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POLARIZATION OF MOLECULAR IONS IN NaTCNQ AND TTF.TCNQ CRYSTALS

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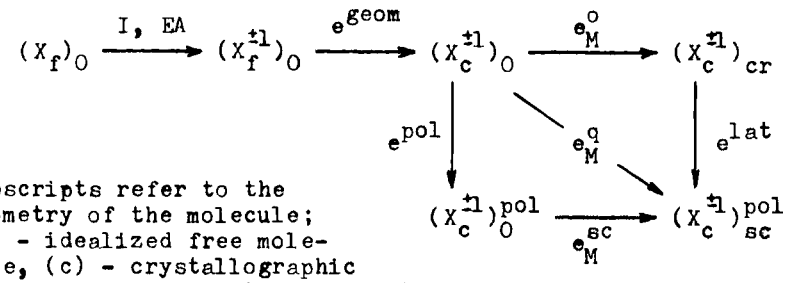
Abstract Self-consistent electrostatic intersite potentials and atomic charges have been calculated. Lattice cohesion energy for NaTCNQ has been reproduced when polarization of $TCNQ^-$ anion in the lattice was taken into account.

The intriguing problem of evaluation the lattice energy (and the charge transfer) in quasi 1-D crystalline materials has long been studied but never definitely resolved.[1] There have been, however, only few attempts toward analysing the electronic structure of the involved molecule/ion located in the electrostatic field of the lattice.[2-5] At the very least, it has been demonstrated that electrostatic intersite potentials,[6] produce a charge redistribution in TTF.TCNQ [2,3] and NMP.TCNQ.[4] This present study is aimed at evaluation of the particular components of the lattice cohesion energy, which has been decomposed into a set of contribution as indicated in the following diagram:



Subscripts refer to the geometry of the molecule; (f) - idealized free molecule, (c) - crystallographic atomic positions. External electrostatic field acting at the molecule is indicated by the outer subscript; (0) - zero field, (sc) - self-consistent field, (cr) - crystalline field in nonpolarized lattice.

Different notation is used for the energy per ion (e) and energy per molecule of complex (E). Intramolecular (pol.) and lattice (lat.) polarization energies were obtained indirectly by two simple relationships:

$$e^{pol} = e_M^q - e_M^{sc} \qquad \text{and} \qquad e^{lat} = e_M^q - e_M^o$$

e_M^o corresponds to the standard Madelung term; e_M^{sc} is the same value for self-consistent charge distribution; e_M^q stands for the difference in total energies of a polarized molecule in the potential field and free molecule. Crystal structures were taken from ref. 7 (TTF.TCNQ) and ref. 8 (NaTCNQ, monoclinic). Assuming the complete charge transfer between donor and acceptor molecule, the electronic structure of respective ions was sought within the framework of the modified INDO method.[9] UHF scheme has been used for the open shell species.[10] The effect of the lat-

TABLE Energies obtained in calculations (all in eV). For the notation see text.

ENERGY	TTF^+TCNQ^-		Na^+TCNQ^-	
	TTF^+	$TCNQ^-$	$TCNQ^-$	Na^+
e_M^o, EWALD	-2.382	-2.374	-5.602	-8.261
e_M^{sc}, EWALD/INDO	-3.002	-2.800	-9.310	-8.136
e_M^q, INDO	-2.886	-2.667	-7.475	-8.136 ?
e^{pol}, intramolecular polarization	0.116	0.133	1.835	0
e^{lat}, lattice polarization	-0.504	-0.293	-1.873	0.125
E_M^{sc}, Madelung self-consistent	-2.776		-7.805	
$I - EA + E_M^{sc}$	0.82		-5.45	
Experiment (ref. 1)	-2.39		-5.43	

tice field was incorporated by computing the intersite electrostatic potentials by Ewald procedure and including them into the diagonal part of the INDO hamiltonian. Potentials and charges became self-consistent after 5 ÷ 6 iterative runs. Calculated energies are given in the TABLE. Self-consistent net atomic charges and intersite potentials are shown in Figs. 1a, b and 2; Δq denotes a departure from atomic charges in a nonpolarized ion due to the charge redistribution. Polarization effect on NaTCNQ is large enough to produce a realistic lattice cohesion energy, surprisingly close to the experimental value. In fact, this is the best result ever obtained for any organic quasi 1-D material. Polarization seems to have much less effect on TTF^+ and $TCNQ^-$ ions in lattice. However, extrapolation to the charge transfer $\varrho<1$ has been avoided here. In contrast to other terms, the $e^{pol}(\varrho)$ dependence cannot be simply rationalized and may perhaps reveal a substantial effect on the lattice cohesion.

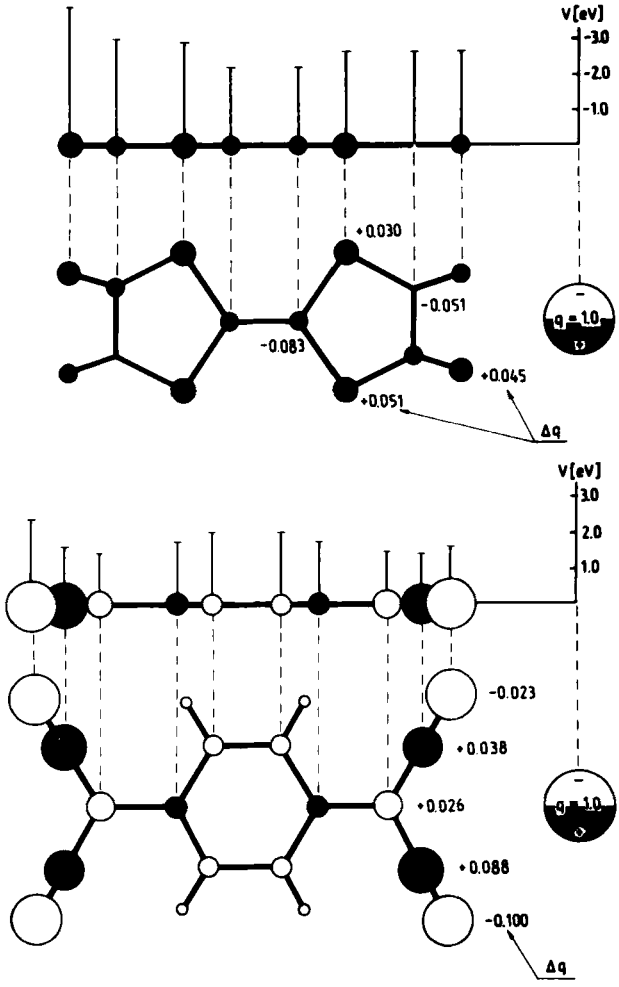


FIGURE 1a, b Polarized TTF^+ and $TCNQ^-$ ions in the lattice TTF.TCNQ.

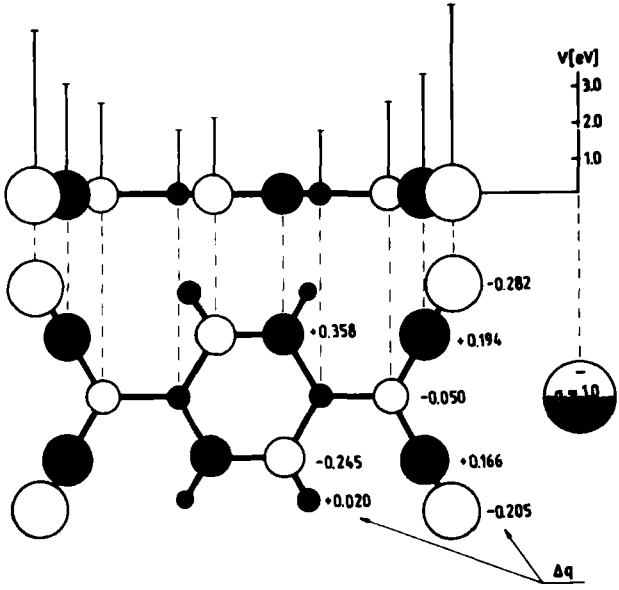


FIGURE 2 Polarized $TCNQ^-$ ion in NaTCNQ latticce

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