Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 21 Mar 2007.

To cite this article: Miklos Kertesz (1985): Changes of Lattice Geometries Upon Charge Transfer, Molecular Crystals and Liquid Crystals, 126:1, 103-110

To link to this article: http://dx.doi.org/10.1080/15421408508084159

Mol. Cryst. Liq. Cryst. 1985, Vol. 126, pp. 103-110
0026-8941/85/1261-0103/$15.00/0

Printed in the United States of America

CHANGES OF LATTICE GEOMETRIES UPON CHARGE TRANSFER

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Abstract General perturbation theoretical arguments are given for the opposite effect of small positive and negative charge transfer on the geometry of solids. Applications to π-conductors, such as intercalated graphites and doped polyacetylenes, indicate C-C bond elongation for donor compounds and shortening for acceptor compounds,in agreement with experiment.

INTRODUCTION

π-electron metals, such as intercalated graphites[1] and highly doped polyacetylenes[2], are good electric conductors because charge transfer creates partially filled energy bands. The charge transfer (electrons from donors or to acceptors) causes some changes in the π-bonding of the carbon frameworks in these systems. Some of these changes have been observed experimentally for the graphite intercalation compounds (GIC)[3] and, to a lesser extent, for doped polyacetylenes ($(CH)_x$)[4]. Pure electrostatic argument would predict the expansion of lattices, due to the repulsion of the charged atoms after charge transfer has taken place, to be independent of the sign

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of the transferred charge. In this communication the inherent asymmetry regarding the change of the bond distances as a function of the sign of the charge transfer (CT) is discussed. Previously, we have indicated[5,6], that the slight antibonding nature of the Bloch one-electron functions at the Fermi level results in a C-C bond lengthening for negative charge transfer (donor compounds) and bond shortening for positive charge transfer (acceptor compounds).

PERTURBATION THEORY OF THE EFFECT OF CHARGE TRANSFER ON THE GEOMETRY OF SOLIDS

Let us make a number of simplifying assumptions about the total energy of a crystal. Suppose that the a semi-empirical one-electron Hamiltonian (e.g., of the extended Huckel type[7]) is used. In that case, the total energy per unit cell may be expressed as

$$E = \sum_{n,k}(occ)\varepsilon_n(k) = \sum_j \sum_{\alpha\beta} P_{\alpha\beta}(j)H_{\alpha\beta}(j) \qquad (1)$$

where $\varepsilon_n(k)$ is the n-th energy band, $H_{\alpha\beta}(j)$ is the matrix element between orbital α in the reference cell, and orbital β in the j-th neighboring unit cell; and finally, $P_{\alpha\beta}(j)$ is the corresponding density matrix element (bond order).

The energy may be expanded into a power series around a given geometry, R, and charge state. The latter may be characterized by q, the number of electrons per unit cell. For simplicity we discuss one geometry parameter only.

$$\delta E(R,q) = \frac{\partial E}{\partial q}\,\delta q + \frac{\partial E}{\partial R}\,\delta R + \frac{1}{2}\,\frac{\partial^2 E}{\partial R^2}\,\delta R^2 +$$

$$+ \frac{1}{2}\,\frac{\partial^2 E}{\partial q^2}\,q + \frac{\partial E}{\partial q \partial R}\,\delta q \delta R \qquad (2)$$

For any given q the equilibrium geometry is defined by

$$\frac{\partial E(q,R)}{\partial R} = 0 \qquad (3)$$

We want to find the effect of CT, i.e., the change in q, δq, on the geometry. δE is a quadratic function of δR. The minimum occurs at

$$\delta R = -\,\delta q\,\frac{\partial^2 E/\partial q \partial R}{\partial^2 E/\partial R^2} \qquad (4)$$

provided (3) is fulfilled. Thus, the change in the equilibrium geometry , δR, is proportional to δq for small amounts of δq and inversely proportional to the force constant, $f = \partial^2 E/\partial R^2$. The effect is also proportional to the coupling of the charge transfer to geometry. For the simple effective Hamiltonian yielding (1), equ. (4) can be expressed as follows (k_f and j are vectors)[8]

$$\delta R = -\,\delta q f^{-1} \sum_{\alpha\beta j} [2C_{\alpha n}(k_F)C_{\beta n}(k_F)e^{ik_F j}]\,\frac{\partial H_{\alpha\beta}(j)}{\partial R} \qquad (5)$$

where $C_{\alpha n}$ is the Bloch orbital coefficient corresponding to the α-th atomic orbital for the k_F wave vector at the Fermi energy, E_F, normalized over a unit cell and $H_{\alpha\beta} = H_{\alpha\beta} - E_F S_{\alpha\beta}$. The expression in [ ] is the contribution of

the Bloch orbitals at the Fermi level to the density matrix $P_{\alpha\beta}(j)$. The sign of δR depends on the sign of this term.

DOPED POLYACETYLENE AND GRAPHITE

Energy band caculations have been done[5] on $(CH)_x$ chains with a varying degree of charge transfer, q, followed by geometry optimizations for different q values using the extended Huckel Hamiltonian. The optimized C-C distances, R_{opt}, as a function of q are given in Fig. 1. The

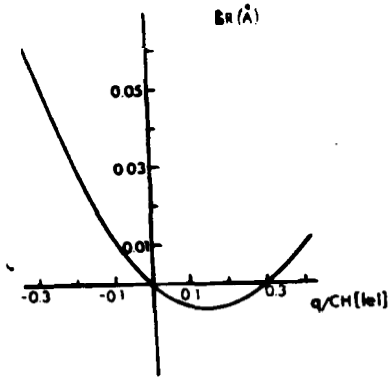


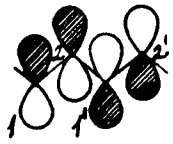
FIG. 1. Variations of the optimal C-C bond length in all-trans-polyacetylene, as a function of the charge transfer q.

zero of q is set for the neutral π-system. For small values of q the deviations of R_{opt} are linear as predicted by the present theory. The slope of the curve is negative, because (5) can be now rewritten as (H is used instead of H' assuming orthonormal atomic orbitals)

$$\delta R = R_{opt}(q)-R_{opt}(0) = - 2qj^{-1} p_{11} \partial H_{11}/\partial R \qquad (6)$$

where 11' is the index pair corresponding to the π orbitals on atoms 1 and 1' in neighboring unit cells. The pattern of the orbital, from which this is calculated, is

illustrated in 1

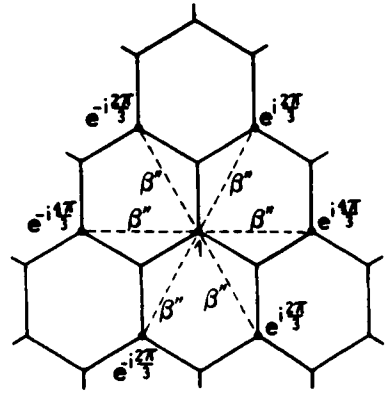


Formula 1. Orbital at the Fermi level in polyacetylene

There is no contribution from the H_{12} matrix element because $p_{12} = 0$. This reduces (5) to (6) and only a slight (second neighbor) antibonding effect remains.

The case of graphite is analogous. The wave function at the Fermi level (at the famous K point in the hexagonal 2D Brillouin zone) is illustrated in 2, where the phase factors for the six neighboring cells are given relative to the reference cell. In a carbon layer first

Formula 2.
Phases of neighbors in graphite at the K point.



neighbor bond orders thus vanish ($1+2\cos 2\pi/3 = 0$). So the largest contributions to the r.h.s. of (5) will come from second neighbors indicated by dashed lines in 2. The result will be now (again assuming orthonormal atomic orbitals).

$$\delta R = -6qf^{-1} p_{11} 2\partial H_{11}/\partial R$$

The effect seems to be 3 times smaller (the difference in the number of second neighbors) in a polymer than a honeycomb lattice. However, here $p_{11} = 2N^2\cos(2\pi/3) = -N^2 = -1/2$. For the polymer $p_{11} = -2N^2 = -1$. Thus, about a 50% difference results from dimensionality. Actually, the 2D layer is more rigid, thus a rather small difference is expected. Fully optimized caculations[6] for a graphite layer with a series of different charge transfer values are given in Fig. 2. The continuous curve corresponds to a π-only charge transfer and agrees very well with the coresponding $(CH)_x$ curve given in Fig. 1.

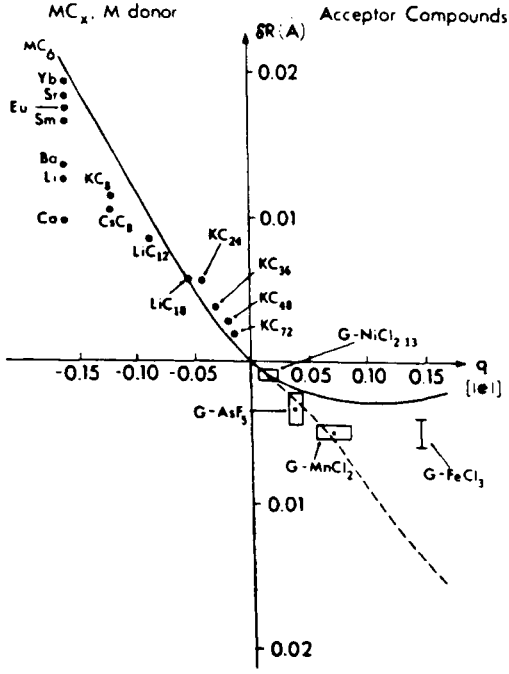


FIG. 2. Variation of the optimal C-C bond distance in intercalated graphites.

The experimental points were taken from different sources[3]. As to the experimental charge transfer (q) values, for the donor compounds full charge transfer has been assumed in representing the points. We would be compelled to assume in some of the cases, that the large deviations from our theoretical curve implies a partial charge transfer. For the acceptor compounds the q values were based on several experimental methods[3]. The agreement with experiment is reasonable in the case of $(CH)_x$ as well, although the evidences there are more indirect[4]. Let us note that in order to arrive at the correct dependency of δR on δq, optimized geometries had to be used.

The asymmetric charge tansfer effect described here has an orbital origin. Especially the shrinking of lattices upon charge transfer can not be explained by electrostatic agruments. The effect of the dopants has to be assessed. In the graphite compounds full band structure calculations indicate[9,10] that large fraction of the transferred charge goes into the rigid bands of graphite. We plan to investigate this question for doped polyacetylene using recently extablished[11] 3D structural models for highly doped $(CH)_x$.

ACKNOWLEDGEMENTS

I am indebted to Professor Roald Hoffman for enlightening dicussions on the graphite compounds and to Dr. Ray Baughman on the polyacetylene compounds. Acknowledgement is made to the Research Corporation for a Cottrell Research Grant and to the donors of the Petroleum Research Fund, administered by the ACS for support of this work.

REFERENCES

1. See e.g. Intercalated Graphite, edited by M.S. Dresselhaus, G. Dresselhaus, J.E. Fisher, and M.J. Moran (North Holland, 1983).
2. See e.g. C.K. Chiang, A.J. Heeger, and A.G. MacDiarmid, Ber. Bunsenges Physik. Chem. 83, 407 (1979).
3. D.E. Nixon and G.S. Parry, J. Phys. C., 2, 1732 (1969).
   D. Guerard, C. Zeller, and A. Herold, C.R. Acad. Sc. Paris, 283, Ser C, 437 (1976)
   R.S. Markiewicz, J.C. Kasper and L.V. Interrante, Synth. Metals 2, 363 (1980)
   L. Pietronero and S. Strassler, Phys. Rev. Lett. 47, 593 (1981)
   T. Krapchev, R. Ogilvie, and M.S. Dresselhaus, Carbon 20, 132 (1982)
   S. Flandrois, J.M. Masson, J.C. Rouillon, J. Gaultier and C. Haw, Solid State Commun. 42, 759 (1982)
4. M.A. Druy, C.M. Tsong, N. Brown, A.J. Heeger, and A.G. MacDiarmid, J. Polymer Sci. Polym. Phys. Ed. 18, 429 (1980)
   S. Pekker and A. Janossy, Mol. Cryst. and Liquid Cryst. 77, 159 (1981)
5. M. Kertesz, F. Vonderviszt and S. Pekker, Chem. Phys. Lett. 90, 430 (1982)
6. M. Kertesz, F. Vonderviszt and R. Hoffmann, in ref. 1, p. 141.
7. See e.g. M.-H. Whangbo, R. Hoffmann and W.B. Woodward, Proc. Roy. Soc. (London) A366, 23 (1979)
8. H. Teramae, T. Yamabe, G. Satoko and A. Imamura, Chem. Phys. Lett. 101, 149 (1983), M. Kertesz, ibid, 106, 443 (1984).
9. See e.g. N.A.W. Holzwarth in ref. 1, p. 107.
10. T. Inoshita, K. Nakao and H. Kamimura, J. Phys. Soc. Japan 43, 1237 (1977)
11. R.H. Baughman, N.S. Murthy, and G.G. Miller, J. Chem. Phys. 79, 515 (1983)
    R.H. Baughman, L.W. Shacklette, N.S. Murthy, G.G. Miller and R.L. Elsenblumer, Mol. Cryst. and Liquid Cryst. (in press)