Dependence of Young's Modulus of *trans*-Polyacetylene upon Charge Transfer

Sung Y. Hong and Miklos Kertesz
Department of Chemistry, Georgetown University, Washington, D.C. 20057

(Received 2 January 1990)

The effect of charge transfer (CT) on the Young's modulus of *trans*-polyacetylene was studied with a molecular-orbital cluster incorporating a charged soliton and with an infinite-chain model using band theory. The results of both models agree with one another very well. The Young's modulus (Y) of *trans*-polyacetylene changes up to 7% with CT of up to 0.25e per CH unit. The calculated changes of the geometry upon CT agree with experiments. The asymmetry of the variation of structure and Y with respect to the sign of the CT is due to second-neighbor antibonding interactions in both the soliton and band models.

PACS numbers: 62.20.Dc, 61.41.+e, 71.20.Hk

Polycetylene (PA) has attracted interest as a conducting polymer because it shows dramatic changes in conductivity[1-3] and magnetic susceptibility[2-4] upon doping. Undoped PA has a dimerized structure with alternating short and long bonds due to Peierls distortion of the π electron system.[5-7] Charge transfer (CT) due to doping of PA with donors or acceptors affects the π electronic system causing changes of geometrical and electronic structures. A soliton model[8] was presented and, especially at low-doping levels, has been demonstrated[9] to be essential for interpreting the unusual experimental observations. As shown in this Letter, however, a simple model using partially filled bands successfully predicts certain properties, such as the Young's modulus and the average geometry of a doped polymer, as can a soliton model. The observed asymmetry with respect to the sign of CT is in agreement with our theoretical predictions.

Improving preparation techniques[2,10] are pushing upward the intrinsic conductivities and elastic properties,[11] such as Young's moduli (Y), of conducting polymers. It would be important to know the upper limit of Y of a conducting polymer in its pristine state and the variation of Y as a function of dopant concentration.

We used an infinite-chain model and a cluster model of $C_{21}H_{23}$. In the latter model, a soliton was incorporated at the center of the cluster with the CT of $\pm e$. For energy-surface calculations, we employed a Hartree-Fock-based semiempirical quantum-chemical method [modified neglect of diatomic overlap[12] (MNDO)] and its solid-state-theory form.[13] The method is very reliable in predicting molecular and polymeric geometries and produces good force constants when used in conjunction with force-constant scaling,[14] a widely used process for empirically correcting the Hartree-Fock force-constant overestimation problem.[15]

The Young's modulus Y for one-dimensional crystals is defined in terms of the second derivative of the potential energy E of a unit cell with respect to the c-axis lattice spacing c; $Y = cA^{-1}(d^2E/dc^2)$, where A is the effective cross-sectional area perpendicular to the c axis. Therefore, information on the energy surface around the equilibrium geometry enables one to calculate Y. Since such information can be obtained from the distortion of geometry and force constants K_{ij}, Y can be also expressed as follows:[16]

$$Y = cA^{-1}\sum\sum K_{ij}Q_i'Q_j', \tag{1}$$

where Q_i are the internal coordinates of atoms making up the unit cell and the prime denotes the first derivative with respect to c. Assuming K_{ij}'s are constant near the equilibrium geometry, a set of Q_i' variables fully determine Y. The optimal Q_i' values can be obtained so as to yield a minimal Y value (that is, minimal change of energy upon longitudinal deformation) while satisfying translational symmetry.

In the band calculations 25 unit cells of C_2H_2 were considered in the lattice sum and the k-space integrals were represented by 21 points (41 points for $q = \pm 0.075e$, where q is the CT per CH unit, the plus sign corresponding to donor doping). The amount of CT is equal to the empty or occupied part of k space for the π or π^* band at the Fermi level. Young's modulus was numerically calculated by changing c by $\delta c = \pm 0.01$ Å around its optimized value while the other geometrical parameters were completely reoptimized. For the effective area A the value of 15.52 Å^2 obtained from x-ray-diffraction analysis[7] of neutral *trans*-PA was used throughout the whole range of CT studied. We adapted a uniform scaling process with a scaling factor of 0.63 from our earlier study[16] of Y for neutral *trans*-PA, based on the empirical force field of Takeuchi *et al.*[17]

Figure 1 shows the variation of Y as a function of charge transferred to the PA chain. The cluster (soliton) model predicts somewhat lower Y values of 352 ($q = -0.048e$) and 359 GPa ($q = 0.048e$) and shows the same trend as the infinite-chain model with partially filled bands. Most striking is the relatively small change of Y upon CT (about 7% increase of Y for $q = 0.25e$ and 3% decrease for $q = -0.25e$ compared to the value for undoped PA). The relative insensitivity of Y for PA and poly(2,5-dimethoxy-*p*-phenylene vinylene) to doping has been experimentally observed.[11] Our calculations show the trend that donor (acceptor) doping increases (decreases) the Y value and that the modulus of the metallic state (i.e., $|q| \gtrsim 0.1e$) varies almost linearly with CT.

The diagonal approximation[16] (i.e., $K_{ij} = \delta_{ij} K_{ii}$) is useful insofar as to qualitatively interpret the variation of Y upon CT. The expression for Y of equidistant PA can then be simplified as

$$Y = \frac{4R\sin\alpha}{A[4\sin^2\alpha/K_{RR} + R^2\cos^2\alpha/K_{\Theta\Theta}]}, \tag{2}$$

where $\alpha = \Theta/2$ and K_{RR} is the force constant for C-C bond stretching and $K_{\Theta\Theta}$ for C-C-C angle bending. The change in Y upon CT can be expressed from Eq. (2) in terms of changes of geometries and force constants as follows. Using

$$B = 4/[A(4\sin^2\alpha/K_{RR} + R^2\cos^2\alpha/K_{\Theta\Theta})^2],$$

we have

$$\begin{aligned}\delta Y(q) = B\{&[\tfrac{1}{2}R^3\cos\alpha(1+\sin^2\alpha)/K_{\Theta\Theta} - 2R\sin^2\alpha\cos\alpha/K_{RR}]\delta\Theta(q)\\ &+ [4\sin^3\alpha/K_{RR} - R^2\cos^2\alpha\sin\alpha/K_{\Theta\Theta}]\delta R(q) + R^3\cos^2\alpha\sin\alpha/K_{\Theta\Theta}^2\delta K_{\Theta\Theta}(q) + 4R\sin^3\alpha/K_{RR}^2\delta K_{RR}(q)\}\\ = {}&E\delta\Theta(q) + F\delta R(q) + G\delta K_{\Theta\Theta}(q) + H\delta K_{RR}(q).\end{aligned} \tag{3}$$

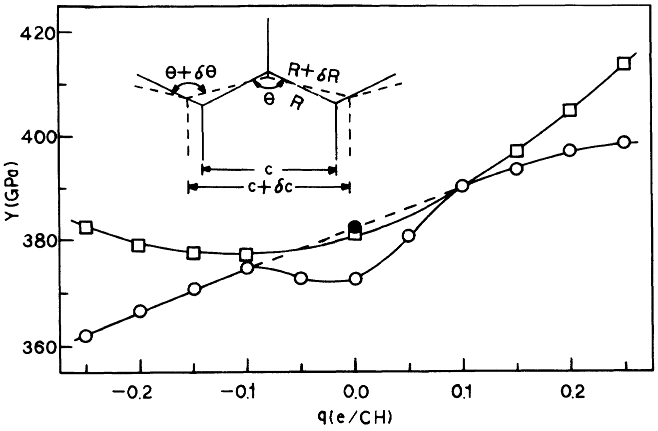

FIG. 1. The variation of the Young's modulus of *trans*-polyacetylene (PA) as a function of charge transfer q. ○ corresponds to full calculations, ● to a metallic model, and □ to calculations with force constants fixed as $q = 0.1e$. Inset: The change of structure of *trans*-PA upon longitudinal deformation.

In the last line numerical values at the optimized structure ($R = 1.405$ Å and $\Theta = 125.0°$) of neutral equidistant PA with force constants[18] $K_{RR} = 5.716$ mdyn/Å and $K_{\Theta\Theta} = 0.763$ mdyn Å are $E = 2.8 \times 10^{-1}$ mdyn Å^{-2}, $F = 1.7 \times 10^{-4}$ mdyn Å^{-3}, $G = 1.9 \times 10^{-1}$ Å^{-3}, and $H = 2.6 \times 10^{-2}$ Å^{-1}. As seen in Figs. 2 and 3, the bond angle changes significantly while the bond length changes negligibly. Thus, we expect a significant change in $K_{\Theta\Theta}$ and a negligible change in K_{RR}. These indicate that Y at low doping is most sensitive to the changes of the bond angle and its bending force constant.

Figures 2 and 3 show the variations, with CT, of the geometry predicted by the MNDO solid-state method. The soliton model with CT of 0.048e to (from) dopants predicts short bond lengths (in Å) of 1.361-1.395 (1.360-1.391), long bond lengths of 1.412-1.461 (1.408-1.460), unit-cell lengths of 2.484-2.505 (2.490-2.509), and bond angles (in degrees) of 124.5-125.1 (125.1-125.9). The average values of these geometric parameters are very close to the predicted values of the infinite-chain model and are indicated by plusses and crosses in Figs. 2 and 3. At small CT, the bond angles increase (decrease) upon doping of PA with donors (acceptors) while the change of (average) bond lengths (for alternant PA) upon CT are negligible. In heavily doped regimes, both bond lengths and angles increase with CT. The trend of geometrical changes with CT can be interpreted from frontier crystal-orbital arguments.[19] Using the geometrical predictions we can interpret the results of Fig. 1. We calculated the modulus of neutral and charged metallic PA using fixed force constants, which show a trend similar to the variation of bond angles as predicted by the diagonal approximation [Eq. (3)]. In heavily doped regimes, the variation of Young's modulus does not follow the prediction based on fixed force constants since the force constants decrease significantly as expected from the bond-order arguments.

The variation of the c-axis lattice spacing c of *trans*-PA upon CT is given in Fig. 3. The metallic states show a parabolic curve with a minimum near the neutral state. However, the alternant system with small CT shows negligible change of c for donor doping and decrease in c with a minimum value between $q = -0.05e$ and $-0.10e$ for acceptor doping. In the heavily doped region with iodine ($q = -0.1e$ assuming I_3^- species), Murthy, Shacklette, and Baughman[20] recently observed about 0.4% contraction of c, which is much smaller than the earlier macroscopic observation (about 8%).[21] The negligible increase of c for pristine PA, which was lightly doped with sodium, was also observed in the x-ray scattering experiments[22] and was ascribed to the formation of a soliton lattice. Our results show excellent agreements with the recent experiment values.[20,22] The

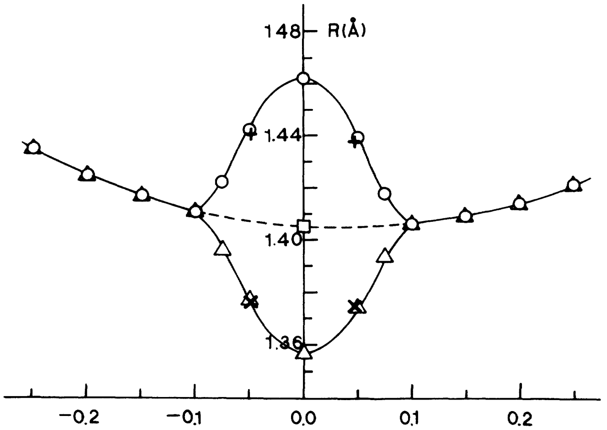

FIG. 2. The variation of the bond lengths of *trans*-polyacetylene upon charge transfer q. △ denotes the length for the short bond, ○ for the long bond, and □ for the bond of the neutral metallic state. + and × indicate the corresponding values predicted from the soliton model.

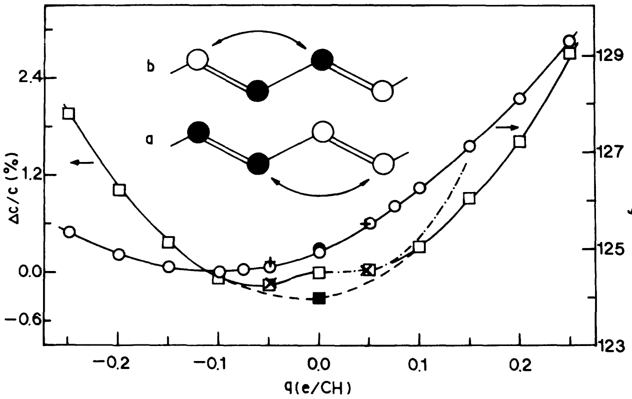

FIG. 3. The variation of the bond angle (○) and the c-axis lattice spacing (□) of *trans*-polyacetylene upon charge transfer q. ● and ■ refer to the neutral metallic state, and + and × to the soliton model. ---- corresponds to the lattice spacings observed by Winokur *et al.* (Ref. 22). Inset: The undulation of the sign of the wave functions (a) below and (b) above the Fermi level. Arrows indicate second-neighbor antibonding interactions.

change of c upon CT is simply understandable in terms of the variations of bond lengths and angles,

$$\frac{\delta c}{c}=\frac{1}{c^2}[(R_1-R_2\cos\Theta)\delta R_1+(R_2-R_1\cos\Theta)\delta R_2+R_1R_2\sin\Theta\,\delta\Theta]. \quad (4)$$

The lattice spacing of lightly doped PA with acceptors slightly decreases mainly due to the decrease of Θ in Eq. (4). However, with donor doping c does not follow the change of Θ because steeper decrease of the long bonds than the increase of the short bonds almost cancels the Θ dependence. At heavy-doping levels (both donors and acceptors) the lattice spacing increases due to the increase of bond angles and bond lengths.

The asymmetrical change of the geometry with respect to the sign of the CT has also been observed for graphite.[23] While the Huckel, the Su-Schrieffer-Heeger,[8] and the Hubbard models include only the nearest-neighbor interactions leading to electron-hole symmetry, inclusion of second-neighbor interactions lifts that symmetry as evident from the inset in Fig. 3. All second-neighbor interactions are antibonding—leading to additional repulsions at donor doping and elimination of such repulsions for acceptor doping. This asymmetry is most obvious for the bond-angle variation. The soliton wave function at the midgap also displays the same kind of second-neighbor antibonding interactions.

The excellent agreement of the two models discussed here suggests that the average size of the unit cell or Young's modulus is rather insensitive to the details of the electronic structure of lightly doped PA. What seems to be essential is that the orbitals around the Fermi level (for both the band model and the soliton model) are slightly antibonding which explains the observed asymmetry with respect to the sign of q.

This work was supported by the U.S. Air Force Office of Scientific Research (Grant No. 89-0229), and the Camille and Henry Dreyfus Foundation.

---

[1] C. K. Chiang *et al.*, Phys. Rev. Lett. **39**, 1098 (1977); D. Moses *et al.*, Phys. Rev. B **25**, 7625 (1982).

[2] T.-C. Chung *et al.*, Phys. Rev. B **29**, 2341 (1984).

[3] X. Q. Yang *et al.*, Solid State Commun. **61**, 335 (1987).

[4] B. R. Weinberger *et al.*, Phys. Rev. B **20**, 223 (1979); S. Ikehata *et al.*, Phys. Rev. Lett. **45**, 1132 (1980); A. J. Epstein *et al.*, Mol. Cryst. Liq. Cryst. **17**, 147 (1985).

[5] R. Peierls, *Quantum Theory of Solids* (Oxford Univ. Press, London, 1955), p. 108; M. Kertesz, J. Koller, and A. Azman, J. Chem. Phys. **67**, 1180 (1977).

[6] A. Karpfen and J. Petkov, Theor. Chim. Acta **53**, 65 (1979).

[7] C. R. Fincher, Jr., *et al.*, Phys. Rev. Lett. **48**, 100 (1982).

[8] W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. **42**, 1698 (1979); Phys. Rev. B **22**, 2099 (1980); M. J. Rice, Phys. Lett. **71A**, 152 (1979).

[9] A. Feldblum *et al.*, Phys. Rev. B **26**, 815 (1982); J. Chen *et al.*, Solid State Commun. **53**, 757 (1985).

[10] K. Agaki *et al.*, Synth. Met. **28**, D1 (1989).

[11] A. J. Heeger (private communication); A. Andreatta *et al.*, Mater. Res. Soc. Symp. Proc. **173**, 269 (1990).

[12] M. J. S. Dewar and W. Thiel, J. Am. Chem. Soc. **99**, 4899 (1977); **99**, 4907 (1977).

[13] M. J. S. Dewar, Y. Yamaguchi, and S. H. Suck, Chem. Phys. **43**, 145 (1979); J. J. P. Stewart, QCPE Bull. **5**, 62 (1985); Y. S. Lee and M. Kertesz, J. Chem. Phys. **88**, 2609 (1988).

[14] P. Pulay *et al.*, J. Am. Chem. Soc. **105**, 7037 (1983); A.

Peluso, M. Seel, and J. Ladik, Can. J. Chem. **63**, 1533 (1985); C. X. Cui and M. Kertesz, J. Chem. Phys. (to be published).

[15] P. Pulay, in *Modern Theoretical Chemistry,* edited by H. F. Schaefer, III (Plenum, New York, 1977), Vol. 4, p. 153.

[16] S. Y. Hong and M. Kertesz, Phys. Rev. B **41**, 11 368 (1990).

[17] H. Takeuchi *et al.*, J. Chem. Phys. **84**, 2882 (1986).

[18] Quoted from Table IX in Ref. 16 and K_{RR} is taken as the average value of the force constants for the double and single bonds.

[19] M. Kertesz, F. Vonderviszt, and S. Pekker, Chem. Phys. Lett. **90**, 430 (1982).

[20] N. S. Murthy, L. W. Schacklette, and R. H. Baughman, J. Chem. Phys. **87**, 2346 (1987).

[21] S. Pekker and A. Janossy, Mol. Cryst. Liq. Cryst. **77**, 159 (1981).

[22] M. J. Winokur *et al.*, Solid State Commun. **68**, 1055 (1988).

[23] D. E. Nixon and G. S. Parry, J. Phys. C **2**, 1732 (1969); S. Flandrois *et al.*, Solid State Commun. **42**, 750 (1982); L. Pietronero and S. Strassler, Phys. Rev. Lett. **47**, 593 (1981); M. Kertesz, F. Vonderviszt, and R. Hoffmann, in *Intercalated Graphite,* edited by M. S. Dresselhaus *et al.* (North-Holland, Amsterdam, 1983), p. 141.