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The structures of organic molecules in crystals: simulations using the electrostatic potential

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Abstract. Studies devoted to simulations of crystal lattice effects on the electronic and spatial structures of organic molecules in molecular crystals with inclusion of the external potential created by the crystal environment into the Hamiltonian of the isolated molecule are surveyed. Various methods for the representation of the charge distribution in a molecule by atomic point charges or multipoles are compared and the necessity of the empirical correction of the molecular electrostatic potential obtained using the Hartree – Fock and semiempirical calculations is substantiated. The procedures for the modification of the Hamiltonian are analysed. The limits of applicability of this approach to simulations of specific intermolecular interactions (hydrogen bonds) are discussed. Examples of the use of methods based on the application of the electrostatic potential in the calculation of the crystal lattice energy, simulations of the molecular conformations in crystals and electronic excitations are presented. The importance of the results of computation of the electronic structures of molecules in crystals for systematisation of the crystal structures and, in particular, for comparative analysis of the structures of polymorph modifications is demonstrated. The bibliography includes 117 references.

I. Introduction

Nowadays, various quantum chemistry methods are widely applied to simulate the spatial and electronic structures of molecules. *Ab initio* calculations of molecules comprising 15 – 25 second-row elements using extended basis sets and taking into account the electron correlations by the Müller – Plesset method have become routine.[1] Calculations within Density Functional Theory (DFT) require less computational resources but are not applicable to specific problems.[2] Semiempirical methods are utilised in calculations of systems composed of a few hundred atoms.[3,4] Since researchers are interested in predicting properties of not only isolated molecules but of molecules in condensed phases (*i.e.*, in solutions, crystals, amorphous films, *etc.*) as well, the last 15 years have witnessed the intensive development of methods that account for the medium effects in quantum-chemical calculations.

Especially tremendous progress has been achieved in the simulations of interactions between solute and solvent molecules in solutions. Such investigations exploit two approaches that make it possible to reduce the duration of calculations to an acceptable level. The first approach uses a hybrid description of the system under consideration, *i.e.*, the central molecule is represented at the quantum-mechanical level, whereas solvent molecules are treated using molecular mechanics.[5] Within the second approach, the solvate environment of the central molecule is represented as a dielectric continuum.[6,7] It is remarkable that the energy of solvation of a number of molecular ions can be predicted quite precisely and, for instance, the fact of the existence of glycine molecules as zwitter-ions in aqueous solutions can be rationalised even within a simple continuum model without taking into account specific interactions between the solute molecule and its first solvate shell.[8] The continuum models are also used to calclulate solvatochromic effects.[9 – 11]

Taking into account that crystals are characterised by long-range ordering, one can suggest that the long-range electrostatic interactions therein play an even more important role than in solutions. Numerous theoretical and methodical procedures developed for solvation models can also be adapted to simulations of the crystalline state.

The strict quantum-chemical approach implies the calculation of the band structure of the crystal under periodic boudary conditions.[12,13] A number of software codes suitable for the solution of this problem are available based on the Hartree – Fock (HF),[14] DFT[15] or semiempirical[16] methods. In organic crystallography, however, this approach is rarely applied, probably, for two reasons: first, the band structure calculations require significantly larger computational resources than respective calculations of isolated molecules; second, direct comparison of the results of the crystal band structure and isolated molecules calculations are difficult. Still, in the majority of cases, the electronic structures of molecules in crystals do not differ, in principle, from those of isolated molecule, and thus the effects of the intermolecular interactions can be taken into account by including the external electrostatic potential (EP) into the effective Hamiltonian. Definitely, this is not valid for crystals of charge-transfer molecular complexes and for homomolecular stacking structures of organic photoconductors. But even in these cases, a one-dimensional representation[17] usually appears sufficient, and

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the interactions between the stacks can be described in terms of the external potential.

The present review is devoted to methods for the calculation of the electrostatic interactions in organic molecular crystals and to the application of these methods to the prediction of the crystal lattice energy and simulations of the spatial and electronic structures of molecules in crystals, including the dependence of the colour of crystals on the molecular packing therein.[18]

II. Two definitions of the crystal electrostatic potential

The crystal electrostatic potential can be defined as an effective potential that is experienced by an infinitely small point charge placed in the crystal lattice. For any point in space with coordinates r, it can be represented by a scalar function $\varphi(r)$, which depends on the charge density distribution $\sigma(r)$

$$\varphi(r) = \int_V \frac{\sigma(r')}{|r - r'|} \mathrm{d}r', \tag{1}$$

where the integration is performed over the entire crystal volume V.

The charge density $\sigma(r)$ contains the nuclear and electronic terms

$$\sigma(r) = \left[\sum_i Z_i \delta(r - R_i)\right] - \rho(r), \tag{2}$$

where Z_i and R_i are the charge and coordinates of the i-th atomic nucleus, respectively, δ is the delta-function, and $\rho(r)$ is the electron density.[19] If a crystal has a finite size, the expression for $\varphi(r)$ should also include the potential φ_0 dependent on the shape and structure of the crystal surface.[20] The distribution $\varphi(r)$ in a crystal can be derived experimentally, for instance, using X-ray diffraction.[21]

A different definition of the electrostatic potential can be formulated from the standpoint of energy. The total energy of a molecular crystal can be represented within the atom–atom approximation as

$$E = E_{\mathrm{r-d}} + E_{\mathrm{e}}, \tag{3}$$

where $E_{\mathrm{r-d}}$ is the sum of the energies of repulsion of complete electronic shells and the dispersion attraction of atoms for all molecules in the crystal, E_{e} is the total energy of the intermolecular Coulomb interactions.[22]

The first term in formula (3) is determined using the empirical pairwise potentials 6–12 or 6–exp, the second term is calculated from the charge density distribution in the crystal given by formula (2):

$$E_{\mathrm{e}} = -\sum_i \sum_j \int_V \int \frac{\sigma_i(r_1)\sigma_j(r_2)}{|r_1 - r_2|} \mathrm{d}r_1 \mathrm{d}r_2, \tag{4}$$

the integration is performed over the entire crystal volume V and the summation is performed over all pairs of molecules ($i < j$) in the crystal. The expression for E_{e} can be reformulated as

$$E_{\mathrm{e}} = -N \int_V U(r)\sigma_{\mathrm{A}}(r)\mathrm{d}r, \tag{5}$$

where N is the number of molecules in the crystal and $U(r)$ is the electrostatic potential experienced by the molecule A, which is created by other $N-1$ molecules in the crystal. Sometimes, the potential $U(r)$ is referred to as the Madelung potential to differentiate it from $\varphi(r)$ (see Ref. 23).

Analysis of topological features of the electrostatic potential distribution $\varphi(r)$ in different crystals gives important information on the electric field inside the crystal,[24,25] and, in particular, on specific features of the intermolecular interactions. However, in the present review we are concerned only with the potential $U(r)$ and focus on the methods for its calculation and inclusion into the computational schemes of quantum chemistry.

III. Calculation of the electrostatic potential and modification of the molecular Hamiltonian

Direct inclusion of a set of point charges (from several tens to several hundreds) around a molecule into the molecular Hamiltonian is the simplest way to model the electrostatic interactions of the molecule within its crystal environment. This does not result in any significant increase in the computational time since only the number of one-electron integrals increases. Such a procedure was used for the first time more than 30 years ago [26] for simulations of distortions of the structure of H_3O^+ ions in crystals of $HCl \cdot H_2O$ and $H_2SO_4 \cdot 2H_2O$ using the HF method. The account of the effects of the environment was realised by specifying 50 point charges located at the van der Waals surface of the molecular ion. A similar approach was used in a study of crystals of cyanoformamide:[27] all atoms of 8 molecules from the closest environment were represented by 84 point charges, which were updated in every cycle of the self-consistent field (SCF) procedure. At present, options on the use of point charges are included in several common software codes for non-empirical calculations, such as Gaussian, Gamess and ADF.

Since the series (4) converges very slowly, the Ewald method is normally applied in crystallography for the calculation of the lattice sums.[28] The Ewald method was adapted to HF calculations in such a way that the calculated 'pairwise Madelung constants' are used for the modification of Coulomb integrals without recourse to redetermine the lattice sums in every SCF cycle.[29,30]

It is of note that calculation of the electrostatic contribution to the crystal lattice energy requires accurate determination of the EP, whereas changes in the structure of a molecule in the crystal are caused primarily by the potential gradients within its boundaries. The series in the expression for the potential gradient converges much faster than series (4), the rate of convergence being dependent on the space group of the crystal. Thus, in some cases, consideration of only closest neighbours (typically, within a sphere of 10–20 Å) gives quite accurate results, which are virtually not improved upon inclusion of more distant molecules into the calculation.[31] However, the error due to the series truncation increases for crystals composed of molecules with large dipole moments and for non-centrosymmetric space groups. In those cases, the summation has to be performed over a sphere of 100–200 Å to achieve satisfactory accuracy.[32]

In early studies,[26,27,33] the EPs of crystals were estimated from the point atomic charges calculated using the Mulliken prescription. Presently, it is widely accepted that the Mulliken charges are inappropriate for calculation of the molecular electrostatic potential (MEP)[34,35] and do not reproduce the dipole moments of molecules.[36] Therefore, alternative schemes for the representation of charge densities in molecules have been developed. Charges obtained by fitting to the MEP calculated from the charge density distribution [37,38] are common in molecular mechanics, however this charge retrieval procedure is an ill-posed problem and cannot be efficiently accomplished for large molecules. A procedure of empirical correction for the Mulliken charges obtained in semiempirical [Austin Model 1 (AM1),[39] Parametrisation 3 (PM3),[40] Intermediate Neglect of Differential Overlap-Spectroscopic Parametrization (INDO/S)[41]] and *ab initio* calculations parametrised versus the experimental dipole moments of small organic molecules has been proposed by Truhlar *et al.*[42,43] These authors hoped not only to overcome the drawbacks resulting from the definition of the Mulliken charge itself but also to largely compensate for the systematic errors intrinsic to the semiempirical and HF calculations as well as for the errors of DFT calculations due to the restricted basis sets. Indeed, the above procedure reproduces the experimental values of the dipole moments with root-mean-square errors of 0.25–0.17 D (depending on the

quantum-chemical method used) for the original sample of 198 small molecules, which is 1.5–2 times smaller than those achieved in the direct calculations of the dipole moments from the charge densities. However the efficiency of the correction procedure decreases for compounds beyond the sample used for the parametrisation. For example, since nitro-compounds were not represented in the sample, the procedure not only fails to compensate for the overestimated dipole moments of compounds with an NO_2 group typically predicted by the AM1 and PM3 methods but gives even increased theoretical dipole moments.[44]

We note that the AM1 and PM3 methods provide nearly the same accuracy of calculation of the dipole moments for molecules composed of only first- and second-row elements as do the *ab initio* methods, which require significantly larger computational resources. Nitriles and nitro-compounds are the exception to this: the semiempirical methods underestimate the dipole moments of nitriles by 0.7–0.9 D and overestimate those of nitro-compounds by 0.6–0.8 D. The dipole moments calculated using the semiempirical methods better correlate with the results of the *ab initio* calculations with account for correlation effects † than those from the HF calculations.[44] Therefore, the semiempirical wave functions with empirical corrections for nitriles and nitro-compounds can indeed be used in the calculations of the MEPs of organic compounds without loss of accuracy.[32] On the other hand, the dipole moments of molecules containing sulfur, phosphorus or chlorine atoms are predicted by the semiempirical methods with significantly lower accuracy than by the *ab initio* methods with polarised basis sets.[42]

Among methods for the determination of atomic charges, the Hirshfeld method [45] is worth a special note, which assumes that the electron density at every point of the molecule should be divided over all constituent atoms proportional to their contributions to the electron density of the 'protomolecule', *viz*., the respective set of atoms that do not interact chemically. Despite this unusual formulation, this method yields atomic charges that often reproduce the energy of the intermolecular interactions better than the Mulliken charges.

An extensive verification of different models based on point atomic charges has demonstrated that none of them is capable of reproducing the MEP with high accuracy.[35] An explicit consideration of the character of the electron density distribution in atoms, in particular its extension and asphericity (*e.g*., lone pairs), is necessary in order to achieve the desirable level of accuracy. For this purpose, Stone proposed [46,47] a model of distributed multipoles, which enables determination of mono-, di-, quadrupole, *etc*. moments of atoms from the molecular wave function. Within the semiempirical methods based on the sp-basis, the quadrupole moment is the highest moment characterising a second-row element.[48] The original version of a common continuum model COSMO (Conductor-like Solvation Model) utilised only monopole and dipole moments of atoms, which gave satisfactory numerical results.[8] Later on,[49] the quadrupole moments were also included in the model.

According to the multi-centre model of point charges [50] also proposed for the semiempirical methods, an atom is represented by an atom core charge placed in the position of the atom nucleus surrounded by four pairs of charges, which mimic the native atomic orbitals.[51] The values of the charges are calculated based on the populations of the respective orbitals, and their distances from the atom nucleus depend on the contribution of the s-orbital into the respective sp^n-hybrid orbital. The main idea behind this model is similar to that of the model of distributed multipoles, and the accuracy of the MEP calculated based on this model is higher than those calculated within any scheme utilising point atomic charges (including those that use fitting to the MEP calculated directly from the electron density distribution). The contribution of higher electrical moments of atoms into the EP rapidly decreases with an increase in the distance; the contribution of quadrupole moments is as low as 1%–2% of the total EP at a distance of ~3.4 Å (which is the typical intermolecular distance in stacks of planar organic molecules). The contributions of quadrupole electrical moments become nevertheless substantial in crystals with short intermolecular contacts. However, the model cannot be applied to such systems, since the basic assumption of negligibly small intermolecular overlap of orbitals, which enables consideration of the intermolecular interactions within the classical theory, is then violated.[52]

Since the hydrogen atoms within the semiempirical calculations are assumed to possess only a 1s-orbital, they are represented in the multipole model as point charges. This representation is insufficient to correctly reproduce the MEP along the C—H direction; in order to reconcile the semiempirical results with the *ab initio* calculations [MP2/6–311+G**, where 6–311+G** is the Pople basis set extended with d- and p-polarisation functions with 1s-atomic orbitals approximated with six Gaussians and 2s- and 2p-orbitals approximated with five Gaussians grouped as (3,1,1)], additional point dipoles of 0.22 D [52] directed along the C—H bonds should be placed at the positions of all hydrogen atoms. As will be shown below, the contribution of the electrostatic interactions C—H···C into the total crystal lattice energy is small, but it has to be considered in simulations of crystal packing of aromatic hydrocarbons.[53]

Within a strict quantum-mechanical representation of a fragment of a crystal lattice by a cluster of N identical molecules composed of M atoms (the exchange interactions between the molecules are neglected), the following modification of the Fock matrix of a single molecule is necessary:[23]

$$F_{\mu\nu} = F^0_{\mu\nu} + \left(\mu\left|\sum_{j=,1}^{M}\sum_{i=2}^{N} -\frac{Z_j}{|r - R^i_j|}\right|\nu\right) + \\ + \frac{1}{2}\sum_{\lambda\sigma} P_{\lambda\sigma}\sum_{i=2}^{N}\left[\left(\mu\nu\middle|\lambda^i\sigma^i\right) + \left(\lambda\sigma\middle|\mu^i\nu^i\right)\right], \tag{6}$$

where μ, ν, λ and σ are atomic orbitals, the superscript index i relates to the ith molecule in the cluster (i varies from 2 to N); Z_j is the nuclear charge of the jth atom; R_j is its radius-vector; P is the matrix of orders of the intramolecular bonds. The numerical solution of Eqn (6) represents a time-consuming task which requires calculation of numerous two-electron Coulomb integrals. The Coulomb integrals at long distances can be approximated with sufficient accuracy by two interacting multipoles, but overlapping charge distributions have to be taken into account at short distances.

Instead of Eqn (6), an approximate expression is often used, which is analogous to that used in many continuum models, *i.e*.,

$$F_{\mu\nu} = F^0_{\mu\nu} + \left(\mu\middle|U(r)\middle|\nu\right), \tag{7}$$

where $U(r)$ is the EP [see formula (5)].

The non-diagonal two-atom terms of the Hamiltonian are calculated within the semiempirical methods using empirical parameters; these terms remain constant upon modification of the Hamiltonian. Thus, the matrix element $F_{\mu\nu}$ changes in the course of the iteration calculation only if both orbitals φ_μ and φ_ν belong to the same atom A.[54] The extension of $U(r)$ in Eqn (7) into the Taylor series in the proximity of atom A indicates that U(A) contributes to $F_{\mu\mu}$, $U'(A)$ contributes to $F_{\mu\nu}$ (where one of the atomic orbitals μ or ν is the s-orbital), $U''(A)$ contributes to $F_{\mu\mu}$ and $F_{\mu\nu}$ (where both are the p-orbitals), *etc*. Higher-order derivatives can be neglected in the calculations, even neglect of the second derivative does not result in substantial errors.[32,55]

† DFT/TZVP and MP2/DZVP, where TZVP and DZVP are the basis sets with triply and doubly split valence atomic orbitals extended with d- and p-polarisation functions, MP2 is a method to account for the electron correlations within the approximation of the Müller–Plesset second-order perturbation theory.

Finally, we point to one fact that is almost ignored in the literature. Representation of the electrostatic contribution to the energy of the intermolecular interactions in the Coulomb form [see Eqn (4)] gives satisfactory results at large interatomic distances, but if the molecules are close to each other, the mutual repulsion of the electrons will be weaker than that predicted by the Coulomb law due to exchange and correlation interactions. It is well known from the practical use of semiempirical methods that the theoretical calculation of two-centre Coulomb integrals yields unsatisfactory results.[56] Thus, such integrals are determined using empirical equations which predict values much smaller than the theoretical ones at short distances. In particular, the Dewar – Sabelli – Klopman formula [57, 58] is used for the calculation of two-centre integrals in the MNDO (Modified Neglect of Diatomic Overlap) family of methods

$$\gamma_{AB} = \left[R_{AB}^2 + 0.25\left(\gamma_{AA}^{-1} + \gamma_{BB}^{-1}\right)^2 \right]^{-1/2}, \qquad (8)$$

where R_{AB} is the distance between atoms A and B. Thus, the modified potential determined according to the equation analogous to (8) rather than the Coulomb potential should be used for the calculation of the energy of interaction between the charge densities of molecules [see Eqn (4)]. Various types of potentials have been tested in calculations of the electronic structures of dimers of organic molecules.[52] In the case of the Coulomb potential, the intermolecular interactions appeared overestimated, whereas the modified potential well reproduced the results of the direct calculation of the electronic structure of molecular dimers, including ones with moderately strong H-bonds (O···H and N···H > 1.80 Å).

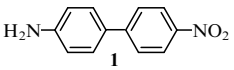
IV. Polarisation of molecules in crystals and the crystal lattice energy

As a rule, the intramolecular charge transfer and the dipole moment of a molecule increase on going from the gas phase to the crystal. In principle, the dipole moments of molecules in crystals can be determined experimentally by an analysis of the electron density distribution from X-ray diffraction data.[59, 60] For simple molecules, this procedure yields results in quite good agreement with the HF calculations of crystals under periodic boundary conditions (taking into account that the Hartree – Fock dipole moments are typically overestimated by 12% – 15%). Several examples are given in Table 1.

Nevertheless, in the case of large molecules, the results strongly depend on the method used for the analysis of X-ray diffraction data. For instance, high-precision diffraction data were collected [67] for *p*-nitroaniline and 4-amino-4′-nitrobiphenyl (**1**), which were further processed using the multipole model developed by Coppens.[68] Depending on the constraints imposed on the parameters κ and κ' of the multipole model (which define the degree of compression of the valence shell) during fitting, a large scatter in the values of dipole moments was observed for *p*-nitroaniline, whereas an unrealistically large value was obtained for compound **1** irrespective of the procedure applied. Probably, this poor reproducibility of the results is due to correlation between the parameters κ and κ' of neighbouring atoms, which results in incorrect assignment of the electron density in the proximity of one atom to another atom. Therefore, the results obtained using the EP can be compared with the experimental data and higher-level calculations only for simple molecules.

The molecular geometry of acetamide in crystal was calculated using the HF/4 – 21G method.[69] The potential $U(r)$ was approximated by point Mulliken charges of 102 neighbouring molecules within a sphere of 10 Å, which were updated every SCF cycle. The account of $U(r)$ lead to an increase in the charge transfer from the amino group to the carbonyl group, which was accompanied by shortening of the C – N bond (by 0.021 Å) and lengthening of the C = O bond (by 0.022 Å). According to the experimental data, the C = O bond length increases by 0.03 Å and the C – N bond length decreases by 0.043 Å on going from the gas phase [70] to the crystal.[71] Apparently, the effects of the crystal environment on the molecular geometry were underestimated in the aforementioned calculation. Probably, this is due to the fact that the model approximating the charge density by point charges is unable to correctly reproduce the effects of the intermolecular hydrogen bonds N – H···O = C, which are present in the crystals of acetamide. It is of note that the maximum discrepancy between the theoretical and experimental data relates to the amino group. This indicates that, first, the neglect of the lone pairs of the oxygen atoms gives rise to underestimation of the strength of the H-bonds and, second, the representation of the hydrogen atoms of neighbouring molecules by point charges is an adequate approximation.

Table 1. The dipole moments (D) of molecules in crystals according to X-ray diffraction measurements and quantum-chemical calculations under periodic boundary conditions (the CRYSTAL[14] code) and those based on the electrostatic potential.

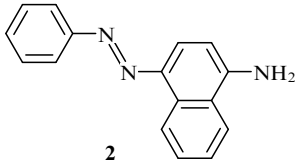
Compound	Experiment and calculation	Isolated molecule	Molecule in the crystal	Ref.
Formamide	experiment	3.7	4.8	61
	CRYSTAL	4.7 [a]	6.7 [a]	62
	SCMP-NDDO [b]	3.9	5.7	63
Urea	experiment	3.8	5.4, 4.2	64, 65
	CRYSTAL	5.1 [a]	7.0 [a]	66
	SCMP-NDDO [b]	4.5	6.5	63
p-Nitroaniline	experiment	–	2.4 – 16.1	67
	CRYSTAL	8.0 [c]	13.3 [d]	67
	AM1	8.1	10.8	52
 **1**	experiment	–	37.3 – 73.5	67
	CRYSTAL	9.2 [c]	23.0 [d]	67

[a] The *ab initio* Hartree-Fock method with the 6 – 31G** basis set. [b] The acronym stands for Self-Consistent Madelung Potential with Neglect of Diatomic Differential Overlap. [c] The *ab initio* DFT method with the Becke functional coupled with the Lee-Yang-Parr correlation functional (B3LYP) and the 6 – 311G** basis set. [d] The *ab initio* Hartree-Fock method with the 6 – 21G** basis set.

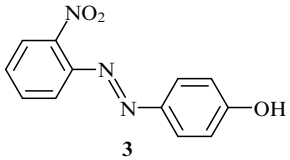
The SCMP-NDDO method, which features the AM1 parametrisation, accounts for the intermolecular van der Waals interactions based on the atom – atom potentials 6 – exp and the Hamiltonian modified according to Eqn (6), was applied to 11 crystal structures formed by small polar organic molecules, including 8 compounds with intermolecular hydrogen bonds.[63] The results of crystal calculations for urea and formamide using this method and the HF method agree well both in terms of the absolute values and increases in the dipole moments due to crystal packing effects (see Table 1). For all 11 compounds, it was found that the increase in molecular dipole moments in the crystals was larger than in simulations of solvation in a polar solvent by the method of the self-consistent reaction field using an ellipsoidal cavity, *i.e.*, it appeared that the crystal lattice effects are stronger than the expected solvent influence.

The AM1 calculations for a sample of 79 organic crystal structures showed the mean increase in the molecular dipole moments in the respective crystals was 37%, but it varied significantly (from 14% to 100%) depending on the crystal packing motif.[52] A comparison of the EP effects with the solvent influence simulated by the COSMO method [8] demonstrated that the effect of the EP consideration exceeded the maximum possible solvent effect for 20% of the structures (half of which contained molecular ions), in an other 20% of cases, the EP effect was equivalent to that of a solvent with a dielectric permeability $\varepsilon > 10$. The influence exerted by the crystal environment on the

packing motif can be traced for *p*-nitroaniline and *o*-methyl-*p*-nitroaniline as examples: both molecules in the isolated state are characterised by nearly identical dipole moments, but the EP induces a significant increase in the dipole moment for the former compound (see Table 1) and a decrease in the dipole moment by 1.1 D for the latter compound. For crystals containing two or more symmetrically independent molecules within the unit cell, the EP-based calculations make it possible to quantify the non-equivalency of the molecules. According to calculations performed for the crystal structures of 4-phenylazo-1-naphthylamine (**2**)[72] and 4-[(2-nitrophenyl)azo]phenol (**3**),[73] the dipole moments of molecules experiencing different crystal environments are also substantially different.

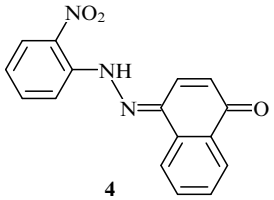


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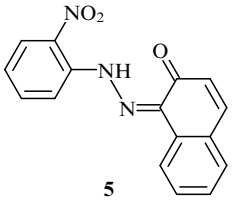


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The crystal lattice effects on the electronic structures of azo dye molecules existing in the crystals in the quinonehydrazone form, 4-[(2-nitrophenyl)hydrazono]-4*H*-naphthalen-1-one (**4**)[74] and 1-[(2-nitrophenyl)hydrazono]-1*H*-naphthalen-2-one (**5**), were simulated using the EP.[75]



4



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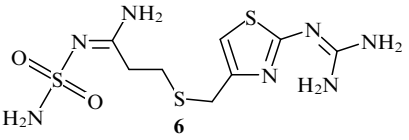
These molecules are characterised by rather large dipole moments (5.6 D and 6.8 D for compounds **4** and **5**, respectively) in the isolated state and form intermolecular hydrogen bonds C—H···O in the crystals. However the molecular dipole moments increase in the crystals by only 24% (**4**) and 22% (**5**).

The intermolecular interactions lead to changes in the molecular polarisability. In a calculation performed for urea crystals, it was assumed that the potential is created only by molecules connected to the central molecule by hydrogen bonds.[33] Under this assumption, one of the components of the molecular quadratic hyperpolarisability tensor (β_{zzz}) doubled nearly (from −44 to −74 a.u.). The EP approach was also utilised in an HF calculation for triaminotrinitrobenzene crystals.[30] This compound is of interest since its centrosymmetrical crystal can generate the second harmonics of laser light.[76] The calculations predicted a 3–4-fold enhancement of the components of the molecular tensor in the crystal; the non-linear optical properties of the crystal can be explained by violations of ordering in terms of the alternation of molecular layers in the crystal along the crystallographic direction *z*.

Applications of the atom–atom potentials method to the calculation of the crystal lattice energies was considered in detail elsewhere.[77,78] Here, we confine ourselves only to discussion of the role played by the electrostatic interactions. Since the empirical parameters of the potentials 6–12 and 6–exp are often determined by fitting to the experimental crystallographic and thermodynamical data, they implicitly include the mean effects of the electrostatic interactions. Some authors suggest (see, for example, Ref. 79) that it is unnecessary to additionally consider electrostatic interactions when these potentials are used. Indeed, the intermolecular interactions in crystals formed by low-polar molecules are quite successfully described based on such potentials. However, simulation of the crystal structures containing moderately strong intermolecular hydrogen bonds within this model required the introduction of six additional pairwise potentials for the systems A···H—B.[80] It is quite possible that further extension of the range of H-bonded systems would require introduction of new types of pairwise interactions.

The explicit consideration of the electrostatic interactions seems more reasonable from the methodological viewpoint. For this purpose, the empirical parameters contained in the expression for the potential should be separated from the Coulomb contribution during their fitting to the experimental data[81] or determined using quantum-chemical calculations.[82] In order to calculate the electrostatic component, either the lone pairs have to be represented by supplementary point charges[81] or the multipole representation of the atomic charge densities should be used.[83] According to the calculations performed within the multipole model,[84] the ratio of the electrostatic and the van der Waals terms strongly depends on the nature of the intermolecular interactions in the crystal. In particular, in the crystal structure of benzene, the electrostatic contribution is as low as 14% of the total crystal lattice energy, whereas it amounts to 43% and 83% in the crystal structures of benzoquinone and uracil, respectively. In those calculations, the multipole moments of atoms were the same as in the isolated molecules, *i.e.*, their polarisation in the crystals was neglected.

This drawback was corrected in the aforementioned SCMP-NDDO method, which used no special parametrisation for the hydrogen bonds.[63] This method was applied to calculate the crystal lattice energies of 11 polar organic compounds forming intermolecular H-bonds; the mean relative error of the determined values was 7%, which is somewhat smaller than that obtained using the empirical potentials without explicit account for the electronstatic interactions (~10%, see Refs 79, 80). The SCMP-NDDO method was also used in a calculation of relative energies of conformational polymorphs of famotidine (**6**).[85]



6

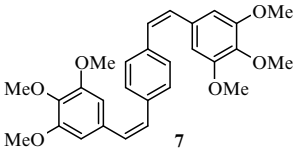
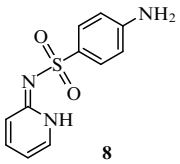
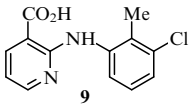
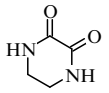
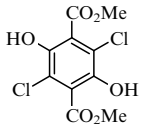
The energy of an isolated molecule in the stable polymorph was higher than that of the metastable polymorph by 17.9 kJ mol^{-1} due to sterical hindrance. However, the total energy of the molecule in the stable polymorph appears only 1.9 kJ mol^{-1} higher than that in the metastable polymorph owing to the more efficient electrostatic interactions therein. These calculations agree with high accuracy with the fact that it is the metastable form of **6** that starts to crystallise first despite being unstable thermodynamically.[86]

V. Conformations of molecules in crystals

Conformations adopted by molecules of organic compounds often change upon transition from the gas phase or a solution into a crystal. Numerous examples of polymorphs formed by different conformers of a compound (so-called conformational polymorphism)[87] as well as the co-existence of several conformers in one crystal structure are known. Obviously, deviation of the molecular geometry in a crystal from the equilibrium geometry of the isolated molecule is caused by intermolecular interactions, including electrostatic ones.

An EP-based approach to the simulation of molecular conformations in crystals was applied for the first time to biphenyl. This example illustrates the importance of consideration of electrostatic interactions even for crystals formed by non-polar molecules. The biphenyl molecule is non-planar in the gas phase: the torsion angle between the planes of the phenyl rings ψ is 44(1)° according to electron diffraction data,[88] the energy barrier to planarisation is 8(2) kJ mol^{-1}. In contrast, the molecule is planar in the crystal and occupies a special position on an inversion centre.[89] However a conformational analysis of the biphenyl

Table 2. Examples of calculations of molecular conformations in crystals based on the electrostatic potential.

Compound	Method	Comment	Ref.
But-3-en-2-ol	HF/4–21G, APC [a]	a clathrate $C_4H_8O \cdot 2\,C_{33}H_{36}O_6$	94
Glycine	HF/6–31G, supermolecule [b]	three polymorphs with similar molecular conformations	95
 **7**	HF/4–21G, APC [a]	*trans*,*trans*- and *cis*,*cis*-isomers	96
 **8**	HF/6–31G, APC [a]	four conformational polymorphs	97
 **9**	HF/6–31G, APC [a]	four polymorphs containing different tautomers and conformers	98
 **10**	HF/4–21G, APC [a]	a change in the conformation of the ring in the crystal	99, 100
 **11**	HF/6–31G, supermolecule [b]	three polymorphs, one of them contains two crystallographically independent molecules	101, 102

[a] APC means atomic point charges determined according to the Mulliken or Hirshfeld prescription. [b] Supermolecule is a cluster composed of 15 molecules surrounded by atomic point charges.

moiety in 68 crystal structures revealed [90] that, despite the majority of molecules is grouped at around $\psi = 40^\circ$, the planar or nearly planar geometry occurs much more frequently than it being allowed by the Boltzmann distribution with the torsion potential of the isolated molecule. A study of the phonon spectrum of crystals of biphenyl showed that the observed planar geometry is a result of dynamical disorder,[91] the energy minimum corresponds to $\psi = \pm 20^\circ$, and the height of the energy barrier to planarisation is 3.4 kJ mol^{-1}.

The quantum-chemical calculation of a crystal of biphenyl was performed using the HF/4–21G method; the coordination shell included 36 neighbouring molecules, their atoms were represented by point Mulliken charges.[92] We note that in this case (the absence of the lone pairs and short intermolecular contacts and the zero dipole moment of the molecule), this approximation is satisfactory. The calculation yielded $\psi = 45.7^\circ$ and a planarisation barrier of 7.9 kJ mol^{-1} for the isolated molecule, which is in good agreement with the experimental data. The barrier height and the torsion angle decreased to 3 kJ mol^{-1} and 27°, respectively, following the introduction of the crystal EP into the calculations.

The biphenyl molecules in the crystal structure are packed in a herring-bone arrangement: the C–H bonds are approximately perpendicular to the planes of the phenyl groups of neighbouring molecules. The C–H$\cdots\pi$ interactions in the crystal structures of aromatic hydrocarbons are sometimes considered as a particular case of very weak hydrogen bonds,[93] which decrease the energy of the π-orbitals and, consequently, promote stronger π-delocalisation over the molecule. Similar packing motifs are observed in a number of other crystal structures containing the biphenyl fragment; the angle ψ exceeds 25° in none of these structures (see Ref. 90). Thus, the simulation of the EP effects on the conformation of the biphenyl molecules established the reason for the planarisation of the biphenyl fragment for the whole class of similar compounds.

Other examples of application of the EP to simulations of molecular conformations in crystals are listed in Table 2.

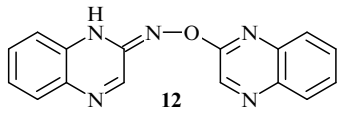
Optimisation of the molecular geometry based on the atomic point charges led in some cases to results contradictory to the experimental crystallographic data. In particular, abnormally short intermolecular contacts were revealed in one out of four polymorphs of **8** and in two out of four polymorphs of **9**. The results were more accurate when a molecular cluster surrounded by point charges was used in the calculation. For instance, both methods were applied to polymorphs of glycine, and the deviations of the calculated torsion angles from the experimental values were 3–5 times larger in the calculation of a single molecule in the field of point charges than in the calculation of a molecular cluster. On the one hand, failures in the use of the model of atomic point charges can be due to the inadequacy of the model for the calculation of the EP in these systems, since all of them contain intermolecular hydrogen bonds. On the other hand, the use of a molecular cluster implicitly takes into account the effects of the van der Waals interactions on the molecular geometry, since too short distances between atoms of neighbouring molecules are avoided in the cluser calculations.

VI. Crystal packing effects on the energy of electronic transitions

The first examples of the existence of organic compounds as crystalline forms with different colours were described in the

beginning of the 20th century.[103] At present, the Cambridge Structural Database[104] stores information on more than 50 families of differently coloured polymorphs and pseudopolymorphs, although solid-state spectral data have been reported for only a few representatives. Various reasons can be responsible for the differences in colours of molecular crystals. Firstly, the molecules in the crystals can adopt different conformations or exist as tautomeric forms which differ substantially in the degree of intramolecular conjugation. For instance, one of the aforementioned polymorphs of **11** is yellow, the second one is pale yellow, whereas the third one is colourless. The molecules in the yellow polymorph are nearly planar; the CO_2Me and OH groups are turned by 68–83° and 32–51°, respectively, in the colourless polymorph due to intermolecular hydrogen bonds and they occupy intermediate positions in the pale yellow polymorph. Secondly, changes in the colour can be due to excitonic effects or intermolecular charge transfer.[105] Finally, by analogy with solvatochromic effects, the absorption bands in a crystal can shift due to polarisation of the molecule in the crystal environment. We consider this phenomenon in more detail below.

Compound **12**

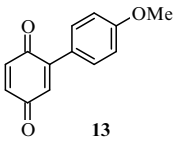
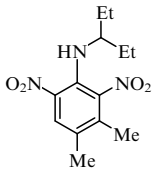
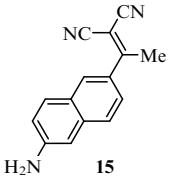
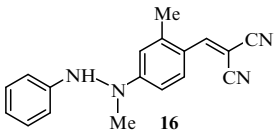


12

exists as orange and pale yellow polymorphs, in which the difference in the conformations of the molecules is not sufficiently large to explain the difference in colours. The effects of the EP on the electronic structure of the molecule were simulated using the SCMP-NDDO method. Only configurations produced upon transfer of an electron from the highest occupied to the lowest unoccupied molecular orbitals were taken into account to calculate the excitation energy. According to the calculation,[106] crystals of the orange form of **12** are characterised by an excitation energy 1700 cm^{-1} lower than that of the yellow form, which is the reason for the different colours of the polymorphs.

The INDO/S method has specially been optimised for calculations of spectra of organic molecules but it is less suitable to calculations of the ground states of molecules and the electron density distribution, in particular, than other semiempirical methods. In this respect, an alternative procedure was proposed,[32] in which the AM1 or PM3 method is used for the calculation of the EP, and the resultant potential is included in the INDO/S type Hamiltonian. The excitation energies for 16 groups of polymorphs and pseudopolymorphs were calculated within this approach.[52] For six groups, it was the EP effects that were shown to be responsible for the experimentally observed difference in colours, and a fair agreement between the calculated changes in the excitation energies and shifts of the absorption bands was observed for those compounds, the solid-state reflection spectra of which were available from the literature (Table 3). For four other compounds, the differences in the molecular geometries and the potential effects considered separately appeared small, but the difference in colours could be attributed to their joint influence. Finally, for the remaining six compounds, the calculations yielded identical excitation energies for different polymorphs. Apparently, the difference in colours in those cases should be attributed to another reason. We note however that the results of computation evidently contradicted the experimental data in none of the 16 cases. Within this approach,[52] bathochromic shifts of the absorption bands of quinacridone [112, 113] and indigo [114, 115] on going from solutions to the crystals can also be rationalised.

Table 3. Examples of compounds forming differently coloured polymorphs for which the excitation energies (cm^{-1}) were calculated using the INDO/S method with the electrostatic potential.

Compound	Colour of the polymorph	Experiment	Calculation		Ref.
			molecule in the crystal	isolated molecule	
 **13**	red	19 190 [a]	31 220	32 013	107, 108
	yellow	20 490 [a]	33 118	32 734	
 **14**	orange	17 730 [a]	26 792	28 137	109
	yellow	19 190 [a]	28 346	27 706	
 **15**	red	15 500 [b]	26 273	29 339	110
	yellow	17 240 [b]	28 599 [c]	29 720 [c]	
			30 432 [c]	31 575 [c]	
 **16**	orange	17 210 [b]	28 456	29 423	111
	yellow	18 420 [b]	28 998 [c]	28 430 [c]	
			30 015 [c]	30 885 [c]	

[a] Postion of the long-wavelength edge of the absorption band. [b] Position of the maximum of the fluorescence spectrum. [c] The crystal structure of the yellow polymorph contains two independent molecules.

The INDO/S method with included crystal EP was also applied to simulate the changes in dipole moments of the electronic transitions for crystals of certain amides, purines and pyrimidines with respect to the isolated molecules.[55, 116, 117] According to the calculations, a crystal-field-induced mixing of the $n\pi^*$ and $\pi\pi^*$ type excited states occurs, which gives rise to changes in the direction of the transition moments by 10° and even more. The calculations using the $U(r)$ potential agree much better with the experimental spectra of the crystals than the respective calculations for the isolated molecules.

* * *

Thus, the use of the crystal electrostatic potential in quantum-chemical calculations enables quite reliable determination of the crystal lattice energies and simulation of the geometry and electronic structure of molecules providing explanations of their changes on going from the isolated molecules to the crystals. The crystal lattice effects vary over a wide range depending on the packing motif and the character of the intermolecular interactions. This determines the difference in the properties of polymorph forms as well as variation of characteristics of crystallographically independent molecules experiencing different crystal environments. The systematic application of the EP-based calculations significantly extends the analytical potential of chemical crystallography as applied to molecular structures and makes it possible to step beyond a mere geometrical description.

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