

mainly caused by the surplus value of the electrostatic contribution in the $C2/m$ model. It suggests that a non-conducting mixed stack TTF–TCNQ structure can be prepared. At the same time it suggests the application of the atom–atom approximation for the prediction of conducting segregated stack structures, when only non-conducting mixed-stack structures are observed (e.g. for anthracene–TCNQ or benzidine–TCNQ). However, in the *Introduction* we have mentioned already some serious limitations of our method. In view of the apparent importance of electrostatic interaction for the relative stabilities of structures we would stress the uncertainties introduced by the assumption of a charge-transfer of $\rho = 0.59 e$ for the $C2/m$ model.

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The Electrostatic Term in Lattice-Energy Calculations for Lithium Formate Monodeuterate: Determination from the Experimental Electron Density

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Abstract

The electrostatic energy of crystalline $\text{LiCHO}_2 \cdot \text{D}_2\text{O}$ has been calculated with three sets of net atomic charges. These sets have been obtained from *ab initio* and extended Hückel calculations as well as by the method of Tsirel'son & Ozerov [*Sov. Phys. Crystallogr.* (1979), **24**, 662–666] from the X-ray electron density. It is shown that only the 'experimental' set of net atomic charges provides good agreement with the experimental evaluation of the lattice energy for $\text{LiCHO}_2 \cdot \text{D}_2\text{O}$.

been given by Tsirel'son & Ozerov (1981). These authors also proposed the determination of the idempotent charge–bond-order matrix from X-ray data (Tsirel'son & Ozerov, 1979). When the idempotent condition is taken into account an antisymmetric many-electron wave function is produced. This function describes the experimental electron density and, as a result, gives physically reliable net atomic charges.

The first application of the method above was realized on a lithium formate monodeuterate (LFD) crystal (Tsirel'son, Zavodnik, Fomitscheva, Ozerov, Kuznetsova & Rez, 1980). This crystal has an exceptional capacity for second harmonic generation. It has no center of symmetry (space group $Pna2_1$) and is pyroelectric, piezoelectric and ferroelectric and also has nonlinear optical properties. In conjunction with its high dielectric strength, these properties are the basis of a wide use of LFD as a laser material. The deter-

Accurate diffraction data allows direct determination of the electron density to be made, leading to the understanding of the nature of the chemical bond. A complete survey of methods used for this purpose has

mination of the valence electron density of LFD had given rise to calculation of its nonlinear optical susceptibilities (Ozerov, Tsirel'son, Varnek, Krasheninikov, Parini & Pozdnjakov, 1981) using the Levine–Van Vechten–Phillips approach (Levine, 1973).

The main aim of this work is to calculate the potential energy in crystalline LFD.

As shown by Kitaigorodsky & Ahmed (1972) the potential energy of an organic molecular crystal may be successfully determined by a well known atom–atom approximation. According to this approximation, the expression for the lattice energy of a crystal may be written as the sum over all molecules in the crystal.

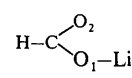
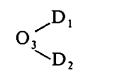
$$U = \frac{1}{2} \sum_i \sum_j \{A_{mn} \exp(-B_{mn} r_{ij}) - C_{mn}/r_{ij}^6 + q_i q_j / r_{ij}\}.$$

The first term represents the exchange repulsion between the *i*th and *j*th atoms; the second describes the dispersion interaction; the last represents the electrostatic interaction (U_{el}) between the two atoms which carry net atomic charges q_i and q_j . This last term is rather large in crystals built up from molecules containing very polar functional atomic groups and can sometimes reach 50–75% of U (Hagler, 1977). Estimation of the net atomic charges (q_i) is hence extremely important.

The usual method of obtaining net charges is by population analysis of molecular orbital calculations. The difficulty in assigning atomic charges arises from the large differences in results obtained at different approximation levels (Hagler & Lapicciarella, 1976; Hirshfeld & Mirsky, 1979). These calculations are carried out essentially for individual molecules and so do not take into account the charge redistribution caused by intermolecular crystal forces. As shown by Tsirel'son *et al.* (1980) this effect can be large.

Here the electrostatic energy calculation was carried out with a set of net atomic charges obtained by Tsirel'son & Ozerov's (1979) method using accurate diffraction data (Tsirel'son *et al.*, 1980). The charge–bond-order matrix was derived with a symmetry-orthogonalized Slater-type orbital basis set. The net atomic charges were calculated from the diagonal

Table 1. Net atomic charges in LFD

Numbering of atoms	Atom	'Experimental'	<i>Ab initio</i>	Hückel*
	Li	0.82	0.70	0.55
	C	0.04	-0.01	-0.01
	O ₁	-0.53	-0.34	-0.30
	O ₂	-0.46	-0.34	-0.26
	H	0.13	-0.02	-0.02
	D ₁	0.11	0.06	0.08
	D ₂	0.07	0.06	0.07
	O ₃	-0.18	-0.12	-0.10

* Based on a molecular-cluster simulation.

Table 2. Interatomic interactions

	<i>A</i> (kJ mol ⁻¹ Å ⁶)	<i>B</i> (kJ mol ⁻¹)	α (Å ⁻¹)
Li–Li	315.27	127802	4.38
Li–C	887.47	149912	3.96
Li–O	585.31	203901	4.28
Li–H	231.95	126910	4.61

elements of this matrix. Table 1 contains these charges, those obtained using *ab initio* calculations for free molecules of HCOOLi and H₂O, and those using the extended Hückel method for a molecular-cluster simulation in a crystal environment.

The van der Waals term (U_c) for the lattice energy has been calculated using parameters for C–C, C–H, C–O, O–O, H–H interactions proposed by Kitaigorodsky & Mirsky (1961, 1964) and Kitaigorodsky, Mirsky & Bereznitsky (1970). In addition we used parameters for the Li–Li interaction which was calculated with expressions: $A = 2.25 \epsilon_0 r_0$; $B = 8.28 \times 10^5 \epsilon_0$; $\alpha = 1/(0.736 r_0)$. The values of ϵ_0 and r_0 were taken from Borisanova's (1965) results ($\epsilon_0 = 0.155$ kJ mol⁻¹, $r_0 = 3.1$ Å). The parameters for Li–C, Li–O and Li–H interactions were found as the mean geometrical value of parameters of the same interaction type. As a result we have the parameters in Table 2.

Afonina, Kuleshova & Zorky (1978) have shown that it is important to take the hydrogen-bond energy component into account. Here the hydrogen-bond energy was calculated using the Popov, Dashevsky, Lipkind & Arhipova (1968) potential: $U_h = \epsilon_0 \{1 - \exp[-n(d_0)]\}^2 - \epsilon_0$, where $\epsilon_0 = 23.03$ kJ mol⁻¹, $d_0 = 1.75$ Å, $n = 5$ Å⁻¹ (Sarkisov, Dahis & Malenkov, 1972).

To be compared with the heat of sublimation (which is the energy of crystal structure decomposition for HCOOLi and H₂O molecules), the lattice energy must be calculated as the sum over all pairs of molecules in the crystal relative to the initial pair HCOOLi and H₂O. Of course the choice of the initial pseudo-molecule HCOOLi is rather arbitrary because of the nearly ionic character of the components in LFD.

In the calculation of the lattice energy the choice of the limiting radius of summation is very important. This is illustrated by Fig. 1, where the dependence of the electrostatic energy ('experimental' charges) on the

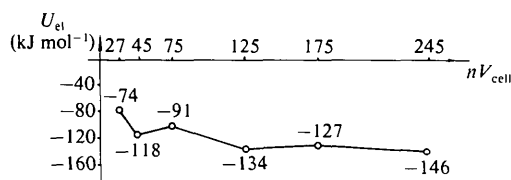


Fig. 1. Electrostatic energy vs the volume of sphere summed.

Table 3. Calculated and experimental lattice energy in LFD (kJ mol⁻¹)

U_c = van der Waals energy; U_{el} = electrostatic energy; U_h = hydrogen-bond energy; $U = U_c + U_{el} + U_h$; ΔH_s = sublimation enthalpy.

Method of net atomic charges calculation	$-U_c$	$-U_{el}$	$-U_h$	$-U$	ΔH_s
'Experimental'	28.9	145.6	35.3	209.8	205.4
Hückel	28.9	37.1	35.3	101.3	205.4
<i>Ab initio</i>	28.9	35.5	35.3	99.7	205.4

volume of sphere summation (nV_{cell}) is presented. Inspection of Fig. 1 shows that the electrostatic energy has converged at a limiting separation of about $n = 245$.

The results of our calculations are given in Table 3. As can be seen from this table, only the 'experimental' set of net atomic charges provides good agreement with the independent experimental evaluation of the heat of sublimation (ΔH_s). This value was derived with the microcalorimeter Kalve (Vorobjov, Miroshnitchenko, Vorobjova, Matuschin & Lebedev, 1977).

Theoretical evaluation of the influence of the crystal environment on a given molecular component is difficult: the energy values derived from two different quantum chemical approaches are almost identical. Moreover, the deformation electron density maps (Ozerov, Tsirel'son, Korkin, Zavodnik & Fomitscheva, 1980) for both cases are also almost identical.

It should be noted that it is possible to determine the lattice-energy value directly from the X-ray electron density function apart from an atom-atom approximation and the use of net atomic charges. Work in this field is in progress.

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