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Low-temperature X-ray diffraction analysis: possibilities in the solution of chemical problems

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ABSTRACT. The possibilities of the modern precision X-ray diffraction method for the determination of the exact geometry, the characteristics of the thermal vibrations, and the distribution of electron density in the crystals of molecular compounds are examined in relation to a number of examples. The role of such investigations in the solution of chemical problems is demonstrated.

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I. Introduction

The development of the X-ray diffraction method for the investigation of the structures of single crystals has been marked in recent years by a significant acceleration and simplification of the procedure used to obtain experimental diffraction data and to elucidate and refine crystal structures. At the same time there has been considerable growth also in the analytical possibilities of the method, which has proved extremely important for the actual solution of many chemical problems. In particular, use of low-temperature recording during a diffraction experiment (T < 100–150 K) made it possible to establish the structures of many fundamentally important simplest low melting and/or thermally labile compounds, including chemically unstable intermediates in chemical reactions,[1–3] which significantly extended the scope of X-ray diffraction analysis.

Acceleration of the measurement of structural data and the extension of the analytical scope of the method and in a certain sense of its routine applications (this includes low-temperature experiments) proved possible by virtue of the development of modern automatic diffractometers with appropriate attachments and highly effective sets of programs for crystal structures calculations on latest generation computers. The considerable increase in the number of structural studies throughout the world on molecular carbon-containing compounds is indicated, in particular, by the fact that the Cambridge Structural Data Centre contains at present information about the structures of more than 73,000 compounds[4] and the Centre receives annually approximately 6000–7000 new structures. Thus X-ray diffraction analysis has become one of the most important and useful methods for the study of structure in modern chemistry.

On the other hand, there has been an appreciable growth in recent years also in the real accuracy of the X-ray diffraction method. This has made it possible to extract from its results information of a new type, namely one can now establish detailed features of the steric structures of molecules and crystals, to discover the characteristics of atomic thermal vibrations, and also to investigate experimentally the distribution of electron density in crystals. In particular, the attainment of a precision in the determination of interatomic distances to within 0.002–0.003 Å permits a reliable detection of different electronic effects in molecules (the anomeric effect, the presence and absence of conjugation, etc.), which alter their geometry.

We emphasise that the standard errors in the interatomic distances obtained on refining crystal structures by the least squares method (LSM) fairly often have similar values. However, in the usual ("routine") experiments a whole series of factors (absorption, extinction, and diffuse scattering of X-rays, the asphericity of the electron distribution of atoms, the librations of the molecules and atomic groups in the crystals, the possible types of disorder, etc.) are not as a rule taken into account. These can introduce errors into the structural, including geometrical, parameters, which can sometimes be several times greater than the standard errors of the LSM. The correct allowance for these factors or reduction of their influence and hence the determination of the most reliable and accurate diffraction data and structural characteristics of the molecules and crystals is the task for modern precision X-ray diffraction analysis which has greatly developed in recent years.[5,6]

In the case of molecular crystals, which include almost all the crystals of organic, organoelement and organometallic compounds, one of the main and in many cases the principal condition governing the measurement of precise diffraction data involves the use of low temperatures (T < 100–150 K)† in X-ray diffraction experiments.[7] The increase in the accuracy of the X-ray diffraction analysis on reducing the temperature is mainly associated with the decrease in the amplitudes of atomic vibrations. The decrease in these amplitudes leads to a sharp rise in the intensities of the diffraction maxima, which permits in practice their measurement with a high statistical accuracy. On cooling molecular crystals to the

† In the vast majority of low-temperature devices, cold nitrogen vapour is used as the cooling agent (T_b = 77 K). X-Ray diffraction studies at helium temperature have so far been few in number (see, for example, Henriksen et al.[8]) in view of the complexity of the corresponding devices.

temperatures indicated, the greatest increase in the intensity of the large angle of reflections ($\sin\theta/\lambda > 0.6-0.7$ Å^{-1}) takes place. They are in fact largely determined by the scattering of X-rays by the electrons of the inner shells of the atoms, which are little perturbed on formation of chemical bonds and therefore the inclusion of such reflections in the LSM refinement of structures is extremely important and leads to the measurement of more correct thermal and positional parameters of atoms which have not been displaced as a result of chemical bonding effects. Such effects can incidentally be considerable for crystals made up of molecules containing multiple bonds of the type C≡C or C≡N. The refinement of structures of this kind only on the basis of "near" reflections, which is frequently the case when the experiments are carried out at room temperature where "far" reflections are absent due to intense thermal vibrations, can lead to a systematic shortening of such bonds by 0.01 Å and more, although the error, determined by the LSM, in the interatomic distances can be almost an order of magnitude smaller.[9]

At low temperatures, where the possibility of a reliable measurement of large angle reflections arises, it is possible to avoid this source of systematic error as a result of the appreciable increase in the contribution of such reflections to the X-ray scattering, which corresponds to a large extent to scattering by spherically symmetrical atoms—this is one of the main approximations in the X-ray diffraction analysis. The cooling of crystals and the associated decrease in the atomic vibration amplitude lead also to a decrease in a series of other effects (anharmonicity, diffuse thermal scattering, the "freezing out" of certain low-frequency vibrations), which also affect the thermal and geometrical parameters. Furthermore, on cooling, there is an increase in the radiation and chemical stabilities of the crystals. In particular, in the case of molecular crystals, a decrease in temperature to 100–150 K decreases the librations of the molecules or their fragments in crystals as a whole and hence there is an appreciable decrease in the so called "librational" shortening of bonds—an effect attaining 0.02–0.03 Å at ~300 K. On the other hand, the introduction into the diffraction data obtained at the usual temperature of corrections applied to the bond length is not always effective, because the corresponding mathematical models, used in the structural analysis for the description of thermal movements and for the calculation of these corrections,[10] are frequently themselves correct only at low temperatures (since they are based on the small displacement approximation). In addition, it is evident that in many cases the determination from X-ray diffraction data (for molecular crystals) of correct values of the parameters of the anisotropic thermal vibrations (more precisely the mean square displacements) of the atoms is in many cases possible only at low temperatures.[11,12] The progress achieved in recent years in the determination of physically significant parameters of atomic mean square displacements or thermal ellipsoids and the development of methods for the theoretical calculation of these parameters[13,14] and of different criteria of their reliability[15,16] have made possible the extraction from the results of the precision X-ray diffraction experiment of additional new information associated in particular with the determination of the types and energy characteristics of different intramolecular movements in crystals (including movements due to the conformational changes in the molecules) and with the study of the nature of the disorder and phase transitions.

The possibility of obtaining accurate X-ray diffraction data, characterised by the accuracy of the determination of the correct set of kinematic structural amplitudes to within ~1–2% makes it possible to find from the experimental X-ray diffraction data the electron density distribution function for the crystal $\rho(r)$.[17–19] It is important to emphasise that this function defines uniquely the structure and physicochemical properties of the test system (the Hohenberg–Kohn theorem[20]). The latter factor provides a basis for the formulation in the language of electron distribution of various chemical problems (together with other problems), the most important of which involves the establishment of the nature of the chemical bond in compounds of different classes. Here too the experimental determination and visualisation of the characteristic features of the function $\rho(r)$, for example, in the form of electron density distribution maps, makes it possible to obtain valuable information about the nature of the chemical interaction and reactivity of molecules.

The method most widely used in such investigations involves the construction and analysis of maps of the so called deformation electron density (DED), defined as the difference $\delta\rho(r) = \rho(r) - \rho^0(r)$, where $\rho(r)$ is the total electron density of the crystal derived from the experiment, while $\rho^0(r)$ is the calculated electron density of spherically symmetrical non-interacting atoms (of the "premolecule"). The function $\delta\rho(r)$ thus describes the character of the redistribution of electron density on formation of chemical bonds between the initially non-interacting atoms, i.e. permits the "visualisation" of the formation of such bonds. It is significant that DEP maps can be constructed from the results of the X-ray diffraction experiment alone, while the quantity $\rho^0(r)$ can be calculated from the results of the large angle refinement of structures by the least squares method (the so called "$X-X$" method for the construction of DED maps). Bearing in mind that the function $\delta\rho(r)$ generally represents a small difference between two large quantities $\rho(r)$ and $\rho^0(r)$, the experimental determination and calculation of the latter should be carried out with a high accuracy, which can be achieved for molecular crystals in most cases only by using low temperatures and by applying the corrections listed above (for absorption, extinction, etc.) to the diffraction data obtained. This review deals with certain examples of the results of precision (low-temperature) X-ray diffraction analysis for the solution of various chemical problems, mainly associated with the determination of the accurate geometry of the molecules and of the detailed features of the steric structure and the characteristics of thermal vibrations in molecular crystals and also with the establishment of the character of the distribution of electron density.

The review does not consider methodological questions involving the employment and application of various low-temperature devices in X-ray diffraction experiments (such devices have already been considered[7,21]) as well as questions associated with the use of low temperatures for the investigation of low melting and/or metastable compounds (other reviews[1,22] have been devoted to these problems). The principal task of this review is the elucidation and consideration, in relation to a number of examples, of the potential of the method associated with its increasing true accuracy in the low-temperature study of crystals of molecular compounds.

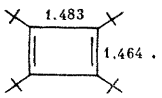
II. Determination of the exact molecular geometry

We shall consider certain examples of studies of molecular crystals carried out in order to obtain the exact molecular geometry (with an error of the determination of the interatomic distances between non-hydrogen atoms in the range 0.001–0.003 Å) from diffraction data.

Such studies are extremely important for the development of modern structural chemistry, since they permit a reliable determination of very detailed and in many instances fundamentally important features of the structures of molecules and crystals. As already mentioned, the use of low temperatures is one of the main conditions for the determination of accurate structural results, because it is then possible to measure a sufficient number of "large angle" reflections.

In particular, a recent low-temperature (123 K) study[23] of tolane Ph−C≡C−Ph established that the length of the C≡C triple bond is 1.211(2) Å according to the results of the large angle refinement ($\sin\theta/\lambda > 0.65$ Å^{-1}), whereas refinement of the structure only in terms of the near reflections, which is equivalent to the employment in the experiment of Cu radiation for which $\sin\theta/\lambda < 0.65$ Å^{-1}, yielded a significantly smaller length of this bond: 1.196(2) Å. Thus the effective shortening of the triple bond in the usual experiment is by 0.015 Å for tolane, which is comparable or can even be greater than the real change in the length of this bond due to the electronic conjugation effects.

An X-ray diffraction study of tetra(t-butyl)cyclobutadiene (I) at room temperature[24] showed that the central ring has a nearly square planar geometry.



(I)

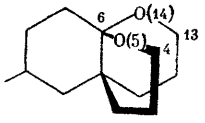
This conflicted with many other experimental (including X-ray diffraction) and calculated data and forced the authors to postulate the presence of dynamic or static disorder in the crystal of compound (I), leading to the superposition of two orientations of the central rectangular (and not square) ring, differing by a rotation in the plane by 90°. A reinvestigation of compound (I) at 123 K [25] confirmed the existence of such disorder and its diminution at a low temperature led to a decrease in the contribution of the alternative form to 15−30%, which made it possible, in its turn, to establish more correct bond lengths in the ring [1.441(2) and 1.527(2) Å; for other known cyclobutadiene derivatives in which there is no disorder the corresponding distances are 1.34 and 1.60 Å]. We may note that the partial disorder in the molecule of compound (I) at low temperatures can be clearly discovered by means of a detailed analysis of the parameters of atomic thermal displacement (see below).

Other examples are associated with the study of the geometry of arene or other π-complexes of transition metals with cyclic polyene ligands. Quantum-chemical calculations have shown[26] that in the case of such π-complexes of the type $(\eta^n\text{-}C_nH_n)M(CO)_m(XY)$ (n = 3−7, m = 1−3, XY = CO, N_2, NO, CN, M = transition metal) the electronic influence of the metal should reduce the symmetry of the coordinated η^n-cyclic ligand and should give rise to a characteristic change in its geometry. In particular, the alternation of the C−C bond lengths in the benzene ring should be observed for η^6-arene complexes.

Indeed, the alternation of C−C bonds in a six-membered ring was observed in a low-temperature study (77 K) of benzenechromium tricarbonyl $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ the C−C bond eclipsed by CO groups are lengthened compared with the other bonds in the ring by 0.017(2) Å. This small change in molecular geometry is correlated with the characteristics of the electron distribution maps near the Cr atom.[28] Subsequently the effect was confirmed[29] also in a low-temperature diffraction study of similar complexes $(\eta^6\text{-}C_6Me_6)Cr(CO)_3$ [Δ = 0.021(4) Å] and $(\eta^6\text{-}C_6Me_6)Mo(CO)_3$ [Δ = 0.036(9) Å]. However, we emphasise that, as a consequence of the considerable librations of η^6-linked rings at room temperature, this extremely fine electronic effect, which is of fundamental importance for the understanding of the nature of the chemical bond in transition metal π-complexes, could not be recorded experimentally in any of the three compounds indicated.

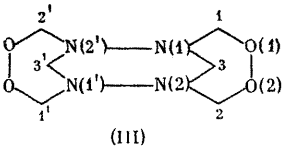
The effects associated with the manifestation of the so called orbital n,σ^*-interactions belong to the class of important stereoelectronic effects which determine to a large extent the characteristic features of the structure and reactivity of certain molecules of organic and organoelement compounds.[30] Interactions of this type can affect also the geometrical characteristics of the molecules. In particular, according to the results of quantum-chemical calculations for methanediol and methoxymethanol[31,32] in the synclinal (*sc*) and antiperiplanar (*ap*) conformations, the C−O bonds located in the *ap*-position relative to the lone electron pairs (LP) of the O atoms are lengthened relative to the other C−O bonds by 0.025−0.030 Å.

The reliable detection of small geometrical effects of n,σ^*-interactions becomes possible in highly accurate low-temperature X-ray diffraction studies. In particular, the O(5) and O(14) oxygen atoms in the structure of dihydroxypropellane ketal (II), investigated[33] at 98 K, are chemically equivalent but conformationally different: the C(6)−O(14) bond has the *sc*-orientation relative to the O(5)−C(4) bond and hence the *ap*-orientation relative to the LP of the O(5) atom; on the other hand, the C(6)−O(5) bond is characterised by the *ap*-orientation relative to the O(14)−C(13) bond and by the *sc*-orientation relative to the LP of the O(14) atom.



(II)

As a consequence of the different effectiveness of the orbital n,σ^*-interactions, the difference between the C−O bond lengths in the molecule of compound (II) is 0.026(3) Å [C(6)−O(5) = 1.412 Å, C(6)−O(14) = 1.438 Å]. A similar difference between the lengths of the chemically equivalent C(1)−N(1) and C(2)−N(2) bonds (0.025 Å) and between the C(1)−O(1) and C(2)−O(2) bonds (0.017 Å) has been observed in a study of the tricyclic compound (III) (data obtained[34] at 96 K), which is also induced by the different effectiveness of the interaction of the LP of the N(1) and N(2) atoms with the σ* orbitals of the C−O bonds:



(III)

The use of low temperatures gives rise to the possibility of investigating the manifestation of such stereoelectronic effects in crystals of the simplest molecular compounds which are in many instances liquid with low melting points or gases. The methodological questions involving the preparation of single crystals of low-melting compounds from liquids (melts) having melting points ranging from room temperature to about −150 °C needed for studies of this kind have been examined in a number of reviews[1,7,22] and will not be discussed here. We may note only that data on the structures of such usually very simple compounds are of special

interest for structural chemistry: they can be used to investigate the characteristic features of the steric structure of molecules (for example, the geometrical manifestation of various electronic effects) and crystals (the specific features of intermolecular interactions) in a "pure" form, i.e. in those cases where the molecules lack different functional substituents, which, on the one hand, enable the compounds to form crystals stable under the usual conditions, but, on the other hand, influence those properties of the test molecules which are difficult to determine beforehand.

As an example, we shall present data obtained in a recent study of the molecular structure of dimethoxyamine $HN(OMe)_2$ (IV) [35] and tetramethoxyhydrazine $(MeO)_2N-N(OMe)_2$ (V) [36]—the simplest (and low melting) alkoxyamines in which n,σ^*-interactions play an important role according to the available chemical data. The molecular structures of compounds (IV) and (V) and their principal geometrical parameters are presented in Figs. 1*a* and 1*b*.

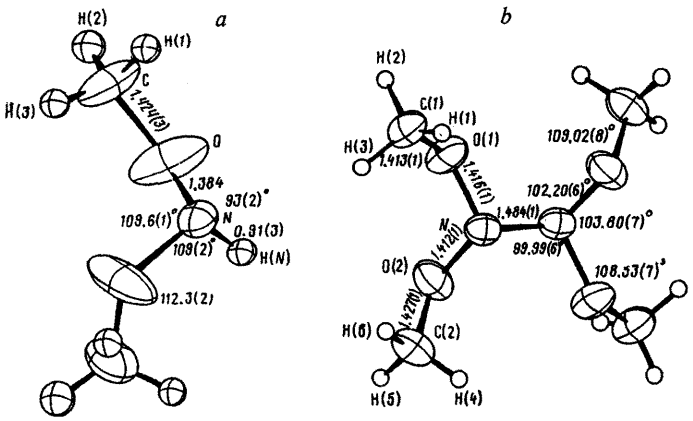


Figure 1. The crystal structure and principal geometrical parameters of the molecules of dimethoxyamine (IV) (*a*) and tetramethoxyhydrazine (V) (*b*).

It has been established that in the crystal of compound (IV) the molecules have a conformation characterised by a CONO torsional angle of 78.7°; the Me groups are then displaced from the ONO plane on either side. Electron diffraction study of this compound in the gas phase and the results of electrooptical measurements in solution established that mainly this conformation of the molecule is retained in the free state and in solution.[35] The preferred retention of this conformation is apparently determined by the fact that it is optimal for the occurrence of the stabilising $n_O-\sigma^*_{NO}$ interaction, as a result of which the N–O bond length in dimethoxyamine is reduced to 1.384(2) Å compared, for example, with 1.496(9) Å in MeO–NH(Me), where there is no such possibility. On the other hand, in the case of tetramethoxyhydrazine (V) (centrosymmetrical molecule, CONO torsional angles of 108° and −132°), the effectiveness of this interaction is smaller than in dimethoxyamine, which lengthens the N–O bonds to 1.414(2) Å. On the other hand, the conformation of compound (V) is favourable for the occurrence of another stabilising interaction of the type $n_O-\sigma^*_{N-N}$ whose occurrence is manifested by the lengthening of the N–N bond in this compound by 0.038 Å compared with hydrazine. It has been noted[37] that the ready homolysis of the N–N bond is a chemical manifestation of this electronic effect.

The interesting question of the relation between the reactivity of molecules, for example, their capacity to undergo dissociation at specific bonds, and the length of such bonds (in the ground electronic state) arises in this instance. A series of studies have been devoted to such questions.[38–42]

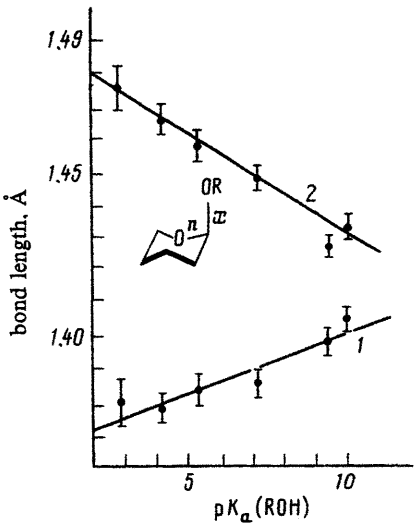


Figure 2. Dependence of the C–O bond lengths in a series of aryl derivatives of tetrahydropyranyl acetals on the pK_a for the corresponding acids ROH:[39] *1*, *n*; *2*, *x*.

For example, structural and kinetic studies of a series of aryl derivatives of axial tetrahydropyranyl acetals established a linear correlation between the lengths of the endocyclic and exocyclic C–O and C–OAr bonds, on the one hand, and the pK_a of the corresponding conjugate acids ArOH (Fig. 2), on the other. According to Briggs et al.,[39] the pK_a determine the rate constants for the hydrolysis of the acetals, i.e. for the reactions involving the heterolytic dissociation of the C–OAr bond, and hence the free energy of activation. With increase in the effective electronegativity of the OAr substituent as a consequence of the increasing effectiveness of the $n_O-\sigma^*_{C-O}$ interaction, the endocyclic C–O bond is appreciably shortened and the axial C–OAr bond is lengthened, which increases the rate of hydrolysis. The profile of the coordinate of this reaction plotted from the experimental data using the method of structural correlations[41,42] made it possible to estimate the slope of the $\Delta E/\Delta r$ curve in the initial stage of the stretching of the C–OAr bond, which proved to be 260 ± 10 kcal mol^{-1} Å^{-1}. Thus the energy expended on the stretching of the bond of the type under consideration by ~0.01 Å is fairly large and amounts to ~3 kcal mol^{-1}, which necessitates the determination of the geometrical characteristics of the molecules with a high accuracy in studies of this kind. We may also note that, when stereoelectronic effects (for example the anomeric effect) in compounds containing elements of the Third Period (O, S, P) are considered, the corresponding effects of the substituents are much weaker. In particular, the energies and geometries of all the possible molecules of doubly substituted methanes XCH_2Y, in which the substituents X, Y = F, OH, NH_2, Cl, SH, or PH_2 contain elements of the

Second and Third Periods, have been calculated[43] by the SCF LCAO-MO method (in terms of the 3-21G* basis set). It was established that the energy of the interaction of the substituents Cl, SH, and PH_2 is significantly lower than for substituents containing the elements of the Second Period. The geometrical manifestation of these effects should also be apparently weaker; this requires an improved reliability of the structural data for their reliable identification.

III. Analysis of atomic thermal parameters

An important characteristic feature of the precision X-ray diffraction method is the possibility of extracting from diffraction data the correct values of atomic thermal parameters[6,7,9,11,16] or temperature factors.‡ Their analysis permits conclusions about the types and characteristics of the low-frequency motions and/or static atomic displacements occurring in the crystals.

In the case of molecular crystals, such analysis is usually carried out within the framework of the familiar "rigid-body" model,[10] the essential feature of which consists in the separation of atomic vibrations into "external" low-frequency and "internal" high-frequency modes and in the neglect of the contribution of the latter to the temperature factors. Here it is also assumed that static displacements, induced, for example, by the disorder among the atoms in the crystals, are absent. Evidently, as a consequence of the smallness of their amplitude the contribution of the high-frequency vibrations to the temperature factor should be much smaller than that of the low-temperature frequency vibrations. For example, typical mean square amplitudes of the stretching vibrations in organic molecules are 0.001–0.002 $Å^2$ for non-hydrogen atoms,[44] which is in many cases smaller by an order of magnitude than the values calculated from the experimental temperature factors. As a result, the vibrations of molecules or the vibrations of their constituent components as a whole make the main contribution to the atomic temperature factors for crystals of molecular compounds.

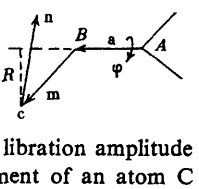
In conformity with the "rigid-body" model considered,[10] the harmonic movement of molecules in the crystal as a whole can be described in the general case with the aid of three tensors: the translational (**T**), librational (**L**), and translational-librational (correlation) (**S**) tensors, containing 20 independent components. The mean square displacements of any atom, i.e. the components of its temperature factor in the harmonic approximation, represented in the form of the so called thermal ellipsoid, can then be expressed in terms of these tensors and also in terms of the equilibrium position of the atom in an explicit form. Thus the description of the thermal motion of a molecule in a crystal containing n independent atoms with the aid of $6n$ temperature parameters of the ellipsoids of thermal vibrations of each atom can be reduced to the consideration of only 20 components of the three **LTS** tensors. These components are determined by the least squares method either using as the "variables" the $6n$ already refined components $U_{ij}(B_{ij}, \beta_{ij})$ of individual temperature factors or by refining the LTS-tensors directly on the basis of diffraction data.[45]

‡ It has recently become common usage to call these parameters the parameters of the mean square displacement amplitudes (the English abbreviation is MSDA), because not only atomic vibrations but also different kinds of static displacements of atoms from equilibrium positions contribute to the Debye–Waller factor (the "temperature" factor).

The agreement between these parameters, obtained from diffraction data (U_{ij}^{exp}) and calculated on the basis of the hard body model (U_{ij}^{theor}) is a measure of the physical significance of the temperature parameters and of the suitability of the **LTS** model. Evidently, if the difference $\Delta U_{ij} = U_{ij}^{exp} - U_{ij}^{theor}$ is small and close to the error of the experimental determination $\sigma(U_{ij})$, the temperature parameters correspond to the rigid-body model within the limits of the accuracy attained.

However, it is evident that the model is too simplified and that the discrepancy between U_{ij}^{exp} and U_{ij}^{theor} should not always be understood merely as an indication of an experimental error in the determination of U_{ij}^{exp}. The slow low-frequency ($\omega \leqslant 500$ cm^{-1}) intramolecular vibrations, not taken into account in the **LTS** model, can introduce an appreciable contribution to the values of U_{ij} and the identification of such movements, which can be precursors of conformational transformations in crystals, is in fact of significant interest. Therefore, subsequently, after the appearance of the rigid-body model, other more complex versions of the description of the thermal motion of atoms and crystals were developed. In particular, they make it possible to take into account the non-rigidity of the molecular skeleton. One of the first attempts to take into account the intramolecular movements in the description of atomic thermal parameters was the "riding" model widely used for the description of the thermal movements of terminal atoms in molecules, especially hydrogen atoms.[46] Next, mention should be made of Johnson's model which has been called the "segmented rigid-body" model[47] and was subsequently developed for the description of the thermal motion of macromolecules,[48] and of the studies of Hamilton and co-workers[49] on the torsional oscillations of methyl groups in different organic molecules (on the basis of neutron diffraction data). A method has been proposed recently for analysing the thermal parameters in which it is possible to calculate the force constants of the slow intramolecular movement. It is based on the inclusion in the least squares procedure of the parameters of the quasi-normal modes of these movements together with the simultaneous refinement of the components of the **LTS** tensors.[50] The procedure has been tested successfully in the description of thermal motion in two lipid derivatives characterised by significant torsional librations about the single bonds linking the rigid cyclic molecular skeleton to the flexible aliphatic chains.

A fairly simple one-parameter model, in which together with the calculation of the corresponding **LTS** tensors there is a possibility of taking into account and calculating the amplitudes of intramolecular torsional vibrations, has been developed in recent years for practical applications in studies of this kind.[51,52] In this model, a single parameter φ (the libration amplitude) is introduced for each atom or group of atoms which can execute torsional vibrations about the given bond (for example, the vibrations of a C atom about an A–B bond).



$$\mathbf{n} = \mathbf{m} \times \mathbf{a} / |\mathbf{m} \times \mathbf{a}|;$$
$$R = |\mathbf{m} \times \mathbf{a}| / |\mathbf{a}|.$$

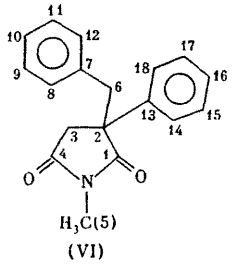
If the libration amplitude is not too great, it can be regarded as the movement of an atom C in the direction of a unit vector **n**. The additional displacement of the atom C as a result of such intramolecular movement is φR and this movement is superimposed on the displacement of the molecule in the crystal as a whole. The mean square amplitude $\langle\varphi^2\rangle$ as well as the components of the **LTS** tensors are refined by the least squares method. The model

considered proved to be extremely efficient and suitable for the description of intramolecular movements in crystals with fairly large torsional amplitudes ($\varphi < 20-25°$).

However, in the general case, in the analysis and interpretation of the temperature parameters within the framework of the simple rigid-body LTS model or when its more complex versions are used, difficulties frequently arise which are both associated with the unduly high degree of simplification of the models and are purely mathematical.[53] Therefore, in the interpretation of the temperature parameters, the search for other criteria of their quality and reliability becomes important.

For molecular crystals, one of the ways of testing the quality of atomic thermal parameters and of discovering the types of intramolecular movements (or disorder) occurring in crystals involves the calculation of the differences Δ between the mean square amplitudes of the opposed vibrations of pairs of atoms in the direction of the chemical bond between them (the so called Hirshfeld test[15] of the "rigidity" of the bond: $\Delta_{AB} = Z^2_{AB} - Z^2_{BA}$, where Z^2 is the projection of the mean square vibration amplitudes of the atoms A and B onto the direction of the A–B bond in the compound investigated). If Δ_{AB} is small ($\lesssim 10^{-4}$ Å^2) for the given chemical bond between the atoms A and B in the molecule, which corresponds to significantly smaller amplitudes of the stretching vibrations of the atoms compared with the vibrations of the molecules in the crystal as a whole, then the thermal ellipsoids for the atoms A and B correctly reproduce the character of the atomic movement. On the other hand, if Δ is significantly greater than 10^{-4} Å^2, then some other additional atomic displacements apparently contribute to the thermal parameters of the atoms A and B or there is a systematic error in their calculation. For structurally rigid systems, for example for molecules with three-dimensional frameworks or for cyclic systems, with correctly determined thermal parameters, the values of Δ should be small also for all pairs of atoms not linked by valence bonds, confirming the rigidity of the entire molecular skeleton. However, if the test of the rigidity of chemical bonds is positive and the calculation of Δ for certain pairs of chemically non-bonded atoms in the molecule yields values of Δ much greater than 10^{-4} Å^2, this result can indicate the occurrence in the given molecule of definite types of intramolecular movements. Such calculation of the values of Δ has been frequently used recently to elucidate the types of such movements.[16]

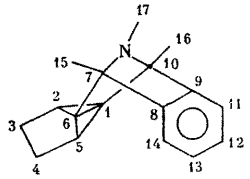
As one of the examples of the analysis of the values of Δ, we shall consider the result of the study of a crystal of 3-benzyl-*N*-methyl-3-phenylsuccinimide (VI) at 100 K:[54]



(VI)

The average value of Δ for all 23 pairs of chemically bonded atoms in compound (VI) is 21×10^{-4} Å^2, which is comparable to the values of $\sigma(\Delta) \simeq 15 \times 10^{-4}$ Å^2. The values of Δ for pairs of atoms linked by valence bonds in three fragments, namely the *N*-methylsuccinimide fragment (8 atoms), the benzyl fragment (7 atoms), and the phenyl fragment (6 atoms), are also small, amounting to 19, 24, and 11 ($\times 10^{-4}$ Å^2) respectively, which indicates their structural rigidity. On the other hand, calculation of the average values of Δ for pairs of non-bonded atoms belonging to different fragments indicates the non-rigidity of the molecular skeleton of compound (VI) as a whole: $\Delta = 71 \times 10^{-4}$ Å^2 (imide–benzyl), 38×10^{-4} Å^2 (imide–phenyl), and 44×10^{-4} Å^2 (benzyl–phenyl). This structural non-rigidity is probably due to the possibility of the torsional vibrations of the three rings relative to the C(2)–C(6), C(7)–C(6), and C(2)–C(13) single bonds of the central fragment of the molecule of compound (VI).

In the study of the structure of the [3.1.1]propellane derivative (VII), it was established (structural data for 95 K [55]) that, for all the pairs of chemically bonded atoms, the Hirshfeld test of the rigidity of the bonds is positive with a high degree of accuracy [$\Delta_{av} = 3(7) \times 10^{-4}$ Å^2], which indicates a high quality of the diffraction data. The molecule as a whole is also fairly rigid — the average value of Δ for all the pairs of atoms not linked by valence bonds [with the exception of pairs with participation of the C(17) atom of the methyl group attached to the N atom] is less than 10×10^{-4} Å^2.



(VII)

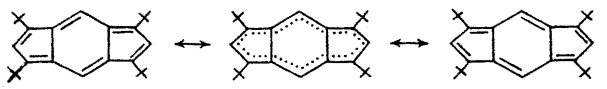
Calculation of the values of Δ for the non-bonded pairs of atoms with participation of the C(17) atom shows, however, that there is an appreciable movement of this atom relative to the C(8)–C(14) carbon atoms on the right-hand side of the molecule [displacement in the direction C(17)...C(8)–C(14)]. On the other hand, such additional countermovement has not been observed relative to the atoms in the left-hand part of the molecule [the C(1)–C(7), C(10), C(15), and C(16) atoms]:

	C(1)÷C(7), C(10), C(15), C(16)	C(8)	C(9)	C(11)	C(12)	C(13)	C(14)
Δ ($\times 10^4$ Å^2)	0—6	17	21	33	39	38	25

Thus the additional movement (detected in the thermal parameters of the structure) of the C(17) atom of the methyl group takes place along an arc around the nitrogen atom, i.e. it corresponds to the beginning of the possible route to the inversion of the configuration at this atom.

Calculation of the differences Δ for the same compound, investigated at different temperatures, makes it possible in a number of instances to establish the most readily "frozen out" types of intramolecular vibrations. In particular, a study[56] of the trigonal-bipyramidal phosphorane $Cl_3P(CCl_3)_2$ (VIII) at 153 K demonstrated the structural rigidity of the molecule: calculation of the differences Δ for all the chemically bonded and also non-bonded pairs of atoms at distances $\lesssim 3.2$ Å yields the mean square value $\Delta = 7 \times 10^{-4}$ Å^2. On the other hand, the analogous calculation using high-temperature data (300 K [57]) leads to $\Delta = 85 \times 10^{-4}$ Å^2; the pairs of atoms not linked by valence bonds and including atoms of only one of the two CCl_3 groups are characterised by the maximum values of Δ [$\Delta = (112-166) \times 10^{-4}$ Å^2]. This evidently indicates the additional libration of this group in the crystal, which was also detected from ^{35}Cl NQR data. The barrier to the rotation of this group, estimated from diffraction data, proved to be approximately 57 kJ mol^{-1}.[58] The possibility of the libration of only one of the two CCl_3 groups is due to their different environments in the crystal.

Naturally, it is difficult to establish the occurrence of a specific type of intramolecular movements (or the presence of disorder) in crystals by analysing only the values of Δ. However, calculation of Δ is a very simple and reliable criterion for discovering the presence of these effects. For example, in the study of the cyclobutadiene derivatives (I) at 123 K [25] already mentioned, the presence of residual ring disorder is manifested by the relatively large value of $\Delta_{C,C}$ (compared with other values) for the carbon atoms of the central ring ($\Delta_{C,C} = 19 \times 10^{-4}$ Å^2). On the other hand, the study of the structure of the derivative of S-indacene (IX) at room and low (100 K) temperatures showed[59] that the molecule in the crystal has the intrinsic D_{2h} symmetry of the carbocycle, which corresponds to the equalised structure (B) and agrees with ^{13}C NMR data:[60]



(IX, A) (IX, B) (IX, C)

Analysis of the differences $\Delta_{C,C}$ for the ring carbon atoms in the molecule of compound (IX) confirmed its structural rigidity ($<\Delta^2_{C,C}>^{1/2} = 7 \times 10^{-4}$ Å^2), which rules out the possibility of the coexistence of the valence isomers (A) and (C) in the crystal. This result forced the authors[59] to put forward the hypothesis that in the case under consideration there is a possibility either of the stabilisation in the crystal of the delocalised non-aromatic 12 π-electron system or the geometry of the molecule corresponds to the transition state of the valence isomerisation reaction stabilised by crystal packing.

In view of the foregoing, it appears useful to analyse the values of Δ for crystals of different tautomeric compounds and also for crystals of compounds with strong hydrogen bonds (for example, of the type O–H...O) and a central H atom. Such analysis makes it possible to discover the contribution to the structure observed in the crystal by possible "limiting" valence forms.

More important information about the intramolecular movements is obtained (which makes it possible to establish not only a qualitative but also a quantitative measure of such movements) using the one-parameter model discussed above,[51,52] on the basis of which it is possible to calculate the mean square amplitudes of the intramolecular torsional vibrations $<\varphi^2>$. Next, it is possible to calculate, using familiar formulae, the force constants f and other characteristics of such movements:[16,61]

$$f = kT/\langle\varphi^2\rangle. \quad (1)$$

Strictly speaking, in the calculation of the libration force constant ($f = 4\pi^2 I\nu^2$, where I is the moment of inertia and ν is the frequency in cm^{-1}), one should use a quantum-chemical expression for $<\varphi^2>$:

$$\langle\varphi^2\rangle = \frac{h}{8\pi^2 I\nu^2}\,\mathrm{Coth}\left(\frac{h\nu}{2kT}\right). \quad (2)$$

However, it has been shown[61] that Eqn. (2) reduces to the classical Eqn. (1) to within at least 1% for frequencies $\nu < 0.2\ T$ (ν is expressed in cm^{-1} and T in K), which is valid at normal temperatures for almost all groups except $-CH_2$, $-CH_3$, $-NH_2$, and $-NH_3$. Having specified the usual form of the rotational potential V [$V = B(1 - \cos n\varphi)/2$], where B is the height of the potential barrier, and having expanded V in series, we obtain

$$V = \frac{B}{2}[1 - (1 - n^2\varphi^2/2 + \ldots)] \simeq \frac{Bn^2\varphi^2}{4}. \quad (3)$$

Having set this expression equal to $V = f\varphi^2/2$, we have in the classical limit

$$B \simeq 2f/n^2 = 2kT/n^2\langle\varphi^2\rangle. \quad (4)$$

Thus, not only the frequencies and force constants but also the heights of the barriers to slow intramolecular vibrations in crystals can be estimated from the values of $<\varphi^2>$ determined from diffraction data. On the assumption that the selected form of the cosinusoidal potential is valid, Eqn. (4) proved to be sufficiently accurate (the error is less than 10%), provided that the height of the barrier B exceeds $12kT/n^2$,[61] i.e. provided that the mean square amplitude $<\varphi^2> < 0.17$ rad^2 ($\varphi < 25$ °C). The possible barriers B as well as the frequencies and force constants for more than 300 groups have been estimated[61] on the basis of the corresponding calculations of the quantity $<\varphi^2>$ from the experimental temperature parameters $U_{i,j}$ for 125 different structures of molecular crystals using data from the Cambridge Crystallographic Data Centre. Certain results, including those obtained recently,[58,62] are presented in Table 1, which shows that the calculated barriers fall within the range found by means of other methods. Such estimates may prove useful, particularly in the absence of the corresponding experimental data obtained by other methods (non-elastic scattering of neutrons, relaxation NMR methods, NQR spectroscopy, etc.), or in comparing the results obtained by different methods. In this connection, we may note the tabulated (Table 1) estimates of the barriers to the rotation of the cyclopentadienyl and permethylated cyclopentadienyl rings in metallocenes, for which a good agreement has been observed with the results found by NMR relaxation methods, as well as the data for the barriers to rotation in phosphazo-compounds, which agree with the studies of these compounds by the NQR method.

Table 1. The barriers to the intramolecular movements of certain atomic groups in crystals estimated from X-ray diffraction data.[58,61,62]

Group	Atom linked to group	Height of barrier, kJ mol^{-1}	
		calc. by Eqn. (4)	from data obtained by other methods
$-CH_3$*	Trigonal C, N Tetrahedral C, N, P O	B_3 = 1.5–9.6 B_3 = 4–26 (cf. Ref.11) B_3 = 1–9 (cf. Ref.4)	1.2–8.5 (crystal) 12–22 (gas) 4.5 (CH_3OH gas) 15–19 (crystal)
$-CF_3$	Trigonal C Tetrahedral C	B_3 = 4–10 (cf. Ref.7) B_3 = 8–66 (cf. Ref.25)	4–7 (gas) 13–25 (gas) 11–17 (crystal, NMR)
$=PCl_3$	Trigonal N in phosphazo-compounds $Cl_3P=NR$	B_3 = 31–58	21–38 (crystal, NQR, NMR)
η^5-C_5H_5	Transition metals, Fe, Ni, Rh, Ru, Os	B_5 = 7–23	10–25 (crystal, NMR non-elastic neutron scattering)
η^5-C_5Me_4	Transition metals, Fe, Ru, Os	B_5 = 9–19	10–30 (crystal, NMR)

*From neutron diffraction data.

Multitemperature studies have played an important role in the investigation of the characteristics and features of the thermal vibrations of atoms in crystals. In the first place, such studies make

it possible to investigate the nature of the disorder,[7] revealing its static (associated with the coexistence in the same positions in the crystal of several different molecular orientations or conformations or with the multidomain nature of the specimen) or dynamic (associated with slow intramolecular movements characterised by a high amplitude) character. Such separation of the different types of ordering is naturally arbitrary because it can be determined only by the height of the barrier separating the crystal different orientations and conformers located in the same position in the crystal; furthermore, there is also a possibility of the presence in the crystal of both types of disorder.

Under the conditions of disordering of a static type, cooling of the crystals to specified temperatures should not lead to a consistent decrease in the temperature factors of the atoms in the disordered groups, which is natural since in the given instance large temperature parameters usually reflect only the presence in the crystal of molecules (or their fragments) with other orientations and conformations and not the occurrence of any atomic movement. On the other hand, in the study of systems with dynamic disorder one may expect a fairly sharp decrease in the temperature parameters of certain atoms in the structure when the temperature is reduced, since usually this type of disorder is associated with movements characterised by a fairly large amplitude and a low frequency, i.e. with the most readily "frozen out" types of vibrations. Certain examples of the use of low-temperature data in order to reduce disorder were examined above.

One may also note that the energy characteristics of the process considered can also be estimated from the analysis of the temperature variation of the populations of the individual sites in dynamically disordered structures. Thus a multitemperature study of 1,3,5-tribenzyl-1,3,5-triazacyclohexane (X) at 293, 268, 250, and 127 K [63] showed that the populations of the axial and equatorial positions of the N atoms change consistently with temperature, which corresponds to their inversion. The values of ΔH° and ΔS° for the inversion of the N atoms were calculated from diffraction data. Other examples of similar estimates were considered elsewhere.[11]

In a number of instances, interesting qualitative conclusions about the character of the conformational and sometimes chemical transformations of molecules in crystals can be reached only by analysing the shape of the thermal atomic ellipsoids. For example, in crystals containing molecules and complexes with saturated flexible five-membered rings, including metallocycles, one observes fairly frequently at room temperature a conformational disorder of the latter as a result of which two conformers coexist in the crystal (each has the half-chair form). The transition between them takes place via a pseudorotation mechanism.[64]

Numerous ethylenediamine complexes of metals constitutes a large group of such compounds. The individual orientations of the rings on electron density maps for such systems are usually not observed and disorder is as a rule manifested by the significant extension of the ellipsoids of the thermal vibrations of the C atoms of the ethylenediamine (en) ligands at right angles to the plane of the effectively flattened five-membered ring. The calculated effective amplitudes of the vibrations of the C atoms at right angles to the plane of the ring are anomalously large and amount to 0.3–0.4 Å; the C–C single bond then proves unrealistically short (~1.4 Å).[64] This disorder evidently has a dynamic nature, since, on cooling the crystals of these compounds, the metallocycles exhibit the half-chair conformation characteristic of them and the geometry of the ring becomes "normal". A similar change has been observed in a study of the complex $Cr(en)_3(SCN)_3.0.75H_2O$ in the temperature range 293–133 K,[65] the transition being fully reversible and continuous in character.

A similar disorder of the five-membered pyrrolidine ring has been observed in an X-ray diffraction study of sodium pyrrolidine-1-carbodithioate dihydrate $Na[S_2CN(CH_2)_4].2H_2O$ (XI) at 295, 150, and 27 K.[66] At 295 K, the ring is effectively flattened [the displacements of the C(4) and C(5) atoms from the plane of the S(1), C(1), and N atoms are 0.245(5) and −0.151(7) Å respectively], and thermal ellipsoids of the C(4) and C(5) atoms are greatly extended in the direction at right angles to the plane of the ring (Fig. 3), and, as a consequence of conformational disorder, the C(4)–C(5) single bond is unrealistically short: its length is 1.394(8) Å. At 150 K, the disorder is only partly frozen out [the displacements of the C(4) and C(5) atoms from the above plane are 0.269(6) and −0.259(6) Å respectively and the bond length C(4)–C(5) = 1.419(8) Å], in agreement with the height of the barrier to the pseudorotation of the pyrrolidine ring, which is commensurate with kT at 150 K. Complete ordering of the structure takes place at 27 K: the ring has the half-chair conformation, the displacements of the C(4) and C(5) atoms from the plane are 0.328(7) and −0.373(7) Å, and the bond length C(4)–C(5) = 1.511(10) Å, i.e. has the usual value for a $C(sp^3)–C(sp^3)$ single bond.

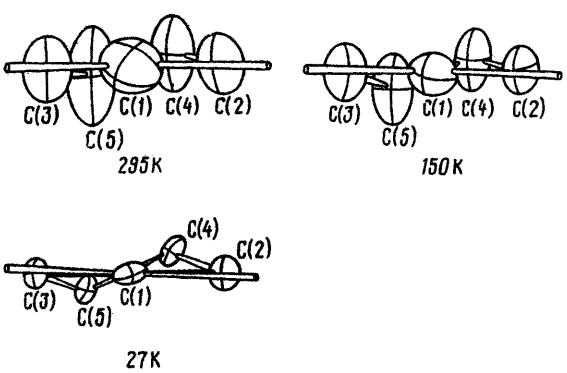


Figure 3. General form of the pyrrolidine ligand along the C(1)–N bond in the structure of sodium pyrrolidine-1-carbdithioate dihydrate (XI) at three temperatures (295, 150, and 27 K); the atoms are represented by thermal vibration probability ellipsoids.[66]

Analysis of the parameters of the atomic thermal displacements has also proved important in the study of many physical properties of crystals,[11] in particular in the study of the mechanisms of the structural and magnetic (spin) phase transitions, in the study of the properties of the liquid crystal state (the mesogen molecules are usually characterised by the presence of a hard central core and mobile side groups, which in the crystal execute much more vigorous vibrations than the central core of the molecule[67]), and in the study of biological macromolecules.[68,69]

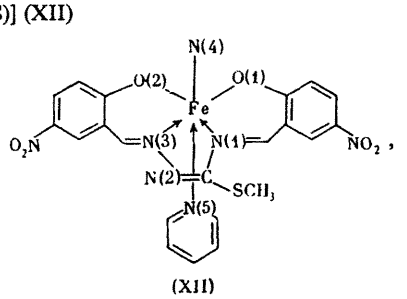
As an example, we shall consider the interesting type of disorder in a crystal, observed in the study of complexes containing Jahn–Teller ions (for example, Cu^{2+}) or compounds with spin transitions of the type "high-spin–low spin" in different octahedral iron complexes.

The degenerate electronic ground state ^2E_g of the Cu^{2+} ion for the ideal octahedral coordination of $[CuL_6]^{2+}$ (L is any ligand) is known to be unstable as a consequence of the Jahn–Teller effect, as a result of which the symmetry of the ion is reduced in order to remove the degeneracy.[70] The octahedral coordination of the ion is distorted, for example, to the tetragonal coordination, and these distortions actually lead to the disordering of the structure (because the tetragonal distortion axis can be any of the three directions in the octahedron). However, these distortions can be frequently small and they can therefore be detected only from the anomalous values of the temperature parameters of the $[CuL_6]$ fragment, which retains the average symmetry of the octahedron. Such anomalies are observed in the calculation of the differences Δ between the mean square "opposed" amplitudes of the atomic vibrations mentioned above. Table 2 presents data[42] for two isostructural compounds of the type $K_2PbM(NO_2)_6$ (M = Cu, Ni) characterised by the ideal octahedral symmetry of the anions $[M(NO_2)_6]^{4-}$ (all the M–N bonds are crystallographically equivalent).[42] The significant difference between the structures consists, however, in the fact that the Cu^{2+} complex is characterised by Jahn–Teller distortions and the existence of the ideal octahedron is therefore impossible for such an ion and the structure observed in the crystal is in essence disordered. As a consequence of this, the differences $\Delta_{M,N}$ for two the isostructural compounds differ almost by an order of magnitude: 0.0208(20) and 0.0022(10) Å^2. The magnitude of the Jahn–Teller distortion can be calculated from these differences (~0.14 Å).

Table 2. The mean square amplitudes U(Å^2) of the vibrations of the M (Cu, Ni) and N atoms in the direction of the bonds between them in the octahedral anions $[M(NO_2)_6]^{4-}$, the differences between them $\Delta_{M,N}$, and the distances R_{M-N}.[42]

Parameter	$[Cu(NO_2)_6]^{4-}$	$[Ni(NO_2)_6]^{4-}$
U_N	0.0380 (20)	0.0132 (9)
U_M	0.0172 (1)	0.0110 (1)
$\Delta_{M,N}$	0.0208 (20)	0.0022 (10)
R_{M-N}, Å	2.111 (4)	2.080 (2)

The study of an octahedral iron complex with a tetradentate asymmetric *S*-methylisothiosemicarbazide ligand L, i.e. [Fe(Py)(L).(NCS)] (XII)



(XII)

at 293 and 163 K showed[71] that, when the temperature is reduced, there is an appreciable change in the geometry of the coordination unit of the Fe atom, which can be caused by the transition of the metal atom to a low-spin state on cooling the specimen.

According to EPR and Mössbauer spectroscopic data, the Fe(3+) atom in compound (XII) is in a high-spin (S = 5/2) state at room temperature, while on cooling the compound a continuous phase transition to a low-spin (S = 1/2) state takes place, the transition being completed only at ~80 K. According to the results of Mössbauer analysis, the content of the high-spin form at 163 K (the temperature of the diffraction experiment) diminishes to ~20%, which alters significantly the geometry of the Fe octahedron: it contracts and the Fe–N bond involving the N(5) atom of the Py ligand is shortened by 0.105(4) Å; the decrease in the length of other Fe–N bonds is by 0.045–0.076(4) Å. At 163 K, the geometrical parameters of the FeN_4O_2 units are found to be close to those characteristic of the corresponding low-spin Fe(3+) complexes. However, the "failure" of the spin transition to reach completion at 163 K, i.e. the presence in the crystal of a residual disorder, is manifested distinctly by the anomalous values of the atomic thermal structural parameters at a low temperature. Thus the average value of the Hirshfeld differences Δ for the Fe–N and Fe–O bonds at 293 K (100% of the high-spin form) is 31 × 10^{-4} Å^2, whereas at 163 K (20% of the high-spin form and 80% of the low-spin form) this value increases by a factor of 3 to 91 × 10^{-4} Å^2. There is a corresponding sharp impairment at 163 K also of the formal parameters of the **LTS** model (R = 5.6% at 293 K and R = 18.6% at 163 K). (In the calculation of the **LTS** tensors, account was taken only of the atoms in the immediate environment of the metal.) The examples presented show that the parameters of the atomic thermal displacements can serve as reliable "indicators" of fine structural changes in crystals, in particular those associated with different phase transitions.

In conclusion of this part of the review, we may note that a real possibility of the extraction from precision X-ray data of quantitative information about the effective (one-particle) potentials of atoms in crystals has appeared recently.[72] The individual atomic temperature factors T(**q**) (**q** is the scattering vector) are Fourier transforms of the distribution function $P(R)$ (the probability density function) of the positions of the nuclei or electron density centroids (in neutron and X-ray diffraction respectively). In the classical high-temperature approximation, the function $P(R)$ can be written in the form

$$P(R) = \exp[-V(R)/kT] \Big/ \int \exp[-V(R)/kT]\, dR, \qquad (5)$$

where $V(R)$ is the potential energy of an atom vibrating in the effective field of its neighbours. Series expansion of $V(R)$ in powers of the displacement relative to the equilibrium position and the use of the quasi-harmonic approximation[72] makes it possible to recover the effective potential of the given atom in the crystal from the coefficients of the expansion. The expansion coefficients are usually refined by the least squares method. It is significant that the expansion need not necessarily be restricted to the harmonic members of the series; within the framework of this approach, it is also possible to take into account the anharmonicity of the atomic vibrations.

The first calculations of the effective atomic potentials were associated with the study of ionic conductivity[73] and the precision study of the electron distribution and anharmonicity of the atomic vibrations in the crystals of simple inorganic compounds.[74] Subsequently this approach was extended to studies on more complex compounds, in particular it was used to calculate the effective potentials of copper atoms in high-temperature

superconductors.[75] On the other hand, the concept of effective atomic potentials can prove useful also for the solution of various crystal-chemical problems. In particular, the force constants and the characteristic frequencies of the chemical bonds are related to the parameters of such potentials. The determination of the specific character of such a bond will probably make it possible to investigate at a higher level the different dynamic processes in crystals.

IV. Study of the distribution of electron density in crystals

The experimental determination of the distribution of electron density $\rho(r)$ in crystals and the discovery of the fine electronic structure of the chemical bond are some of the most important aspects of modern X-ray diffraction analysis.[6,17–19,76] Such studies make it possible to examine the principal ideas, which have become traditional, concerning the nature of the chemical bond in the language of the observed distribution $\rho(r)$. As already mentioned, the commonest method of investigation of the characteristics of the function $\rho(r)$ is the analysis of maps of the deformation electron density $\delta\rho(r)$ (DED), which has a simple significance. In particular, the form, position, and height of the $\delta\rho(r)$ maxima and/or minima relative to the atomic nuclei and lines connecting the chemically bound atoms make it possible to "visualise" the most important features of the electronic structure of molecules and crystals in the region of chemical bonds of different types.

The main principles of the interpretation of electron distribution maps have been described in a number of reviews[76–79] and monographs[17–19] and therefore there is no need to dwell on them in detail. We shall confine ourselves to characteristic examples of studies in recent years, referring mainly to the precision low-temperature study of the distribution of electron density in the crystals of simplest (usually low-melting) molecular compounds as well as certain more complex compounds of new types for which experimental electron distribution data were lacking until recently.

The importance of such investigations of the simplest compounds is determined primarily by the possiblity of carrying out for the purpose of such research of non-empirical quantum-chemical calculations of the electron distribution with a high level of accuracy, which makes it possible to compare theoretical and experimental data and to test the principal theoretical concepts developed for the description of the nature of the chemical bond. A critical comparison of such theoretical and experimental results has been made.[80,81] In addition, the fraction of valence electrons is frequently a maximum precisely in the crystals of the simplest compounds and the corresponding characteristic features of the DED maps, associated with the redistribution of the outer electrons of the atoms and the formation of chemical bonds, can therefore be recorded experimentally with a high accuracy and reliability.

We may note that the modern non-empirical calculations for molecules with a small number of electrons ($\sim$20–25) make it possible to evaluate the electron density in the internuclear space to within 0.05–0.10 e Å^{-3}. The possibilities of the diffraction experiment in the determination of the function $\rho(r)$ are somewhat greater — the accuracy of the determination of electron density in the region of the chemical bond reaches 0.02–0.04 e Å^{-3}.[18]

Apart from this, the X-ray diffraction method is applicable to the study of the electron distribution in complex polyatomic crystals and also in crystals containing the atoms of heavy elements ($Z < 70$). Non-empirical quantum-chemical calculations for such compounds, which require a high level of accuracy, are so far extremely laborious and few have been performed. Because of this, the precision X-ray diffraction method frequently proved to be the only available procedure whereby data can be obtained on the electron distribution in the study of complex compounds. The latter factor is extremely significant in the investigation of the distribution of electron density and of the characteristic features of the chemical bond in crystals of compounds of new types.

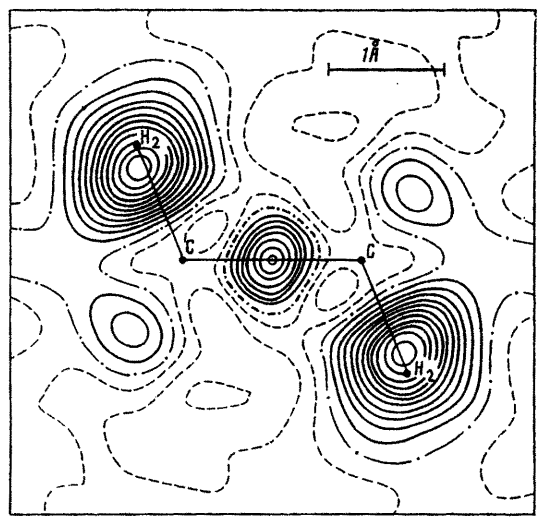


Figure 4. DED section through the transoid H–C–C–H fragment of the ethane molecule.[82] In this and subsequent figures, the continuous contours on the DED maps correspond to positive DED, the dashed lines correspond to negative DED, and dot and dash lines correspond to zero DED. The isolines are drawn at 0.05 e Å^{-3} intervals. [In the calculation of the DED for the ethane molecule, the electron density of the H atoms was not subtracted from the total density $\rho(r)$.]

Examination of the characteristic DED maps in the region of different chemical bonds can be usefully begun with the analysis of the results of the study of ethane, ethylene, and acetylene crystals — the simplest organic molecules containing single, double, and triple bonds between carbon atoms.[82] For the ethane molecule (data at 85 K), the DED section in the plane of the H–C–C–H transoid fragment is characterised by the presence of a distinct symmetrical maximum 0.35(4) e Å^{-3} high and located midway between the C atoms (Fig. 4). This result is consistent with the concept of the formation in ethane of a single covalent σ-bond (the C–C bond length in the crystal is 1.532 Å). In ethylene, the DED maximum on the C=C double bond with a length of 1.313 Å (data at 85 K) is characterised by a greater height (0.50 e Å^{-3}, Fig. 5*a*) and the presence of the π-component in the bond is manifested by a distinct extension of the DED maximum in the direction at right angles to the plane of the molecule and the bond line (Fig. 5*b*). The effectiveness of this π-interaction can probably be estimated from the degree of elongation of the ellipsoidal section (the ratio of the half-axes of the ellipse) in the plane at right angles to the

bond line. It is of interest to compare the result with the value of the so called bond "ellipticity" (ε) in ethylene $\varepsilon = \lambda_1/\lambda_2 - 1 = 0.74$, calculated quantum-chemically from electron density $\rho(r)$ data, where λ_1 and λ_2 are the eigenvalues of the $\rho(r)$ Hessian matrix in two mutually perpendicular directions at right angles to the bond line.[83]

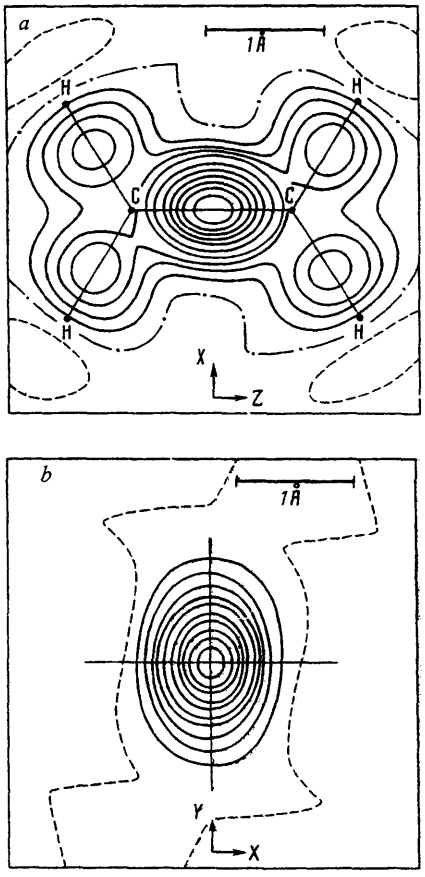


Figure 5. DED sections through the ethylene molecule in the plane of the latter (*a*) and in the plane perpendicular to the C—C bond and passing through its centre (*b*). The contours are drawn at 0.05 e Å^{-3} intervals.

The DED sections through the acetylene molecule (data at 141 K) are presented in Figs. 6*a* and 6*b*. The height of the DED maximum at the centre of the C≡C triple bond (1.182 Å) is 0.60 e Å^{-3} and the DED map actually coincides quantitatively with the results of the theoretical calculation for C_2H_2.[82] We emphasise that, since two π-bonds are formed in ethylene in mutually perpendicular directions, it follows that in the section normal to the C≡C bond line the characteristic ellipticity of the DED maximum is no longer observed (Fig. 6*b*).

The DED section in the plane of the C atoms of the cyclopropane molecule is illustrated in Fig. 7 (structural data[84] obtained at 94 K). It is characterised by the presence of distinct maxima located between the nuclei of the C atoms and displaced from the C—C bond line to the outer side of the triangle. The magnitude of the

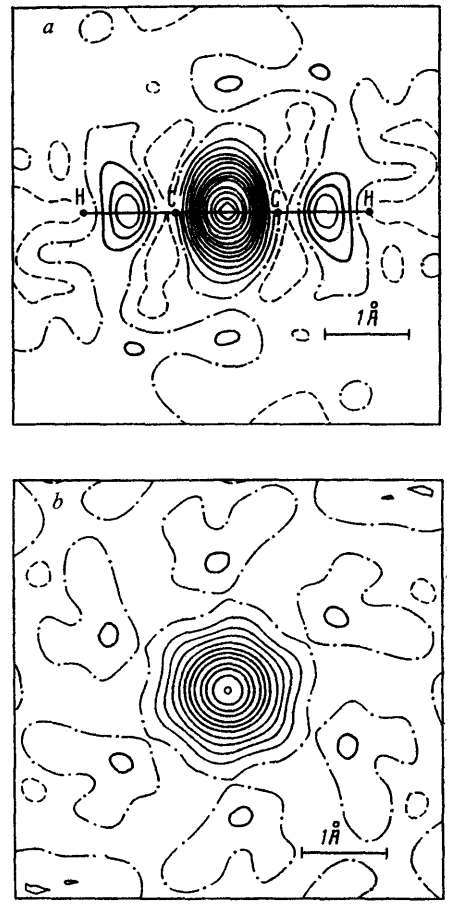


Figure 6. A DED map for the acetylene molecule (*a*) and the section in the plane perpendicular to the triple bond and passing through the centre of the molecule (*b*). The contours have been drawn at 0.05 e Å^{-3} intervals.

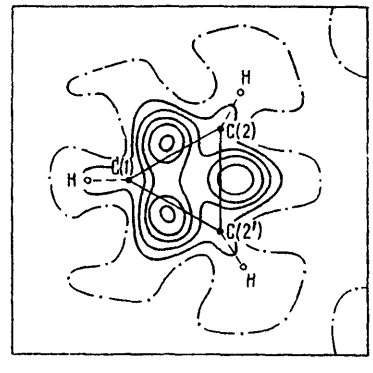


Figure 7. DED section through the plane of the C atoms of the cyclopropane molecule. The contours have been drawn at 0.05 e Å^{-3} intervals.

displacement is ~0.20 Å which constitutes clear confirmation of the ideas concerning "bent" bonds in strained small rings. A similar displacement of the DED maxima from the C–C bond line has been observed also in a series of other investigations of compounds with small rings or with strained three-membered frameworks. For example, in the tetra(t-butyl)tetrahedrane molecule, the DED maxima are displaced to the outer side of the tetrahedral molecular framework by 0.36 Å.[85] In perfluorotricyclooctane C_8F_{12} (XIII) (Fig. 8), investigated[86] at 163 K and containing condensed saturated four-membered rings, the DED maxima are displaced from the C–C bond line to a much lesser extent (~0.15 Å), which indicates a smaller bond strain in four-membered carbocycles compared with the three-membered rings.

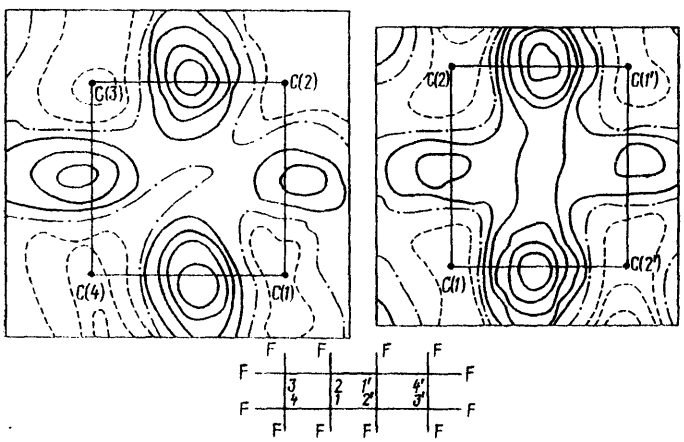


Figure 8. DED section in perfluorotricyclooctane (XIII) drawn through the planes of the four-membered rings of the molecule. The contours have been drawn at 0.1 e Å^{-3} intervals.

The examples considered above referred to molecules of organic compounds whose chemical bonds can be described within the framework of ideas concerning the formation of such compounds via the generation of localised two-centre bonds in them. In compounds where significantly **many-centre bonds with electron delocalisation** are formed according to existing ideas (for example in the molecules of borane or carbaboranes and in the cluster compounds of metals), the distribution of DED in the region of the bond is different. Figs. 9*a* and 9*b* present DED maps in sections drawn through the carbaborane nucleus (Fig. 9*a*) and the triangular B_3 and B_2C faces (Fig. 9*b*) of the icosahedron in the structure of 9-azido-*m*-carbaborane (XIV) [87] (the structural data were obtained at 163 K). In compound (XIV), the DED maxima are not distinctly localised on the B–B and B–C edges of the icosahedron or near the line connecting the atomic nuclei, as happens in the examples considered above. The excess (positive) DED is in fact distributed continuously in the region of the triangular faces but with a slight displacement of the DED on the B_2C face in the direction of the more electronegative C atom. The section through the centre of the icosahedron (Fig. 9*a*) shows that within the carbaborane framework the DED has a negative value (–0.16 e Å^{-3}) and the entire excess electron density is concentrated in a small spherical surface layer of the icosahedron and its distribution is virtually continuous. Thus, judging from the DED maps, the bonds in carbaboranes are formed as a result of the surface delocalisation of electron density, which agrees with the theoretical ideas put forward previously.[88]

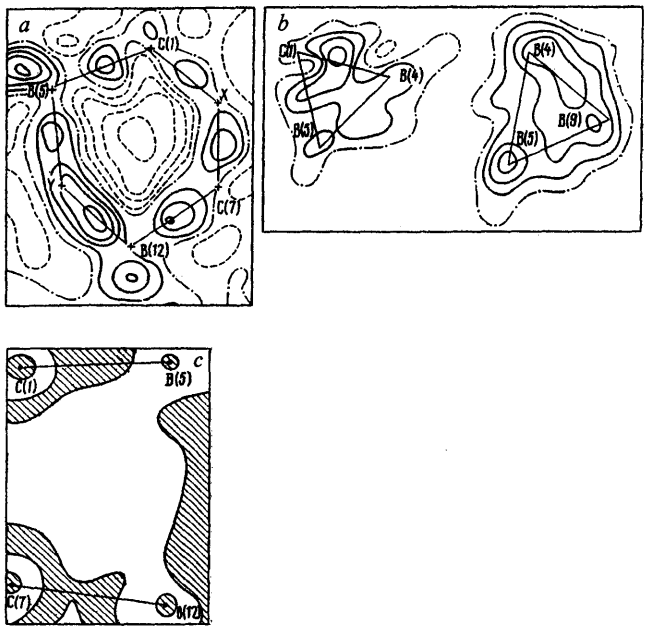


Figure 9. Distribution of electron density in 9-azido-*m*-carbaborane (XIV): *a*, DED section through the centre of the icosahedron passing through the C(1), B(5), C(7), and B(12) atoms and the centres of the B(2)–B(3) (*X*) and B(9)–B(10) (*Y*) bonds (the contours have been drawn at 0.04 e Å^{-3} intervals); *b*, DED section through the B_3 and B_2C triangular faces; *c*, $\nabla^2\rho(r)$ Laplacian section through the centre of the icosahedron passing through the C(1), B(5), C(7), and B(12) atoms (in the shaded regions, $\nabla^2\rho < 0$).

An additional confirmation of the results for compound (XIV) is provided by the calculation from the experimental data of maps of the electron density Laplacian $\nabla^2\rho(r)$ characterising the curvature of the function $\rho(r)$ in three mutually perpendicular directions. By definition, the Laplacian of the function $\rho(r)$ is the sum of the second partial derivatives:

$$\nabla^2\rho(r) = \frac{\partial^2\rho}{\partial x^2} + \frac{\partial^2\rho}{\partial y^2} + \frac{\partial^2\rho}{\partial z^2}, \qquad (6)$$

and, in conformity with the local formulation of the virial theorem for the energy of electrons $2E_{kin}(r) + E_{pot}(r) = {}^1/_4\nabla^2\rho(r)$,[89,90] the negative values of the function $\nabla^2\rho(r)$ in the molecular systems correspond to the parts of the space in which the local electron density is enhanced and in which the contribution of the potential energy stabilising the system predominates. Compared with the difference DED maps, the $\nabla^2\rho(r)$ maps have an important advantage: their construction does not necessitate the calculation of the electron density of the reference state

$$\rho^0(r) = \sum_{at} \rho^0_{at}$$

(of the premolecule), which is subtracted from $\rho(r)$ in the calculation of DED. For this reason, the $\nabla^2\rho(r)$ maps constitute an important and sometimes even a more informative complement of the DED maps used in the study of the electron distribution in crystals.[18] Fig. 9*c* presents the $\nabla^2\rho(r)$ map (the section was drawn through the carbaborane nucleus) of the molecule of compound (XIV), characterised by a wide range of positive values of the Laplacian within the carbaborane nucleus, i.e. the concentration of electron density is reduced within the nucleus, which is consistent with the form of the analogous DED map (cf. Fig. 9*a*). We also emphasise that in the vicinity of the C atoms there are in Fig. 9*c* regions $\nabla^2\rho(r) < 0$, i.e. regions of a local enhanced concentration of $\rho(r)$, which agrees with the greater electronegativity of these atoms compared with B atoms.

In the study of the electron distribution in compounds containing atoms with filled or more than half-filled valence shells (N, O, F, P, S, Cl, etc.), DED maxima are frequently observed near such atoms. They can be attributed to the sites where **the lone electron pairs (LEP) of these atoms are located.** Depending on the nature of the atom and the molecule and on the character of the crystal structure, the DED maxima can have significantly different heights, orientations relative to other bonds in the molecule, and degrees of diffuseness.

The characteristics of the manifestation of the lone electron pairs of the N and O atoms on the DED maps have been investigated frequently and in detail (see, for example, Breitenstein et al.[81]). These LEP are in fact always clearly seen on electron density maps and conclusions about the degree of hybridisation of the corresponding atoms can be reached from the character of their disposition.

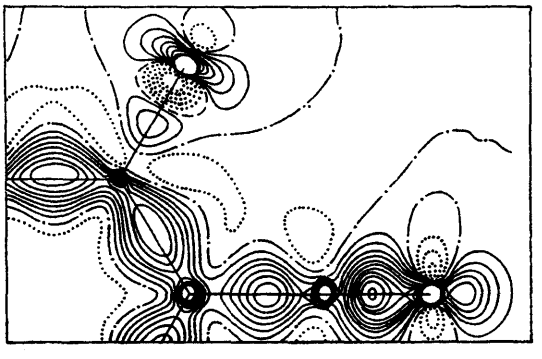


Figure 10. A static DED map in the plane of the $C_6F_4(CN)_2$ molecule (multipolar model). The contours have been drawn at 0.1 e Å^{-3} intervals.

We shall consider the characteristic features of the electron distribution in the region of LEP of halogen atoms. In the vicinity of the fluorine atoms, the LEP are as a rule manifested less distinctly, particularly in the construction of the DED maps by the traditional "$X-X$" method (see above), which is partly caused by their location near the F nuclei, where the error of the experimental determination of $\delta\rho(r)$ is large. Nevertheless, when more flexible, for example multiparameter multipolar models are used for the representation of DED, excess density maxima are observed near the F atoms and are disposed at right angles to the bond lines involving these atoms. As an example, one may quote data[91,92] obtained in the study of the electron distribution in a tetrafluoroterephthalodinitrile $C_6F_4(CN)_2$ (XV) crystal at 98 K [the error of the determination of the DED in compound (XV) in the region of chemical bonds is 0.02 e Å^{-3}; the DED maps were constructed using Hirshfeld's model[93] (Fig. 10)].

We may note that, in constructing the $\delta\rho(r)$ maps using the different multipolar models mentioned above, the electron density of the crystal is represented analytically by an expansion of $\rho(r)$, for example, in terms of angular harmonics or their combinations. The parameters of this expansion (the populations of the multipoles and the exponential multiplier in their radial components), as well as all the remaining positional and thermal parameters of the structure are refined by the least squares method. The first term in the expansion of the function $\rho(r)$ corresponds either to the electron density of the free atom $\rho^0(r)$ (Hirshfeld's deformation model[93]) or to the electron density $\rho_{int}(r)$ of the atomic core (the Stewart[94] or Hansen–Coppens[95] model).

More complex models for the analytical representation of $\rho(r)$ have also been proposed recently (see Porai-Koshits's review[18]) and it is significant that the analytical representation of the functions $\rho(r)$ and $\delta\rho(r)$ does in fact simplify the problem of the calculation of the properties of crystals which depend on these functions.[79] On the other hand, the multipolar representation of electron distribution data requires the refinement of a much greater number of independent parameters in least squares schemes. As a result of this, the use of low-temperature diffraction data in such studies on molecular crystals is sometimes essential, since only this makes it possible to secure a sufficient number of reflections (including large angle reflections) which are necessary for a significant refinement of additional multipolar parameters.

Characteristic examples are provided by data for $LiNO_3.3H_2O$ (at 295 and 120 K [96]) and imidazole (at 293 and 103 K [97]) crystals in which electron density was modelled with the aid of the Hirshfeld and Stewart multipoles respectively. In both cases, the authors pointed out the inadequate accuracy and amount of experimental data obtained at room temperature, which distorted the picture of the electron distribution.

Near the nuclei of covalently bound Cl atoms, the peaks corresponding to the LEP of the latter are shown clearly. In particular, in the study of the phosphorane $Cl_3P(CCl_3)_2$ at 153 K [56] the presence of effectively localised positive DED maxima, with a height of 0.2–0.3 e Å^{-3}, was established in the vicinity of the nuclei of Cl atoms. The maxima are at distances of 0.7–0.8 Å from these nuclei and are oriented in directions at right angles to the P–Cl and C–Cl bonds (Fig. 11).§ In terms of the character of their dispositions, these peaks should correspond to the LEP of Cl atoms having an appreciable p character. Furthermore, beyond the nuclei of the Cl atoms on the lines obtained by producing the P–Cl and C–Cl bonds, there are DED minima indicating the involvement of the p_σ orbitals of the Cl atoms in the formation of the corresponding bonds. We may also note an interesting feature of Fig. 11 associated with the presence on the axial "hypervalent" P–C bonds in this

§ The study of compound (VIII) at room temperature[57] indicated appreciable intramolecular vibrations of the CCl_3 groups, which hindered a reliable determination of the characteristic features of the DED maps.

compound of two intense DED maxima with heights of 0.35 and 0.40 e $Å^{-3}$. The presence of these maxima is consistent with the known fact that the axial disposition of electronegative substituents in pentacovalent phosphoranes is preferred.

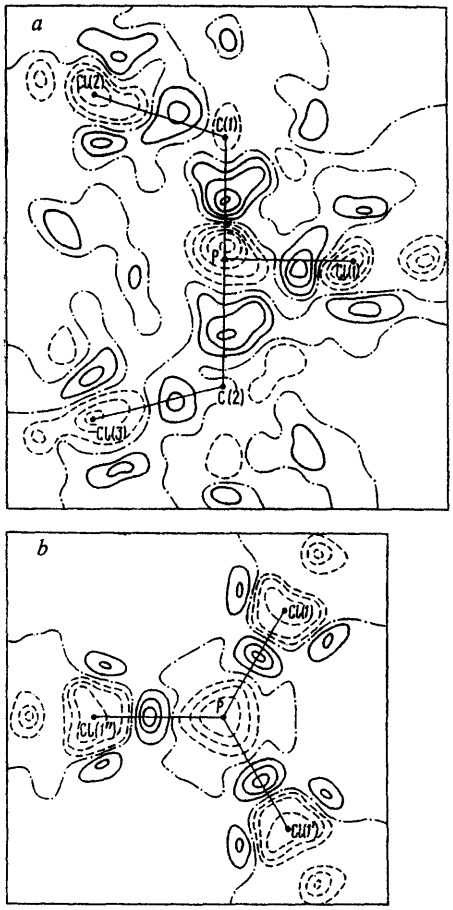


Figure 11. DED sections in the axial (*a*) and equatorial (*b*) planes of the phosphorane $Cl_3P(CCl_3)_2$ (VIII) molecule. The contours have been drawn at 0.1 e $Å^{-3}$ intervals.

An interesting example of the manifestation of the LEP of the Cl atoms on the DED maps has been observed in a study of the crystal of difluorochloronium tetrafluoroborate $ClF_2^+BF_4^-$ (data obtained[98] at 153 K). At room temperature, this readily hydrolysed compound consists of an equimolar mixture of gaseous ClF_3 and BF_3. On the DED map drawn in the bisector plane of the "angular" ClF_2^+ cation (with the angle F–Cl–F = 96.4°), there are in the vicinity of the Cl atom two maxima located at an angle of ~150° (Fig. 12), whose positions can be attributed to the localisation of the two LEP of the Cl atom. By building up the electron environment of the central atom to a distorted tetrahedron, these LP should occupy (according to Gillespie's ideas about the repulsion of electron pairs of the chemical bonds and the LP [99]) a larger solid angle in space than the electrons of the Cl–F bonds, which in fact increases the LP–Cl–LP angle in the ClF_2^+ cation compared with the tetrahedral value.

The data obtained agree with the results of a quantum-chemical calculation[100] of the positions of the regions of local higher concentration of electron density, i.e. with the calculation of the distribution of the Laplacian $\nabla^2\rho(r)$, according to which the angle between the minima in $\nabla^2\rho(r)$ in the region of the Cl–F bonds is 99° (the location of the valence electrons of the Cl–F bonds is consistent with this), while the angle between the $\nabla^2\rho(r)$ minima in the bisector plane of the cation is ~143° (the distance from the nucleus of the Cl atom to the centres of these minima is 0.604 Å).[100] Certain new data obtained in calculations of the $\nabla^2\rho(r)$ maps in order to locate the electron pairs of the halogen atoms have been discussed.[101]

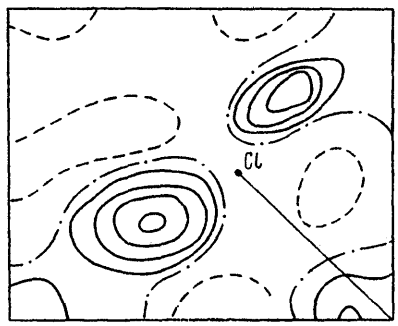
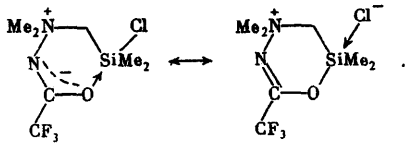


Figure 12. DED section in the structure of $ClF_2^+BF_4^-$ in the plane at right angles to the plane of the ClF_2^+ cation along the bisector of the F–Cl–F angle (the right-hand line). The contours have been drawn at 0.07 e $Å^{-3}$ intervals.

As a result of the improvement of the experimental diffraction method as well as the advances in the synthesis of compounds of fundamentally new types, which are frequently extremely unstable and have an unusual and complex structure, it has been possible in recent years to expand the research into the electron distribution in such compounds. In many cases, their great complexity precludes quantum-chemical calculation of the distribution of electron density in compounds of this kind, which makes the determination of experimental characteristics of their electronic structure of current interest. We shall consider examples of such studies in the series of **organoelement compounds.**

The study of the DED distribution in the trigonal-bipyramidal derivative of pentacoordinate silicon (XVI) was undertaken[102] as part of systematic structural investigations[103] of organosilicon compounds with additional intramolecular Si...O coordination in the "hypervalent" [O–Si–X] fragment. A precision study of compound (XVI) at 163 K showed that the Si atom is involved in trigonal-bipyramidal coordination with an axial disposition of the Cl and O atoms (the Cl–Si–O angle is 172° and the deviation of the Si atom from the equatorial plane of the three C atoms in the direction of the O atom is 0.076 Å). The Si–Cl = 2.434(1) Å bond in the molecule of compound (XVI) is very greatly lengthened, while the Si–O = 1.880(1) Å bond is close to the length of the covalent bond, although its length still exceeds somewhat the typical value for this bond. The C=O carbonyl bond in compound (XVI) has been lengthened to 1.285(2) Å, while the C=N = 1.289(1) Å bond actually corresponds to a double bond of the type $-N=C(sp^2)$.

The results suggest that the electronic structure of the molecule of compound (XVI) can be represented by the superposition of the "limiting" valence forms (A) and (B):



(XVI, A) (XVI, B)

The DED section in the axial plane of the molecule containing Cl, Si, O, and C(1) atoms shows (Fig. 13*a*) that one of the DED maxima near the O atom, whose height is 0.24 e Å^{-3} and which is usually attributed to the LP of this atom, is oriented precisely in the direction of the Si–O axial bond. On the other hand, an individual maximum was not observed on the Si–O bond, although its appearance might have been expected in the case of the formation of the usual covalent Si–O bond in compound (XVI). On the other Si–Cl bond, distinct positive DED peaks are visible only in the immediate vicinity of the nucleus of the Cl atom, while in the centre of the Si–Cl bond the DED is close to zero. In this respect, the DED map in the region of the bonds under consideration differs significantly from that found for similar but shorter (2.09–2.15 Å) Si–Cl bonds in the previously investigated trigonal-bipyramidal trichlorosilyltetrahydrophenanthroline derivative of pentacoordinate silicon.[104] The DED map in the region of the Si–Cl bond in this compound contains distinct maxima on the Si–Cl lines as well as maxima in the region of the LP of the Cl atoms located at right angles to the Si–Cl bond.

A similar picture of the DED distribution, characteristic of a covalently bound Cl atom, has been observed also in the region of the P–Cl and C–Cl bonds in the phosphorane (VIII) (Fig. 11). The data obtained for compound (XVI) evidently show that the Si–Cl bond in compound (XVI) can no longer be regarded as appreciably covalent and it is more likely that in this case a coordination interaction $Cl^- \rightarrow Si$ is observed [contribution by the form (B)]. This conclusion agrees with the increased length of the Si–Cl bond in compound (XVI) and also with the known fact[105] that, in nucleophilic substitution at a tetracoordinate silicon atom, the Cl atom is a "readily eliminated group" (as the Cl^- anion) from the axial position in the trigonal bipyramid of silicon.

The degree of electron delocalisation in the N(1)–C(1)–O amide group of compound (XVI), between the atoms of which there is a possibility of π-conjugation, can be estimated from the form of the DED sections passing at right angles to the C(1)–O and N(1)–C(1) bonds through their midpoints (Figs. 13*b* and 13*c*). A characteristic feature of these sections is the ellipsoidal form of the DED maxima, extended along the (*ab*) and (*cd*) lines perpendicular to the N(1)–C(1)–O plane illustrated by dashed lines in Figs. 13*b* and 13*c*. The form of the maxima constitutes clear confirmation (cf. the analogous section for ethylene—Fig. 5*b*) that the π-component contributes to the formation of the bonds under consideration and that in the case of the N(1)–C(1) bond this component is much more distinct than for the C(1)–O bond [contribution by the form (B)]. Thus the character of the electron distribution in the molecule of compound (XVI) clearly indicates the possibility of representing its electronic structure by a superposition of the forms (A) and (B) presented above. The data obtained from the analysis of the DED maps in compound (XVI) can be evidently used to model the character of the distribution of the electron density of the "transition state" of a S_N2 substitution reaction at the tetrahedral Si atom, which proceeds via the formation of intermediate trigonal-bipyramidal structures.

Another example is associated with the study of the electron distribution in a derivative of dicoordinate phosphorus in the phosphaalkene $(NMe_2)_2C{=}P{-}H$ (VIII) (structural data obtained[106] at 163 K). Phosphaalkenes—compounds with the $>C{=}P$-group are a comparatively new class of phosphorus derivatives and their simplest representatives, including compound (XVII), are as a rule low-melting and unstable. X-Ray diffraction study of a large group of phosphaalkenes demonstrated previously the high tendency of these compounds to conjugate the P=C double bond with the substituents at the P and C atoms,[107] which can lengthen appreciably the double bond to ~1.76 Å [in compound (XVII), the bond length P=C = 1.740(2) Å compared with the usual value of ~1.66 Å in the absence of conjugation]. In order to determine the qualitative characteristics of the electron distribution in phosphaalkenes, DED maps were constructed[106] in the region of the P=C and C–N bonds of the molecule of compound (XVII). Fig. 14*a* illustrates the DED section in the H–P=C plane [the displacement of the N(1, 2) from this plane is ±0.3 Å]. A characteristic feature of this map is the presence of the DED maximum on the P=C bond with a height of 0.39 e Å^{-3} and located approximately in the middle of the bond, and

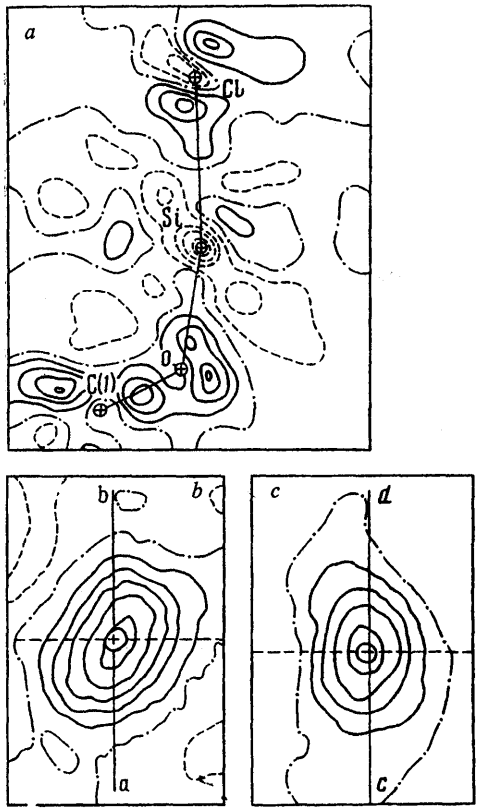


Figure 13. DED sections in the molecule of compound (XVI): *a*, in the axial plane through the Cl, Si, O and C(1) atoms (the contours have been drawn at 0.07 e Å^{-3} interval; *b*, and *c*, at right angles to the C(1)–O and C(1)–N(1) bonds and through the centres of the latter. The contours have been drawn at 0.05 (*b*) and 0.07 (*c*) e Å^{-3} intervals.

also of a maximum A (0.18 e Å^{-3}) located beyond the nucleus of the P atom at a distance of ~0.65 Å, lying in fact on the prolongation of the C=P bond line. In the plane of the π-bond (Fig. 14*b*), the DED maximum is characterised by an appreciable ellipticity, indicating a significant contribution of the π-component to the bond. A π-component of this kind can be seen also in the single C–N(1, 2) bonds, shortened to 1.348(4) and 1.391(4) Å, which is evidence for the occurrence of conjugation in the P=C=N chain.

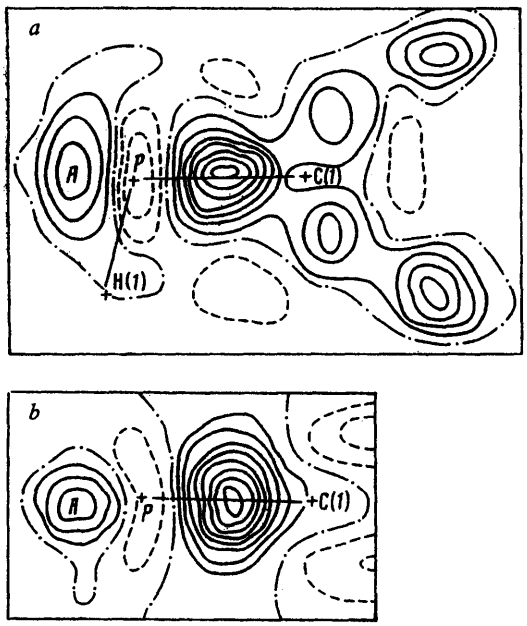


Figure 14. DED maps in the $(NMe_2)_2C=P-H$ (XVII) molecule: *a*, section in the plane of the H(1), P, and C(1) atoms (the contours have been drawn at 0.05 e Å^{-3} intervals); peak A—region of the LP of the P atom; *b*, section in the π-plane of the C=P bond (the contours have been drawn at 0.05 e Å^{-3} intervals).

The maximum A in the vicinity of the P atom is evidently associated with the location of the LP of this atom and from the character of its position one may conclude that the LP has appreciable *s* character. This conclusion agrees with the results of non-empirical quantum-chemical calculations for the simplest alkylidenephosphines.[106,108]

We may note that the significant *s* character of the LP of the P atom can explain the finding that, in the large series of structurally investigated phosphaalkenes (see the review of Chernega et al.[107]), the bond angle at the dicoordinate phosphorus atom is appreciably smaller than the value of 120° characteristic of the sp^2-hybridisation of this atom. Furthermore, the enhanced *s* character of the phosphorus LP in the compounds considered can be the reason why phosphaalkenes exhibit a lower reactivity than phosphines in oxidative addition reactions.[109]

Thus analysis of the DED maps made it possible in many instances to discover clearly the principal features of the electron distribution in the series of compounds of different types, agreeing with the traditional ideas about their electronic structure. In the language of electron distributions, particularly in terms of DED data, typical features of localised and delocalised (many-centre) bonds, strained (bent) bonds, π-bonds, hypervalent, coordinate, and dative bonds, etc. have been formulated and clear confirmation of many qualitative electron ideas used in chemistry has been obtained.

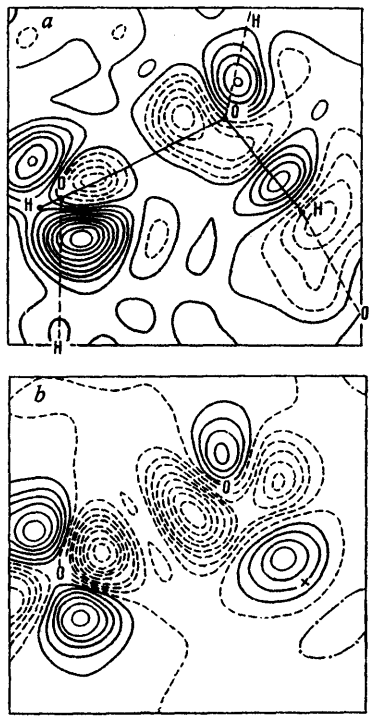


Figure 15. DED maps in the O–O–H plane of the hydrogen peroxide molecule: *a*, experimental data;[111] *b*, calculation.[113] The contours have been drawn at 0.1 e Å^{-3} intervals.

On the other hand, as DED data for different classes of compounds have accumulated, a series of **"strange" results** have appeared (see the review of Tsirel'son and Antipin[76]), which did not fit within the existing ideas about the electron distribution in the region of the chemical bond. In particular, the presence of only weak DED maxima or their complete absence from certain single covalent bonds between atoms whose valence shells are more than half-occupied proved to be difficult to understand. This result was observed in the study of the N–N bonds in a large group of hydrazine derivatives and on C–F, C–O, N–O, etc. bonds. For example, in the precision low-temperature study of 1,2,7,8-tetraaza-4,5,10,11-tetraoxatricyclo[6.4.1.1]tetradecane (III) (see above), it was found that the heights of the DED maxima on the bonds diminish systematically in the sequence C–N > C–O > N–N > O–O and in the region of the O–O bond the DED is actually negative.[110] In a series of other peroxide compounds, including hydrogen peroxide H_2O_2 (data obtained[111] at 100 K), the DED on the O–O bond is also negative (Fig. 15). These facts conflict with the traditional ideas about the formation of the covalent bond as a simple concentration of electron density in the space between nuclei, originating from early theoretical studies of the electron distribution

in the H_2 molecule; nevertheless the absence of significant DED maxima in the region of the bonds considered has been satisfactorily reproduced in quantum-chemical calculations.[81,112–114]

Detailed analysis of this problem carried out in a number of studies,[17–19,76,112–117] showed that the formation of a bond in the H_2 molecule has a number of specific features as a consequence of the absence from the molecule of steric restrictions on $\rho(r)$ imposed by the Pauli principle, and the H_2 molecule can therefore probably be regarded as a "classical" example in the study of the formation of a covalent chemical bond. The absence of DED peaks in the region of the bond considered is due to the fact that in such systems the rearrangement of electron clouds of the atom on formation of bonds proceeds in such a way that the outflow of electrons from the internuclear space as a consequence of the Pauli principle exceeds the effect associated with the increase in electron density in the same region as a result of the interference of the atomic electron clouds.[115] Since the DED maps illustrate the character of the redistribution of electron density relative to the "premolecule"[116] (an assembly of non-interacting atoms), the formation of the covalent bond proper is in many instances masked by other electronic effects (in particular, the transfer of part of the electron density from the internuclear space to the region of the LP), whose magnitude is greater the greater the degree of occupation of the valence shells of the atoms forming the chemical bond.

The foregoing permits the conclusion that the absence of positive DED in the region of the chemical bond is not essential evidence for the absence of a covalent bond and is frequently merely a result of the "oversubtraction" of the electron density, which is naturally not zero in the internuclear space of covalently linked atoms. Nevertheless, the information content of the DED maps is reduced in such cases.

We also emphasise that the presence of the DED maxima between atomic nuclei is likewise not always a sufficient condition for the formation of a covalent chemical bond.[118] In particular, the form of a theoretical DED map for the unstable Be_2 molecule does not differ qualitatively from the DED in stable diatomic molecules, for example in N_2: in both cases, $\delta\rho(r) > 0$ in the internuclear space.[119] Furthermore, even on formation of the simplest diatomic molecules, such as C_2, N_2, O_2, etc.,[84] the positive DED peaks are concentrated not only between the nuclei but also beyond them in the so called "non-bonding" regions, which diminishes, in conformity with Berlin's ideas,[120] the electrostatic forces linking the nuclei. Thus, in the analysis of DED maps and in their interpretation, it is essential to examine in detail all the positive and negative regions of such maps in the vicinity of the atomic nuclei, between which chemical bonds may (or may not) be formed.

It has been noted[118] that analysis of the changes in the electron distribution in the immediate vicinity of the atomic nuclei ($r < 0.4$ Å) is in many instances important for the understanding of the causes of the formation of a chemical bond. The electron density in these regions mainly determines the electrostatic forces acting on the nuclei, but this part of $\rho(r)$ is in fact fairly difficult to establish experimentally and theoretically with a high degree of accuracy. For example, in the multipolar analysis of the DED in the $C_6F_4(CN)_2$ (XV) molecule, it was found that the presence of a very weak $\delta\rho(r)$ maximum on the C–F bond (Fig. 10) cannot ensure the balance of electrostatic forces in the molecule required in accordance with the familiar Hellmann–Feynman theorem. In order to achieve this balance, one must take into account the polarisation of the inert electron clouds of the F atoms and, according to Hirshfeld,[92,121] such polarisation (deformation) of the atomic core can be detected experimentally when accurate X-ray and neutron diffraction data are used jointly and when the accuracy of the determination of the locations of the nuclei is to within $\sim 10^{-4}$ Å. Such an error may be attained only when diffraction data obtained at helium temperatures are used.

As a consequence of the difficulties in the interpretation of the DED maps listed above, other versions of the analysis of the experimental electron distribution data were developed in recent years, in particular methods for the calculation of maps of the **electron density Laplacian** $\nabla^2\rho(r)$ (see above) whose construction does not require the subtraction from $\rho(r)$ of the electron density of the "reference" state selected in a specific manner. Analysis of the Laplacian $\nabla^2\rho(r)$ is part of the study of the topological characteristics of the function $\rho(r)$ within the framework of Bader's theory,[88–90] which has now made possible the most rigorous definition of molecular structure, of an atom in a molecule, and of the chemical bond. A detailed discussion of the results of the analysis of the properties of the functions $\rho(r)$, $\delta\rho(r)$, and $\nabla^2\rho(r)$ within the framework of Bader's theory in relation to the study of the nature of chemical bonds of different types has been considered in a number of reviews.[18,76,83] Here we shall only emphasise that the joint analysis of the functions $\delta\rho(r)$ and $\nabla^2\rho(r)$ derived from the results of a precision diffraction experiment made it possible to deepen the existing ideas about the chemical bond.

In conclusion of the review, we shall consider briefly the possibility of using precision diffraction data, including DED maps, for the interpretation of the characteristic features of **the chemical reactivity of compounds.** We may note that so far there are few examples of such studies, although problems of the relationship between the reactivity of molecules (for example, their capacity for protonation) and their quantum-chemically calculated electrostatic properties, in particular their molecular electrostatic potential (MEP), have been considered in fair detail in the literature.[122] The MEP maps, calculated by quantum-chemical methods, have a simple physical significance, namely the MEP minima must correspond to protonation centres in the compound considered.

The similarities and differences between the corresponding MEP and DED maps for relatively simple molecular compounds have been investigated in a number of studies[122–125] and it has been shown that in many cases such maps are topologically similar. Thus, by formulating, using the procedure of Weber et al.,[125] the electrostatic potential $V(r)$ at a point r for the molecular system, characterised by the electron density distribution function $\rho(r)$, as the sum of the electronic and nuclear components, we have

$$V(r) = -\int \frac{\rho(r')}{|r-r'|}\,dr' + \sum_A \frac{Z_A}{|R_A - r|}, \qquad (7)$$

where Z_A is the nuclear charge of the atom A with the coordinates R_A (summation with respect to all the atoms in the molecule). After introducing the electron density of the premolecule

$$\rho^\circ(r') = \sum_A \rho_A^\circ(r'),$$

the expression for $V(r)$ can be put in the equivalent form

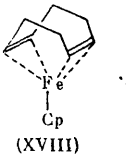
$$V(r) = -\int \frac{\rho(r') - \sum_A \rho_A^\circ(r')}{|r-r'|}\,dr' + \sum_A \left(\int \frac{-\rho_A^\circ(r')}{|r-r'|}\,dr' + \frac{Z_A}{|R_A - r'|} \right). \qquad (8)$$

The expression in round brackets in the last sum is the atomic electrostatic potential $V_A(r)$ and Eqn. (8) can therefore be written thus:

$$V(r) = -\int \frac{\delta\rho(r')}{|r-r'|}\,dr' + \sum_A v_A(r). \qquad (9)$$

It has been shown by Politzer[126] that in the vicinity of an atom the quantity $V_A(r)$ is positive and the sign of the potential is therefore determined by the sign of $\delta\rho(r)$ (the DED function) and by the integral in Eqn. (9). It follows from Eqn. (9) that the negative regions of MEP (the possible centres for protonation or electrophilic attack) in molecules can be mutually related to regions in which there are electron density maxima on the corresponding DED maps.

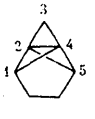
We shall consider certain examples confirming the foregoing. Thus, a precision study of the DED (data obtained[78] at 100 K) of the 17-electron π-cyclopentadienyl-η^4-cycloocta-1,5-dienyl iron complex (XVIII) and its adduct with Li(TMEDA) (TMEDA = tetramethylethylenediamine) established that the Li atom in the adduct is located in the direction of the sterically most accessible (least shielded) of the group of DED maxima near the Fe atom of the initial complex (XVIII), in which these maxima, associated with the populated 3*d* orbitals of the metal atom, are arranged octahedrally.



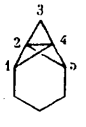
(XVIII)

The results may indicate a significantly electrostatic character for the Fe...Li interaction and may illustrate the possible direction of electrophilic attack on the metal atom. Another similar example is a study[127] of the DED in the "cubane-like" tetrahedral chromium cluster $(\eta^5\text{-}C_5H_4Me)_4Cr_4(\mu_3\text{-}S)_4$ (XIX). On the DED map of this compound, DED maxima were observed on the outer side of the SCr_3 tetrahedra beyond the S atom. They were interpreted as corresponding to the LP of these atoms. As a result of precisely this feature of the electron distribution, the μ_3-ligand of the cluster retains the capacity for weak additional "external" S...Cu coordination in complex (XIX) with $CuBr_2$.

An interesting result has been obtained recently in a study of two highly reactive [1.1.1]propellane derivatives (XX) and (XXI) (data obtained[128] at 81 K):



(XX)



(XXI)

The lengths of the C(2)–C(4) bridge bonds between the "inverted" carbon atoms in these molecules are 1.587 and 1.585 Å, the DED in the region of the C(2)–C(4) bonds being negative and close to zero (Fig. 16). On the other hand, on the outer side of the bridge bonds near the C(2) and C(4) atoms there are DED maxima 0.10–0.15 e Å^{-3} high. Indeed, according to Wiberg et al.,[129] the ease of the protonation of [1.1.1]propellane is responsible for the marked tendency of this compound to undergo acetolysis. The presence of the above non-bonding electron density maxima at the inverted carbon atoms in propellane derivatives has been confirmed[130] by calculations of maps of the electron density Laplacian for such compounds.

A new approach to the theoretical study of the nature of chemical reactivity, based on the analysis of the characteristic features of the electron distribution $\rho(r)$ and the characteristics associated with $\rho(r)$, in the first place the Laplacian $\nabla^2\rho(r)$, was proposed by Bader et al.[100] This approach proved to be closely related to the familiar method of Fukui's "frontier orbitals".[132] It was shown that the regions where the HOMO and LUMO frontier molecular orbitals are located in space correspond in the case of many compounds to regions of local concentration or rarefaction of electron density and the positions of the latter can be determined from the analysis of $\nabla^2\rho(r)$. In particular, analysis of the characteristic features of the function $\rho(r)$ for a series of carbonyl compounds indicates the presence in the valence environment of the C atom of the so called "critical" saddle points in the distribution of $\rho(r)$, where $\nabla(\nabla^2\rho) = 0$; they are distributed near the C atoms at an angle of ~110° relative to the C=O bond line above and below the plane of the carbonyl group.[100] Nucleophilic attack on the carbon atom actually takes place at this angle, which has been confirmed by the results of structural studies.[42] In addition to the foregoing, we may note also the results of studies[133,134] in which analysis of the quantum-chemically calculated $\nabla^2\rho(r)$ maps led to a conclusion about the mechanism of the opening of the three-membered ring in the protonated dimethyloxiran $(CH_3)_2\overline{CCH_2OH}^+$ on treatment with nucleophiles.

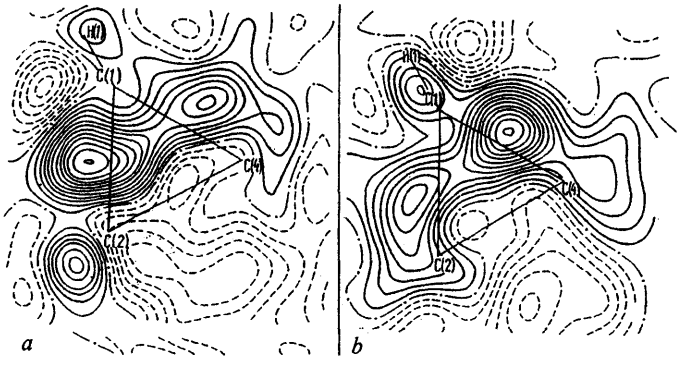


Figure 16. DED sections in the [1.1.1]propellane derivatives (XX) (*a*) and (XXI) (*b*) drawn through the C(1)–C(2)–C(4) atoms of the three-membered rings. The contours have been drawn at 0.025 e Å^{-3} intervals.

The above examples show that, in the field of study of the physicochemical properties of various compounds, the precision X-ray diffraction method can yield new interesting information about the character and features of the distribution of electron density in molecules. However, only the first steps have been taken in this direction. The expansion of the range of compounds investigated and also further improvement of the experimental accuracy of the method and of its computational techniques should evidently lead to the appearance of new and important results in the immediate future.

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