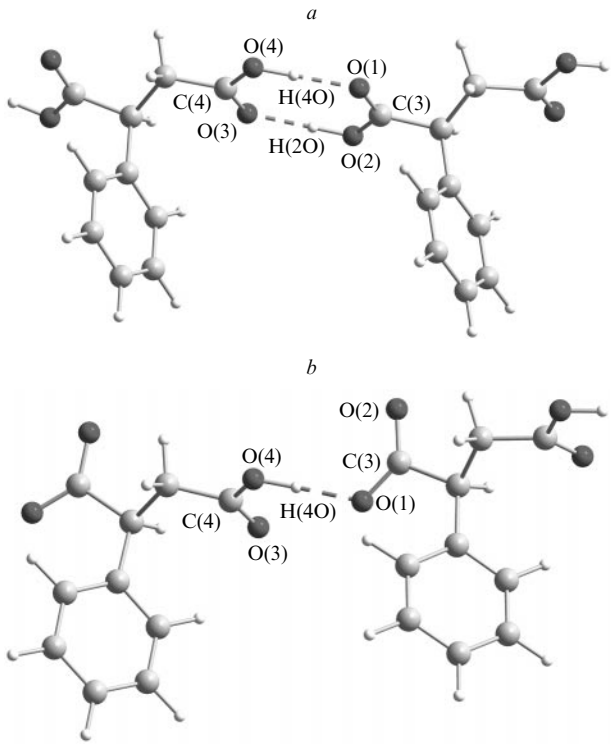
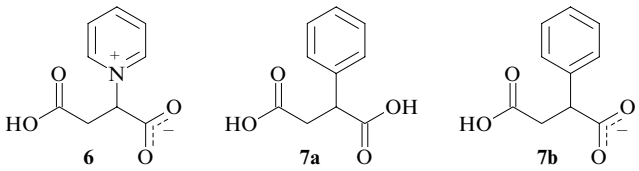


Figure 24. A general view of the hydrogen-bonded dimers of the model acid **7a** (*a*) and its anion **7b** (*b*).[137]



It is to be mentioned that although the calculations of dimers formed by monoanions of dicarboxylic acids suggest the non-existence of the hydrogen-bonded AA associates,[2] the modelled[137] AA dimer, which was geometrically equivalent to the dimer of ions **6** in the isolated state and in the crystal, appeared to be stable in the gas phase (according to the Pbe1Pbe/6-311G(d,p) calculation). The topological analysis of the function $\rho(\mathbf{r})$ in crystal carried out for derivative **6** and for the three types of the calculated associates showed that these interactions between zwitterions and between anions meet all the criteria of hydrogen bonding and are equivalent to the classical hydrogen bonds. In all cases, the CP (3,$-$1) and the corresponding bond paths were located, the dimer formation was accompanied by the structural rearrangements of species, by changes in atomic charges and energies that were similar for all three types of species (molecules of the acid, zwitterions, and anions).[138] The only significant difference was observed in the case of the energies of the hydrogen bonds calculated as the difference between the energy of a dimer and twice the energy of a monomer (ΔE). The values obtained (Table 1) for the dimers of zwitterions and molecules of acid (15.4 and 19.1 kcal mol^{-1}) showed the considerable stabilization owing to the formation of the hydrogen bond, while the dimerization of the isolated anions destabilized the system by $\sim$21.2 kcal mol^{-1}. The interaction energy (E_{int}) estimated by means of the Eqn (1) reproduced well the value

Table 1. The energies of hydrogen bonds calculated as the difference between the energy of dimer and twice the energy of a monomer (ΔE) and using equation (1) (E_{int}).[137]

System	$d_{O\cdots O}$ /Å	ΔE /kcal mol^{-1}	E_{int} /kcal mol^{-1}
Crystal of **6**	2.5219(5)	–	23.2
Dimer of zwitterion **6**	2.597	19.1	18.7
Dimer of acid **7a**	2.631	15.4	16.3
Dimer of anion **7b**	2.634	−21.2	15.3

ΔE for the former (16.3–23.2 kcal mol^{-1}) and, moreover, correlated with the distance O···O for all the four systems. The energy of the hydrogen bonds between the anions thus calculated appeared to be 15.3 kcal mol^{-1}. Thus, the destabilization of the AA dimer is not caused by the 'electrostatic' component of the hydrogen AA bond, which was also expected from the literature analysis.[139–141] As a result, the conclusion was made that for the estimation of the interaction energy the approach based on the AIM theory should be used instead of, or at least in addition to, the difference in the energies of the dimer and the monomer. This approach not only allows estimating the strength of the interaction with rather high accuracy (see the energies obtained using both these methods for the neutral species), but also indicate the bonding nature of AA hydrogen bonds that are considered by the majority of researchers to be stabilizing ones. This agrees entirely with the data from NMR and IR spectroscopy[139, 140] indicating the close resemblance between the classical and anion–anion hydrogen bonds. Therefore, the latter are, to the full extent, the hydrogen bonds, *i.e.*, strong and directional interactions that can play the decisive role in the formation of crystal packing of the corresponding compounds.

The similarity between AA and CC interactions and classical CA bonds was additionally demonstrated on the basis of the detailed investigation of the electron density in the crystals of glycinium trifluoroacetate, glycinium naphthalene-1,5-disulfonate monohydrate and glycine α-polymorph.[142] In the first two structures, a great number of bonding CC and AA interactions, mainly the contacts C–H···O, were found in addition to the CA bonds. On the basis of their energies estimated from the X-ray diffraction data,[142] it was shown that the strength of the interactions C–H···O is independent of their type (CC or CA). This followed from the close values E_{int} for the similar interactions C–H···O (between oppositely charged species as well as like-charged ones) in the above crystals. Although the conclusion made is intuitive, any quantum chemical calculation of a CC pair formed by such a contact C–H···O will show that it does not lead to the gain in energy.

The presence of numerous hydrogen bonds and interactions C–H···O with different geometry and nature of the fragments involved in the three above structures allowed testing whether the length (d) of the O···H bonds correlates with the attributed energy (E_{cont}).[142] The linear correlation is observed for 25 symmetry-independent interactions with the distance O···H up to ~1.9 Å with the abrupt change in the slope when this value is achieved (Fig. 25); one can see that the interaction energy is indeed independent of the type of the interactions (CC or CA). Some deviations near the value of the distance O···H of ~1.9 Å are caused by the fact that the strength of such an interaction is determined by both the distance between the interacting centres and its directionality, *i.e.*, the degree of overlap of the lone electron pair of the oxygen atom and the electron density on the hydrogen atom. The results obtained[142] illustrate the potential mistakes in locating and estimating the strength of interactions based exclusively on their classification according to the charges of the interacting species.

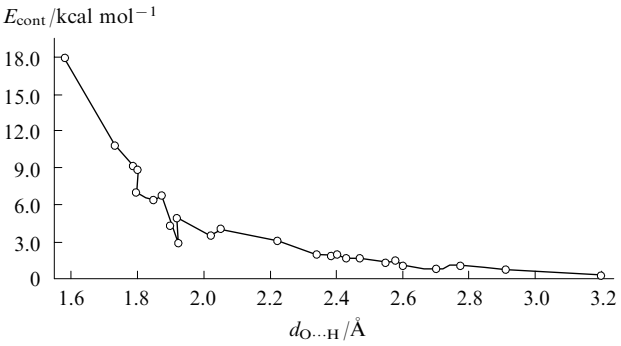


Figure 25. The dependence of the interaction energy on the interatomic distance O···H for the hydrogen bonds and the interactions C–H···O in the crystals of glycinium trifluoroacetate, glycinium naphthalene-1,5-disulfonate monohydrate and α-polymorph of glycine.[142]

* * *

The information summarized in the review clearly demonstrates that bonding interactions between like-charged species, in addition to the expected CA bonds, in the crystals of salts make significant contribution to the crystal packing stabilization. Anion–anion interactions are observed in crystals with cations and anions of nearly the molecular nature as well as in the case of mainly ionic compounds. The AA interactions are not the 'exotic' feature of several structures only or the 'artifact' of the methods used for the investigation. In contrast, their manifestation can be expected for numerous organic and inorganic salts with the anions CO_3^{2-}, NO_3^-, ClO_3^-, or $[FeNO(CN)_5]^{2-}$. In the latter case, the AA association is apparently the characteristic feature of the corresponding crystals and solutions. The data obtained are independently confirmed by other physicochemical methods, such as electronic absorption spectroscopy, NMR and IR spectroscopy. Moreover, dividing the contacts into types CA, CC, and AA is arbitrary and is based on the primitive concepts of the theoretical chemistry, which are hardly applicable to the real systems, in particular, to the crystals of the salts with numerous hydrogen bonds. In the case of the latter, the strength of the AA interactions can be comparable with that for the CA bonds and sometimes can exceed it. Thus, the strong hydrogen bonds between anions, which do not differ dramatically from the classical hydrogen bonds, can play the structure-forming role in the crystal packing stabilization. Moreover, even weak AA interactions can lead to the formation of certain AA associates (for instance, heterochiral ones) and, hence, significantly affect the physicochemical properties of crystals, solutions, materials. Thus, the problem of locating and qualitatively describing non-classical types of interactions in general and the AA association in particular is rather important, and further investigations are likely to create a greater variety of 'tools' for the specialists in the field of the crystal engineering, supramolecular chemistry and the directional design of materials with predetermined properties.

References

1. A M Pendas, A Costales, V Luana *J. Phys. Chem. B* **102** 6937 (1998)
2. D Braga, F Grepioni, J J Novoa *Chem. Commun*. 1959 (1998)
3. M A Carvajal, I Garcia-Yoldi, J J Novoa *J. Mol. Struct. (THEOCHEM)* **727** 181 (2005)
4. L Puntus, K Lyssenko, I S Pekareva, J-C G Bunzli *J. Phys. Chem. B* **113** 9265 (2009)
5. M Meot-Ner *Chem. Rev*. **105** 213 (2005)
6. P Hobza, J Sponer *J. Comput. Chem*. **16** 1315 (1995)
7. S Grimme *Angew. Chem., Int. Ed*. **45** 4460 (2006)
8. M D Wodrich, C Corminboeuf, P R Schleyer *Org. Lett*. **8** 3631 (2006)
9. R Hoffmann, P R Schleyer, H F Schaefer III *Angew. Chem., Int. Ed*. **47** 7164 (2008)
10. N N Krot, M S Grigoriev *Usp. Khim*. **73** 94 (2004) [*Russ. Chem. Rev*. **73** 89 (2004)]
11. V Yu Kotov, S I Gorel'skii *Izv. Akad. Nauk, Ser. Khim*. 823 (1999) [a]
12. I Alkorta, J Elguero *Struct. Chem*. **15** 117 (2004)
13. R F W Bader *Atoms in Molecules. A Quantum Theory* (Oxford: Clarendon Press, 1990)
14. E Espinosa, E Molins, C Lecomte *Chem. Phys. Lett*. **285** 170 (1998)
15. E Espinosa, I Alkorta, I Rozas, J Elguero, E Molins *Chem. Phys. Lett*. **336** 457 (2001)
16. P A Gale, K Navakhun, S Camiolo, M E Light, M B Hursthouse *J. Am. Chem. Soc*. **124** 11228 (2002)
17. J Sanchez-Quesada, C Seel, P Prados, J de Mendoza *J. Am. Chem. Soc*. **118** 277 (1996)
18. B Hasenknopf, J M Lehn, B O Kniesel, G Baum, D Fenske *Angew. Chem., Int. Ed. Engl*. **35** 1838 (1996)
19. B Hasenknopf, J M Lehn, N Boumediene, A Dupont-Gervais, A van Dorsselar, B Kniesel, D Fenske *J. Am. Chem. Soc*. **119** 10956 (1997)
20. S Camiolo, P A Gale, M B Hursthouse, M E Light, A J Shi *Chem. Commun*. 758 (2002)
21. K A Lyssenko, D A Lenev, R G Kostyanovsky *Tetrahedron* **58** 8525 (2002)
22. R G Kostyanovsky, K A Lyssenko, Yu I El'natanov, O N Krutius, I A Bronzova, Yu A Strelenko, V R Kostyanovsky *Mendeleev Commun*. 106 (1999)
23. M J Chmielewski, J Dobrzycki, J Jurczak, K Wozniak *Cryst. Growth Des*. **5** 1339 (2005)
24. J-P Behr, J M Lehn, A-C Dock, D Moras *Nature (London)* **259** 526 (1982)
25. M W Hosseini, R Ruppert, P Schaffer, A DeCian, N Kyritsaka, J Fischer *J. Chem. Soc., Chem. Commun*. 2135 (1994)
26. T Akutagawa, T Hasegawa, T Nakamura, S Takeda, T Inabe, K Sugiura, Y Sakata, A E Underhill *Chem. – Eur. J*. **7** 4902 (2001)
27. M J Chmielewski, J Jurczak *Tetrahedron Lett*. **45** 6007 (2004)
28. J M Williams, J R Ferraro, R J Thorn, K D Carlson, U Geiser, H H Wang, A M Kini, M-H Whangbo *Organic Superconductors (Including Fullerenes). Synthesis, Structure, Properties, and Theory* (Englewood Cliffs, NJ, 1992)
29. K Muller-Dethlefs, P Hobza, T Reschel *Chem. Rev*. **100** 143 (2000)
30. I A Charushnikova, N N Krot, V P Perminov *Radiokhimiya* **43** 193 (2001) [b]
31. G Nocton, P Horeglad, J Pecaut, M Mazzanti *J. Am. Chem. Soc*. **130** 16633 (2008)
32. R T Butcher, J J Novoa, J Ribas-Arino, A W Sandvik, M M Turnbull, C P Landee, B M Wells, F F Awwadi *Chem. Commun*. 1359 (2009)
33. S I Gorel'skii, T G Kim, T P Klimova, V Yu Kotov, B V Lokshin, Yu D Perfil'ev, I I Sherbak, G A Tsirlina *Mendeleev Commun*. 86 (2000)
34. A Vegas, R L Martin, D J M Bevan *Acta Crystallogr., Sect. B* **65** 11 (2009)
35. M A Carvajal, S Alvarez, J J Novoa *Chem. – Eur. J*. **10** 2117 (2004)
36. M A Carvajal, S Alvarez, J J Novoa *Theor. Chem. Acc*. **116** 472 (2006)
37. P Pyykko, T Tamm *Organometallics* **17** 4842 (1998)
38. J Zank, A Schier, H Schmidbaur *J. Chem. Soc., Dalton Trans*. 323 (1998)
39. J P Fackler *Inorg. Chem*. **41** 6959 (2002)
40. A Vegas *Crystallogr. Rev*. **7** 189 (2000)
41. I Garcia-Yoldi, J S Miller, J J Novoa *J. Phys. Chem. A* **113** 484 (2009)
42. P M B Piccoli, A J Schultz, H A Sparkes, J A K Howard, A M Arif, L N Dawe, J S Miller *CrystEngComm*. **11** 686 (2009)
43. J J Novoa, P Lafuente, R E Del Sesto, J S Miller *CrystEngComm*. **4** 373 (2002)
44. J J Novoa, I Nobeli, F Grepioni, D Braga *New J. Chem*. **24** 5 (2000)
45. D Braga, L Maini, F Grepioni, F Mota, C Rovira, J J Novoa *Chem. – Eur. J*. **6** 4536 (2000)
46. S Ansell, G W Neilson *J. Chem. Phys*. **112** 3942 (2000)
47. S Ansell, R H Tromp, G W Neilson *J. Phys. Condens. Matter* **7** 1513 (1995)
48. J Gao, S Boudon, G Wipff *J. Am. Chem. Soc*. **113** 9610 (1991)
49. V G Tsirelson, R P Ozerov *Electron Density and Bonding in Crystals: Principles, Theory and X-Ray Diffraction Experiments in Solid State Physics and Chemistry* (Bristol, Philadelphia: IOP Publ., 1996)
50. P Hohenberg, W Kohn *Phys. Rev. B* **136** 864 (1964)
51. I S Bushmarinov, K A Lyssenko, M Yu Antipin *Usp. Khim*. **78** 307 (2009) [*Russ. Chem. Rev*. **78** 283 (2009)]
52. R F W Bader, T T Nguyen-Dang, A Tal *Rep. Prog. Phys*. **44** 893 (1981)
53. R F W Bader, P L A Popelier, T A Keith *Angew. Chem., Int. Ed. Engl*. **33** 620 (1994)
54. R F W Bader *Chem. Rev*. **91** 893 (1991)
55. R F W Bader *Chem. – Eur. J*. **12** 2896 (2006)
56. R F W Bader, E Essgn *J. Chem. Phys*. **80** 1943 (1984)
57. D Cremer, E Kraka *Croat. Chem. Acta* **57** 1259 (1984)
58. K A Lyssenko, M Yu Antipin, V N Khrustalev *Izv. Akad. Nauk, Ser. Khim*. 1465 (2001) [a]
59. K A Lyssenko, M Yu Antipin, V N Lebedev *Inorg. Chem*. **37** 5834 (1998)
60. S Pillet, G Wu, V Kulsomphob, B G Harvey, R D Ernst, P Coppens *J. Am. Chem. Soc*. **125** 1937 (2003)
61. K A Lyssenko, M Yu Antipin *Izv. Akad. Nauk, Ser. Khim*. 1 (2006) [a]
62. V G Tsirelson *Acta Crystallogr., Sect. B* **58** 632 (2002)
63. K A Lyssenko, A A Korlyukov, M Yu Antipin *Mendeleev Commun*. 90 (2005)
64. K A Lyssenko, M Yu Antipin *Izv. Akad. Nauk, Ser. Khim*. 400 (2001) [a]
65. E A Pidko, R A van Santen *ChemPhysChem*. **7** 1657 (2006)
66. E A Pidko, J Xu, B L Mojet, L Lefferts, I R Subbotina, V B Kazansky, R A van Santen *J. Phys. Chem. B* **110** 22618 (2006)
67. L Sobczyk, S J Grabowski, T M Krygowski *Chem. Rev*. **105** 3513 (2005)
68. A O Borissova, A A Korlyukov, M Y Antipin, K A Lyssenko *J. Phys. Chem. A* **112** 11519 (2008)
69. L N Puntus, K A Lyssenko, M Y Antipin, J-C G Bunzli *Inorg. Chem*. **47** 11095 (2008)
70. V G Tsirelson, P F Zou, T H Tang, R F W Bader *Acta Crystallogr., Sect. A* **51** 143 (1995)
71. V G Tsirelson *Can. J. Chem*. **74** 1171 (1996)
72. P F Zou, R F W Bader *Acta Crystallogr., Sect. A* **50** 714 (1994)
73. A M Pendas, A Costales, V Luana *Phys. Rev. B* **55** 4275 (1997)
74. V Luana, J M Recio, L Pueyo *Phys. Rev. B* **42** 1791 (1990)
75. V Luana, A M Pendas, J M Recio, E Francisco, M Bermejo *Comput. Phys. Commun*. **77** 107 (1993)
76. J M Recio, A M Pendas, E Francisco, M Florez, V Luana *Phys. Rev. B* **48** 5891 (1993)
77. A Vegas, D Santamaria-Perez, M Marques, M Florez, V G Baonza, J M Recio *Acta Crystallogr., Sect. B* **62** 220 (2006)
78. A Vegas, M Jansen *Acta Crystallogr., Sect. B* **58** 38 (2002)

79. A Vegas, V Garcia-Baonza *Acta Crystallogr., Sect. B* **63** 339 (2007)
80. Z W Su, P Coppens *Acta Crystallogr., Sect. A* **51** 27 (1995)
81. Y A Abramov *J. Phys. Chem. A* **101** 5725 (1997)
82. R F W Bader *J. Phys. Chem. A* **102** 7314 (1998)
83. L Pauling *The Nature of the Chemical Bond* (Ithaca, NY: Cornell University Press, 1960)
84. KL Geisinger, M A Spackman, G V Gibbs *J. Phys. Chem.* **91** 3237 (1987)
85. J W Downs, R J Swope *J. Phys. Chem.* **96** 4834 (1992)
86. R D Shannon *Acta Crystallogr., Sect. A* **32** 751 (1976)
87. E Francisco, J M Recio, M A Blanco, A M Pendas, A Costales *J. Phys. Chem. A* **102** 1595 (1998)
88. E Francisco, A M Pendas, A Costales *J. Phys. Chem. A* **106** 335 (2002)
89. V Luana, A Costales, A M Pendas, M Florez, V M G Fernandez *Solid State Commun.* **104** 47 (1997)
90. V Luana, A Costales, A M Pendas *Phys. Rev. B* **55** 4285 (1997)
91. J Cioslowski, L Edgington, B B Stefanov *J. Am. Chem. Soc.* **117** 10381 (1995)
92. I Alkorta, J Elguero *J. Am. Chem. Soc.* **124** 1488 (2002)
93. I Hargittai *The Structure of Volatile Sulphur Compounds* (Dordrecht: Reidel, 1985)
94. J E Peralta, R H Conteras, J P Snyder *Chem. Commun.* 2025 (2000)
95. V Tsirelson, Y Abramov, V Zavodnik, A Stash, E Belokoneva, J Stahn, U Pietsch, D Feil *Struct. Chem.* **9** 249 (1998)
96. V G Tsirelson, A S Avilov, G G Lepeshov, A K Kulygin, J Stahn, U Pietsch, J C H Spence *J. Phys. Chem. B* **105** 5068 (2001)
97. V G Tsirelson, A V Shishkina, A I Stash, S Parsons *Acta Crystallogr., Sect. B* **65** 647 (2009)
98. V G Tsirelson, A S Avilov, Y A Abramov, E L Belokoneva, R Kitaneh, D Feil *Acta Crystallogr., Sect. B* **54** 8 (1998)
99. G V Gibbs, D F Cox, K M Rosso, N L Ross, R T Downs, M A Spackman *J. Phys. Chem. B* **111** 1923 (2007)
100. G V Gibbs, R T Downs, C T Prewitt, K M Rosso, N L Ross, D F Cox *J. Phys. Chem. B* **109** 21788 (2005)
101. Y Aray, J Rodriguez *ChemPhysChem.* **2** 599 (2001)
102. S Gottlicher, A Vegas *Acta Crystallogr., Sect. B* **44** 362 (1988)
103. G V Gibbs, A F Wallace, D F Cox, P M Dove, J W Downs, N L Ross, K M Rosso *J. Phys. Chem. A* **113** 736 (2009)
104. R Bianchi, G Gervasio, D Marabello *Inorg. Chem.* **39** 2360 (2000)
105. V G Tsirelson, O A Evdokimova, E L Belokoneva, V S Urusov *Phys. Chem. Miner.* **17** 275 (1990)
106. R Nada, C R A Catlow, R Dovesi, C Pisani *Phys. Chem. Miner.* **17** 353 (1990)
107. G V Gibbs, M B Boisen, K M Rosso, D M Teter, M S T Bukowinski *J. Phys. Chem. B* **104** 10534 (2000)
108. G V Gibbs, R T Downs, D F Cox, N L Ross, M B Boisen, K M Rosso *J. Phys. Chem. A* **112** 3693 (2008)
109. C F Matta, N Castillo, R J Boyd *J. Phys. Chem. B* **110** 563 (2006)
110. Y Kuwayama, K Hirose, N Sata, Y Ohishi *Science* **309** 923 (2005)
111. G V Gibbs, M A Spackman, D Jayatilaka, K M Rosso, D F Cox *J. Phys. Chem. A* **110** 12259 (2006)
112. V Luana, A Costales, P Mori-Sanchez, A M Pendas *J. Phys. Chem. B* **107** 4912 (2003)
113. D S Kosov, P L A Popelier *J. Chem. Phys.* **113** 3969 (2003)
114. D S Kosov, P L A Popelier *J. Phys. Chem. A* **104** 7339 (2000)
115. R Bianchi, A Forni, R Oberti *Phys. Chem. Miner.* **32** 638 (2005)
116. G R Desiraju, T Steiner *The Weak Hydrogen Bond* (New York: Oxford University Press, 1999)
117. E A Zhurova, V G Tsirelson, A I Stash, A A Pinkerton *J. Am. Chem. Soc.* **124** 4574 (2002)
118. A H Pakiari, K Eskandari *J. Mol. Struct. (THEOCHEM)* **806** 1 (2007)
119. E A Zhurova, A I Stash, V G Tsirelson, V V Zhurov, E V Bartashevich, V A Potemkin, A A Pinkerton *J. Am. Chem. Soc.* **128** 14728 (2006)
120. R G A Bone, R F W Bader *J. Phys. Chem.* **100** 10892 (1996)
121. Yu V Nelyubina, M Yu Antipin, K A Lyssenko *J. Phys. Chem. A* **111** 1091 (2007)
122. P Metrangolo, H Neukirch, T Pilati, G Resnati *Acc. Chem. Res.* **38** 386 (2005)
123. Yu V Nelyubina, K A Lyssenko, A S Sigachev, M Yu Antipin, A N Kravchenko *Izv. Akad. Nauk, Ser. Khim.* 387 (2006) [a]
124. A N Kravchenko, G K Kadorkina, A S Sigachev, E Y Maksareva, K A Lyssenko, P A Belyakov, O V Lebedev, O N Kharybin, N N Makhova, R G Kostyanovsky *Mendeleev Commun.* 114 (2003)
125. L Perez-Garcia, D B Amabilino *Chem. Soc. Rev.* **31** 342 (2002)
126. Yu V Nelyubina, K A Lyssenko, D G Golovanov, M Yu Antipin *CrystEngComm.* 991 (2007)
127. Yu V Nelyubina, M Yu Antipin, K A Lyssenko *Izv. Akad. Nauk, Ser. Khim.* 1 (2009) [a]
128. Yu V Nelyubina, K A Lyssenko, V Yu Kotov, M Yu Antipin *J. Phys. Chem. A* **112** 8790 (2008)
129. A B Nikol'skii, V Yu Kotov *Mendeleev Commun.* 139 (1995)
130. A B Nikol'skii, V Yu Kotov *Koord. Khim.* **23** 706 (1997) [c]
131. P T Manoharan, H B Gray *J. Am. Chem. Soc.* **87** 3340 (1965)
132. Yu A Pentin, L V Vilkov *Fizicheskie Metody Issledovaniya v Khimii* (Physical Methods of Investigation in the Chemistry) (Moscow: Mir, 2003)
133. D B Soria, O E Piro, E L Varetti, P J Aymonino *J. Chem. Crystallogr.* **31** 471 (2001)
134. Yu V Nelyubina, K A Lyssenko, R G Kostyanovsky, D S Bakulin, M Yu Antipin *Mendeleev Commun.* 29 (2008)
135. Yu V Nelyubina, K A Lyssenko, M Yu Antipin *Kristallografiya* **53** 29 (2008) [d]
136. J W Steed, J L Atwood *Supramolecular Chemistry* (2nd Ed.) (New York: Wiley, 2009)
137. Yu V Nelyubina, M Yu Antipin, K A Lyssenko *J. Phys. Chem. A* **113** 3615 (2009)
138. U Koch, P L A Popelier *J. Phys. Chem.* **99** 9747 (1995)
139. T Steiner *Chem. Commun.* 2299 (1999)
140. J Baran, M M Ilczyszyn, M K Marchewka, H Ratajczak *Spectrosc. Lett.* **32** 83 (1999)
141. P Macchi, B B Iversen, A Sironi, B C Chakoumakos, F K Larsen *Angew. Chem., Int. Ed.* **39** 2719 (2000)
142. K A Lyssenko, P Yu Barzilovich, Yu V Nelyubina, E A Astaf'ev, M Yu Antipin, S M Aldoshin *Izv. Akad. Nauk, Ser. Khim.* 31 (2009) [a]

[a] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*
[b] — *Radiochemistry (Engl. Transl.)*
[c] — *Russ. J. Coord. Chem. (Engl. Transl.)*
[d] — *Crystallogr. Rep. (Engl. Transl.)*