PCILO conformational energy calculations on model polyacrylonitrile molecules

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The quantum chemical method perturbative configuration interaction using localized orbitals (PCILO) is applied to models for polyacrylonitrile molecules. Calculations of conformational energies were carried out on 2,4-dicyanopentane. The values and the positions of the energy minima are determined and discussed in terms of Coulombic interactions due to conformation dependent side group charges and interactions between hydrogen atoms and lone pairs or π-orbitals.

INTRODUCTION

The lack of stereoregularity in conventional (radically polymerized) polyacrylonitrile (PAN)[1] hinders the growth of sufficiently large crystalline regions in solid PAN and thus makes a crystal structure analysis difficult to accomplish. As far as we know, the crystallographic data obtained (see, for example, ref. 2 and references cited therein) do not allow atomic coordinates in the unit cell or, in many cases, even a space group to be determined. Therefore, conformational energy calculations on small model PAN molecules seem to be a reasonable first step towards an elucidation of preferred conformations in PAN.

The quantum chemical method employed here is PCILO (perturbative configuration interaction using localized orbitals[3-7]). It has been successfully applied (among other things) to the very similar case of polyvinylchloride model molecules[8]. All comments on the PCILO method given in ref. 8 therefore also fully apply to the present case. The only conformational energy calculations on PAN model molecules which we are aware of are those made by Krigbaum and Tokita[9] (not the main topic of their paper) and McMahon and Tincher[10]. In their calculations Krigbaum and Tokita[9] used simple, empirical rotational potentials and a point dipole interaction of cyano groups according to classical electrostatics. McMahon and Tincher[10] evaluated steric energies of disubstituted pentanes for all possible *trans* and *gauche* conformers utilizing Lennard–Jones (6–12) potentials and compared energy differences with their own n.m.r. results.

CONFORMATIONAL ENERGY CALCULATIONS

The PCILO method represents a special quantum chemical technique which is capable of taking into account configurational interactions. Proceeding from the notion of the chemical bond, the ground, singly and doubly excited configurations are built up from a set of localized bonding and antibonding orbitals (determinant basis). The ground state energy expressed in terms of physically interpretable contributions, the wave function and other characteristics derived from it (for instance, the charge distribution of the molecular system) are evaluated by means of a Rayleigh–Schrödinger perturbation expansion up to the third order. Because they are the free parameters of the wave function, the bond polarities are optimized by an iterative minimization process for the polarization energy.

In the present work, this method has been applied to meso- and racemic-2,4-dicyanopentane as models for iso- and *syn*diotactic PAN. *Figures 1* and *2* show these model molecules with all skeletal bonds in the *trans* conformation. The signs of the angles ϕ_1 and ϕ_2 are taken as positive for right hand rotations for both meso and racemic dyads, starting from zero in the *trans* conformation. The numbers written beside the atoms denote the PCILO calculated excess charge in e (elementary charge) in this bonded state compared with the free atom. Here, and in all the following figures showing molecular models, the arrow depicts the predicted (negative) dipole moment (for its value see *Tables 1* and *2*).
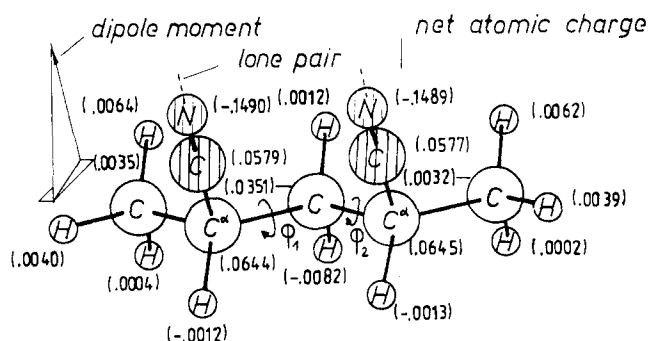

Figure 1 Model of meso-2,4-dicyanopentane in the planar *trans* conformation

In our calculations fixed bond angles and bond lengths according to standard geometry (see ref. 11) were assumed for all conformations. Only for the *trans* and the absolute minimum conformations has the C^α–C–C^α angle been optimized. The C≡N bond length was taken to be 1.16 Å (ref. 12).

RESULTS AND DISCUSSION

Conformational energy maps for the meso and racemic forms are shown in *Figures 3* and *4*, respectively. In the meso map there is one pronounced minimum at $\phi_1 = -82.5°$, $\phi_2 = 27.5°$ separated from the others by a considerable gap of 16.5 kJ/mol. A further lowering of 1.6 kJ/mol in energy is achieved by decreasing the C^α–C–C^α bond angle from 109.5° (used in *Tables 1* and *2*) to 107°.

The racemic form has two deep minima at $(-32.5°, -32.5°)$ and $(-87.5°, -87.5°)$ with a 18.5 kJ/mol gap below the others. Again, a decrease in the
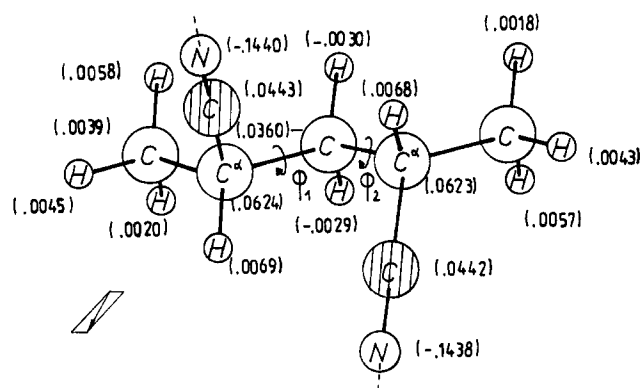
C^α–C–C^α angle (here the minimum is reached at 106.5°) decreases the energy, in this case by 1.8 kJ/mol.

In the *trans* conformations the above effects are stronger, but in the opposite direction. On increasing the angles to 116° and 113.7° the energies are lowered by 6.4 kJ/mol and 2.4 kJ/mol for the meso and racemic forms, respectively.

Table 1 lists the angle coordinates, some energies of interest (as differences from those of the *trans* conformation) and the dipole moments of all the local minima found for the meso molecule. The Coulombic
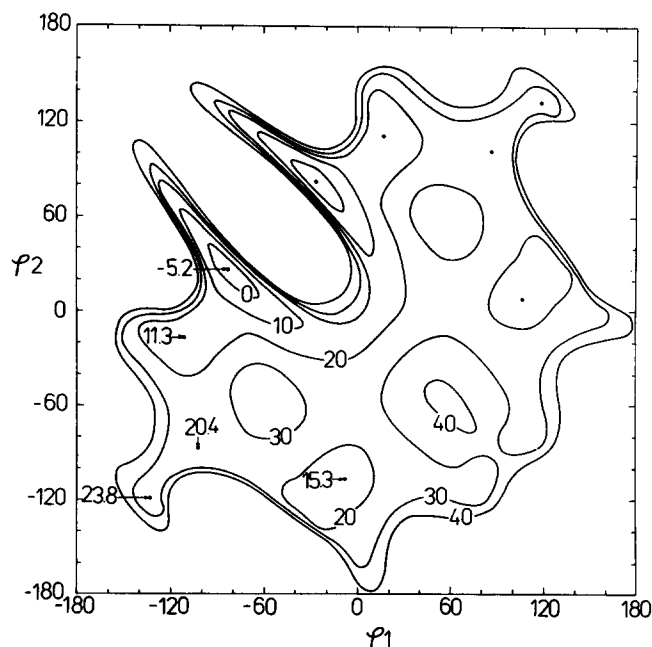

Figure 2 Model of racemic-2,4-dicyanopentane in the planar *trans* conformation

Figure 3 Conformational energy contours for meso-2,4-dicyanopentane. The angles ϕ_1 and ϕ_2 are defined in *Figure 1*. The contour interval is 10 kJ/mol

Table 1 Calculated conformational energies in kJ/mol scaled to the *trans* conformation and dipole moments in Debye of meso-2,4-dicyanopentane (ΔE, total conformational energy relative to *trans*; ΔE_0, energy of the fully localized determinant with optimized bond polarities before perturbative calculation; ΔE_C^{before}, Coulombic interaction energy of the net atomic charges of the two nitrile groups before perturbative calculation; $\Delta(\Delta E_C)$, difference between Coulombic energy of the two nitrile groups after and before perturbative calculation; ΔE^{deloc}, delocalization energy)

Conformation	(ϕ_1, ϕ_2) (°)	ΔE	ΔE_0	ΔE_C^{before}	$\Delta(\Delta E_C)$	ΔE^{deloc}	Dipole moment
tt	(0, 0)	0	0	0	0	0	5.79
$(g^-t)_+$	(−82.5, 27.5)	−28.5	9	−3	−23	−24	5.52
$(g^-t)_-$	(−111, −17)	−11.0	1	−4	4	−1	3.12
tg^-	(−8, −107)	−7.0	−2	−4	9	5	3.72
$(g^-g^-)_+$	(−102, −87)	−2.0	0	−4	7	3	2.62
$(g^-g^-)_-$	(−133, −119)	1.5	−6	−4	5	−4	3.23

Table 2 Calculated conformational energies in kJ/mol scaled to the *trans* conformation and dipole moments in Debye of racemic-2,4-dicyanopentane (ΔE, total conformational energy relative to *trans*; ΔE_0, energy of the fully localized determinant with optimized bond polarities before perturbative calculation; ΔE_C^{before}, Coulombic interaction energy of the net atomic charges of the two nitrile groups before perturbative calculation; $\Delta(\Delta E_C)$, difference between Coulombic energy of the two nitrile groups after and before perturbative calculation; ΔE^{deloc}, delocalization energy)

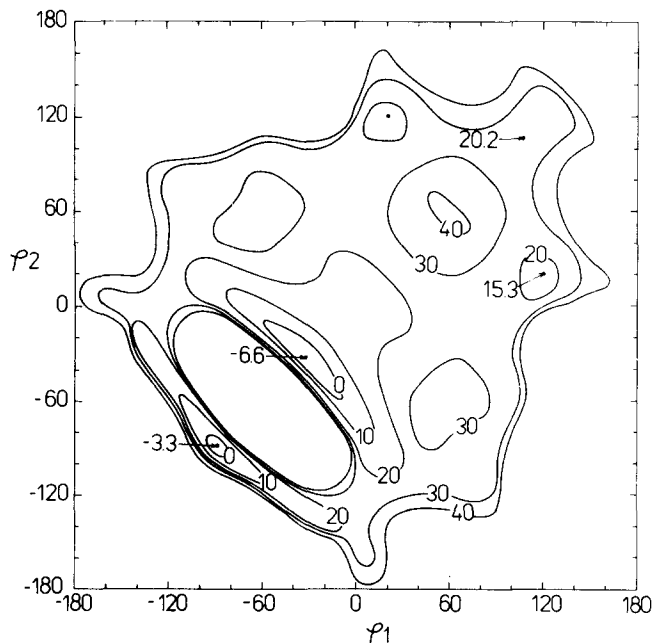| Conformation	(ϕ_1, ϕ_2) (°)	ΔE	ΔE_0	ΔE_C^{before}	$\Delta(\Delta E_C)$	ΔE^{deloc}	Dipole moment
tt	(0, 0)	0	0	0	7	0	3.45
$(tt)_-$	(−32.5, −32.5)	−20.3	21	−2	−42	−43	5.74
g^-g^-	(−87.5, −87.5)	−16.2	12	0	−20	−28	5.42
g^+t	(117, 20)	2.3	3	−2	7	−3	3.10
g^+g^+	(106, 106)	7.3	2	−2	10	3	3.10

Figure 4 Conformational energy contours for racemic-2,4-dicyano-pentane. The angles ϕ_1 and ϕ_2 are defined in *Figure 2*. The contour interval is 10 kJ/mol

interaction energies have been calculated by treating the atoms of the nitrile groups as point charges carrying the PCILO predicted net atomic charges. The delocalization energy E^{deloc} emerges as a second order term in the perturbation expansion. Other terms of the energy perturbation expansion are not given in the table, because they do not differ significantly from one conformation to another.

It should be noted that the energy map (*Figure 3*) and *Table 1* show the appearance of 'split' minima for the *gauche* states (denoted by $(\ldots)_{\mp}$) of the meso molecule. As can be clearly seen, the absolute minimum is due to the Coulombic interaction between the nitrile groups, which can only be properly estimated after performing the perturbative calculation of the atomic charges (giving also E^{deloc}) for each conformation. The conformational dependences of these net atomic charges are given (in parenthesis) in *Figures 5* and *6* in units of e. Small asymmetries are due to numerical effects. The distance between the nitrile group carbon atoms is as small as 2.26 Å for the lowest minimum, as depicted in *Figure 5*.

The other minima can be explained by an effect which was studied separately using the methane–cyanomethane system (*Figures 7* and *8*) and called by us the π-club-H-effect. It is a charge transfer interaction between
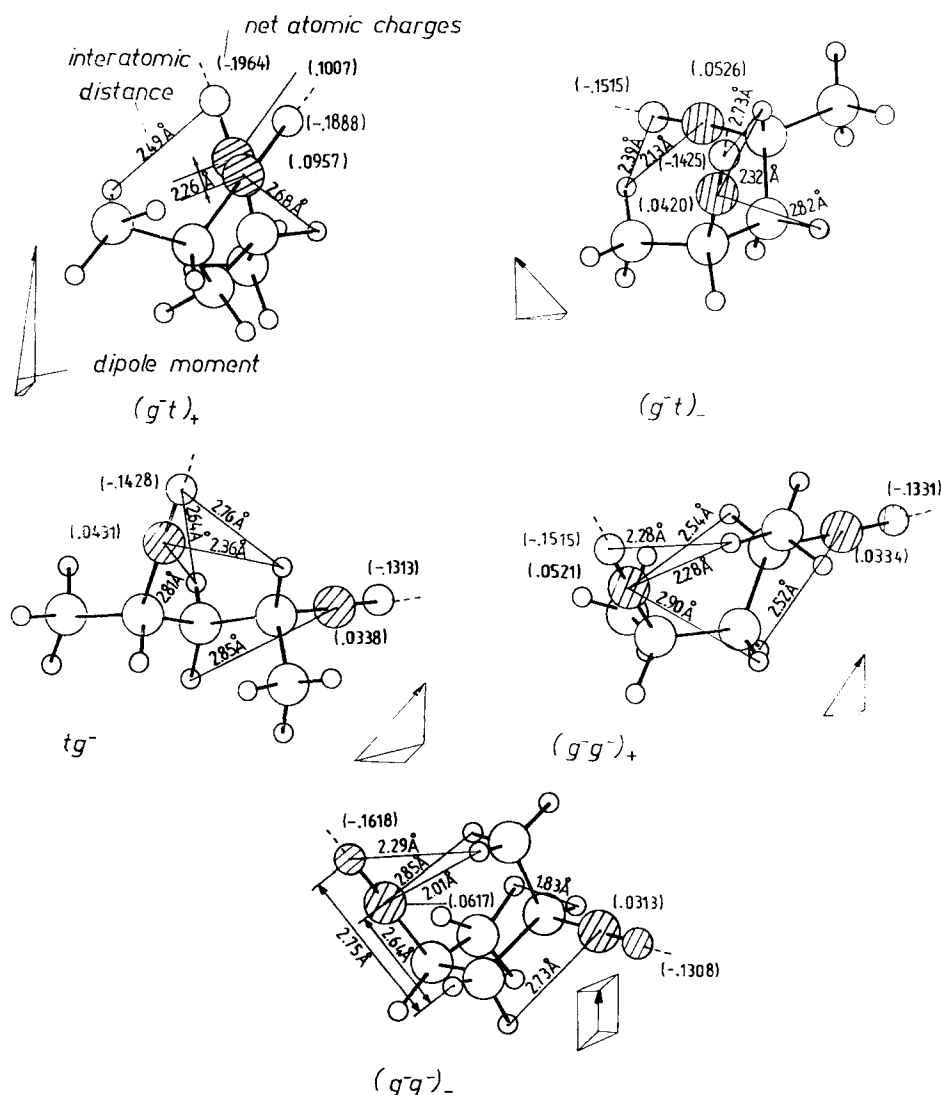

Figure 5 Minimal energy conformations of meso-2,4-dicyanopentane according to *Table 1*
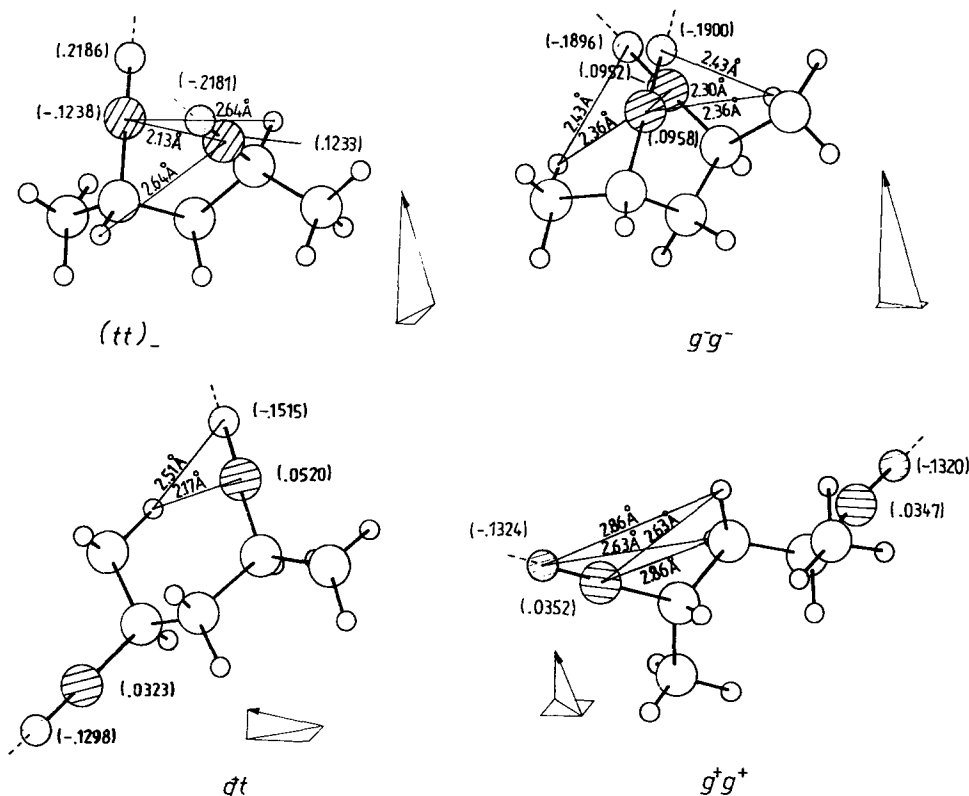
Figure 6 Minimal energy conformations of racemic-2,4-dicyanopentane according to *Table 2*
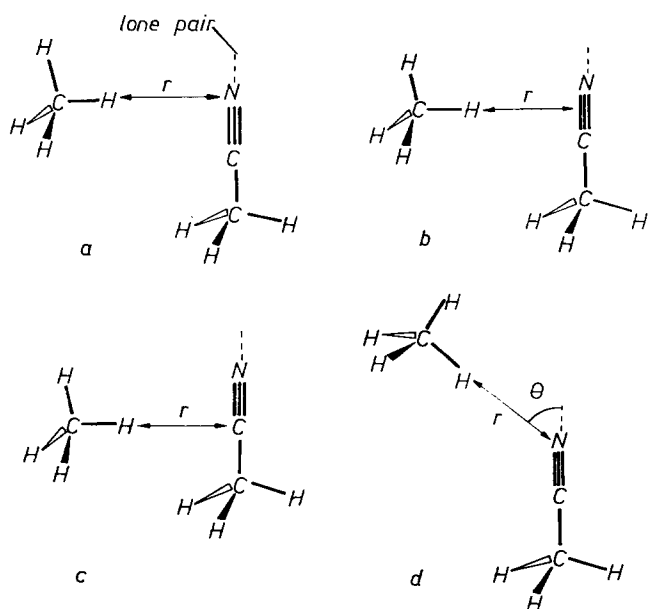

Figure 7 Different kinds of the hydrogen–nitrile group approaches modelled with methane and cyanomethane

Figure 8 Interaction energy of methane and cyanomethane *versus* distance for the arrangements a–d depicted in *Figure 7*

the CH bond and the nitrile π bond. A further decrease in energy is obtained by adding a hydrogen bond contribution from the CH bond and the nitrile group lone pair by allowing the angle between C–H and C$\equiv$N to be changed. However, the minimum conformation formed in this way (*Figure 7d*) is not attainable in 2,4-dicyanopentane. All C–H or H–N distances giving rise to an appreciable π-club-H-effect (< 3 Å) are given in *Figure 5*. The barrier heights between the minima $(g^-t)_+$ and $(g^-t)_-$, $(g^-t)_-$ and $(g^-g^-)_+$, $(g^-g^-)_+$ and
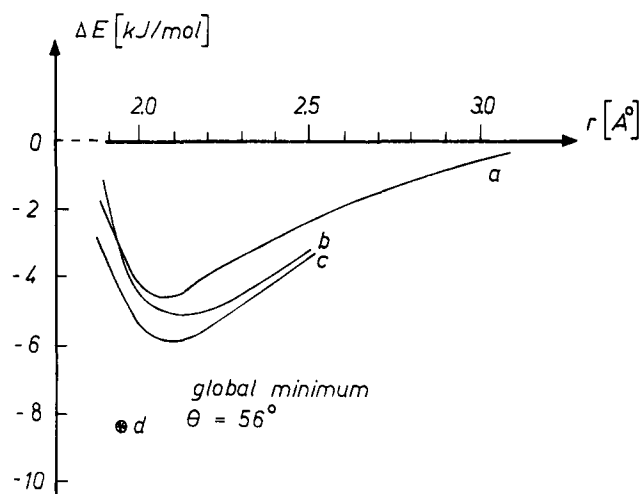
$(g^-g^-)_-$, $(g^-g^-)_+$ and tg^- are about 1 kJ/mol, 4 kJ/mol, 2 kJ/mol and 5 kJ/mol, respectively.

For the racemic molecule the situation is very similar, the main difference being the occurrence of two deep minima caused by Coulombic nitrile group interactions and the absence of 'split' minima (see *Table 2*). The barrier between them amounts to about 25 kJ/mol. The other two minima are readily explained by the π-club-H-effect with the distances given in *Figure 6*.

In order to model the shielding proposed in ref. 1 for meso sequences, we have varied the bond and dihedral angles simultaneously for both nitrile groups from 180° to 120°. No lowering in energy was found.

Comparing the results from refs 9 and 10 with ours, we do not find much resemblance, probably owing to

the simplicity of the assumptions made in those papers. The significance of our results for the local conformations of PAN polymer chains is based on the assumption that next-but-one neighbours have only little influence on the angle under consideration. Of course, this will be true only to a certain degree, but qualitative changes in the local chain conformation should not be expected (see, for example, ref. 13 for the case of PVC). Investigations concerning this point for PAN are in progress.

CONCLUSIONS

It was shown that the quantum chemical PCILO method yields minima of conformational energy for PAN model molecules which would not be expected using classical physics. The deepest minima are characterized by a relatively close approach of the nitrile groups, accompanied by a charge shift in the triple bonds increasing the bond dipole moment. The minimum-energy conformations found are considered as giving the local conformations of the PAN polymer chain.

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