SHORT COMMUNICATION

^{13}C NMR Chemical Shifts and Electronic Structure of Poly(*t*-butylacetylene)

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Recently, a variety of polyacetylene derivatives, so-called synthetic organometals, have been synthesized for use as semiconductors. They possess high conductivity when dopped with halogens. However, unlike metals, the conductivity of these polymers is anisotropic and its temperature dependence is complicated.

The main chains of these conductive polymers comprise conjugated double bonds about which there are *cis* and *trans* isomers. Therefore, their electronic structure should depend on geometrical isomerism. Polyacetylene is insoluble in ordinary organic solvents. Higashimura *et al.*[1] synthesized poly(*t*-butylacetylene), and controlled its geometrical structure by adjusting the polymerization conditions including solvents and catalysts. Since this polymer is soluble in organic solvents such as chloroform and toluene, it is possible to determine its electronic structure by the ^{13}C NMR method.

The purpose of the present work is to discuss the relation between the geometrical and electronic structures of poly(*t*-butylacetylene) by comparison of calculated and measured ^{13}C NMR chemical shifts.

The electronic structure and ^{13}C NMR chemical shift calculations were carried out on trimer model compounds for the polymer using the CNDO/2 method.[2] For the chemical shift calculation, the Pople–Karplus theory was used employing the average exicitation energy (ΔE) approximation.[3]

The geometrical structure of the trimer was assumed to be determined by *cis* and *trans* isomers about the conjugated double bonds. For the *cis*

isomer, it was assumed that (1) three consecutive double bonds are planar, (2) the four carbons of the side chain are tetrahedral, (3) the carbon pairs of (1, 4), (7, 10) and (13, 16), defined in Figure 1, take on the *cis*-conformation, and (4) the side chain protons are located in such a way that steric hindrance is a minimum.
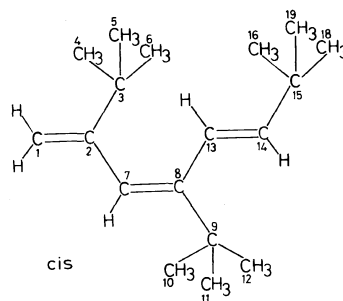

Figure 1. Definition of the *cis* conformation in poly(*t*-butylacetylene).
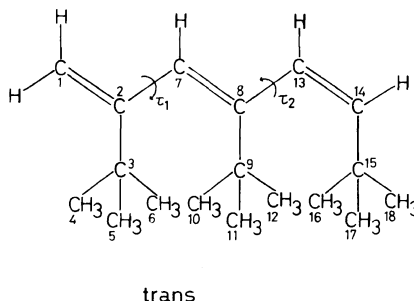

Figure 2. Definition of the *trans* conformation in poly(*t*-butylacetylene).

For the *trans* isomer, the planar zigzag conformation was excluded because of the large steric hindrance it creates. With the rotational angles τ_1 and τ_2 about the skeletal bonds defined in Figure 2, the calculation was carried out to determine the dependence of τ_1 and τ_2 on the total energy and also on the chemical shift of the *trans* isomer.

Figure 3 shows the calculated dependence of τ_1 ($=\tau_2$) on the total energy. As seen from Figure 3, an energy minimum appears at $\tau_1 = \tau_2 = 120°$. Figure 4 illustrates the dependence of τ_1 ($=\tau_2$) on the calculated ^{13}C NMR chemical shifts of the central carbons of the trimer. It is evident that the calculated chemical shifts for the carbons (b), (c), and (d) do not change appreciably with the angles τ_1 and τ_2,
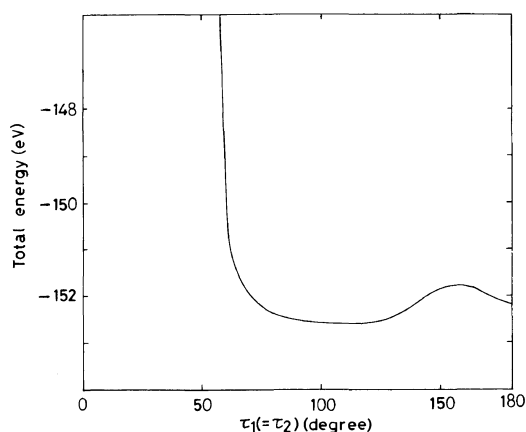
but the calculated chemical shifts for the carbon (a) at τ_1 ($=\tau_2$) below 60° undergo marked change with τ_1. This region of τ_1 is energetically unfavored because of the steric hindrance it gives rise to. In energetically stable regions, the solid curves do not intersect with each other. Although there is some uncertainty in the determination of τ_1 and τ_2, the order of chemical shifts can be determined accurately. Hereafter, we assume $\tau_1 = \tau_2 = 120°$ for the stable form of the *trans* isomer.

Table I shows the calculated ^{13}C NMR chemical shifts for the above-defined *cis* and *trans* isomers along with the corresponding experimental data obtained by Higashimura et al.[1] It can be seen that (1) for both isomers, the calculated shifts are different for different carbons as in the case of the experimental shifts, and (2) the calculated and experimental shifts for a given carbon change with isomer form in the same direction for carbons (a) and (b) and in the reverse direction for carbons (c)

Figure 3. Relation between rotational angle τ_1 ($=\tau_2$) and total energy of poly(*t*-butylacetylene).

Table I. Observed and calculated ^{13}C NMR chemical shifts

	(a)	(b)	(c)	(d)
Observed				
cis	31.26	38.20	144.56	128.08
trans	32.7	37.4	Downfield	128.02
Calculated				
cis	−160.27[a]	−193.86	−277.45	−253.23
trans	−160.69[a]	−193.31	−271.31	−253.62

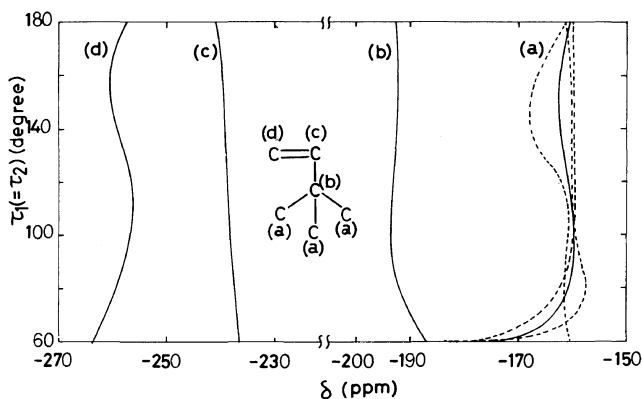[a] Average values over three methyl carbons.

Figure 4. Relations between rotational angle τ_1 ($=\tau_2$) and chemical shift δ for individual carbons in poly(*t*-butylacetylene). Dashed lines indicate chemical shifts for three methyl carbons. The solid line indicates chemical shift averaged over the three methyl carbons.
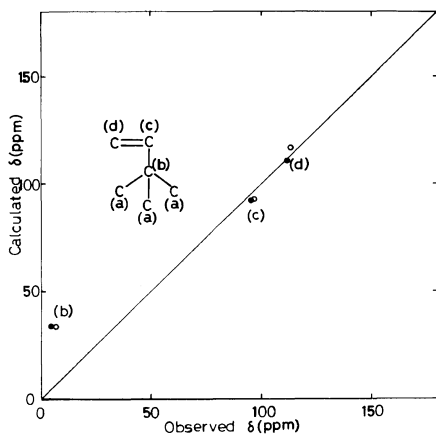
Figure 5. Relation between measured and calculated chemical shifts for individual carbons in poly(t-butylacetylene) relative to the average over three methyl carbons: ●, for *trans* isomer; ○, for *cis* isomer.

Table II. Calculated total π and σ electron densities

	(a)ᵃ	(b)	(c)	(d)
cis				
Total	4.0056	3.9482	3.9583	4.0583
π	0.9991	1.0036	0.9547	1.0746
σ	3.0065	2.9394	3.0035	2.9837
trans				
Total	4.0089	3.9472	3.9886	4.0507
π	0.9858	1.0074	1.0044	0.9907
σ	3.0231	2.9398	2.9842	3.0600

ᵃ Average values over three methyl carbons.

and (d). In Figure 5 is shown the relation between the calculated and experimental chemical shifts, both relative to the averages over the three methyl carbons. Except for carbon (b), the plotted points fall close to the line with an inclination of unity.

Table II gives the calculated total π and σ electron densities for each carbon atom. It is seen that (1) the total electron density in each carbon is independent of the form of isomer, (2) π and σ electron densities in the *cis* isomer are smaller and larger, respectively, than in the *trans* isomer for carbon (c), and (3) π and σ electron densities in the *cis* isomer are larger and smaller, respectively, than in the *trans* isomer for the carbon (d). Empirically, it has been proposed that the shielding, $\Delta\delta$, of a carbon atom in conjugated systems increases linearly with its π electron density $\rho^{4,5}$ *i.e.*,

$$\Delta\delta = \alpha(\rho - 1)$$

where α is a positive constant. The relation contradicts our results, suggesting that the relation must be applied with care to chemical shifts in long linear conjugated systems.

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