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(39) The values of H_{11}, H_{22}, and S_{12}, utilized in this study were chosen in such a way as to correspond closely to situations of chemical significance. Thus the values of H_{11} were fixed at −0.5, −0.4, and −0.3 au because the ionization potentials of various heteroatom lone pairs range between 0.579 and 0.371 au. The values of S_{12} for the heteroatoms studied range between 0.1 and 0.2. Finally, the values of H_{22} typically range from −0.36 au (planar radical) to −0.48 au (tetrahedral radical).

(40) See footnote *b* of Table I.

The Temperature Dependence of Carbon-13 Nuclear Magnetic Resonance Shifts. Limiting Factors and Stereochemical Applications[1]

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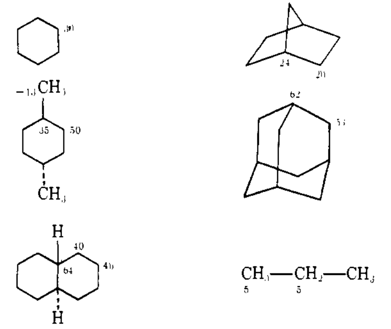
Abstract: With conformationally homogenous alicyclic hydrocarbons, a linear deshielding of up to 0.006 ppm/K with increasing temperature is observed. In contrast upfield shifts as large as −0.02 ppm/K are found with functionally substituted carbon atoms. These findings are compared with solvent dependences and discussed mainly on the basis of square electrical field effects. In sterically inhomogenous compounds carbon atoms which are involved in gauche/trans equilibria are characterized by upfield shifts nonlinear with temperature. The temperature dependence can be used for stereochemical and ^{13}C NMR spectroscopic assignments, as illustrated with *n*-pentylcyclohexane. The methyl carbon shifts in *n*-butane are computer simulated with gauche/trans differences of 300 to 700 cal/mol (enthalpy) and of 2.5–4.7 ppm (shifts). Other hydrocarbons show shift dependences for which empirical parameters are given, reflecting the number of gauche conformations occurring.

Although chemical shifts are known to be intrinsically temperature dependent,[2] there is a paucity of pertinent data on ^{13}C NMR shieldings.[3] For many molecules carbon shifts can be determined more accurately than proton shifts; knowledge of their temperature dependence is a prerequisite particularly in investigations of equilibria and rates of chemical reactions which are fast on the NMR time scale. Besides holding promise for practical applications including

Table I. ^{13}C Shift Temperature Gradients for Conformationally Homogenous Hydrocarbons[a, 6]



Cycloheptane	40
Cyclooctane	30

[a] In 10^{-4} ppm/K units vs. Me_4Si ($\Delta\delta_{Me_4Si} \equiv 0$); positive sign denotes downfield shifts with increasing temperature; standard deviation ±2 to ±6 [10^{-4} ppm/K]. Measured as neat liquids with added lock and reference compounds (see Experimental Section).

^{13}C signal assignments, a study of the temperature dependence of carbon shifts could provide data for the understanding of shielding mechanisms.

As internal reference throughout this investigation, tetramethylsilane (Me_4Si) is used, which *below* 300 K shows a deshielding of $\Delta\delta/\Delta T$ = 0.012 ppm/K with increasing temperature, as recently found[4] by comparison with temperature independent[5] NMR frequencies. In a series of conformationally homogenous and fairly nonpolar hydrocarbons, a strictly linear deshielding (correlation coefficient $r \geq 0.99$) with increasing temperature is observed for all carbon signals[6] (Table I). The values (as compared with Me_4Si with $\Delta\delta/\Delta T \equiv 0$) range between (−0.001 ± 0.0005) and (0.006 ± 0.0005) ppm/K and show no regular trends except being smallest for methyl carbons. The observed deshielding could be connected to an effect of bond length increase,[7a] or, more likely for unpolar single bonds, to a decreasing mean excitation energy ΔE,[8] which could enhance the paramagnetic σ_p term.

The interpretation of carbon shifts in *polar* compounds is particularly complicated by the change in macroscopic properties of the solution with temperature. The deshielding of a carbon nucleus by a fluctuating dipole can be approximated on the basis of square electrical field effects.[9,10]

$$\Delta\delta_{(E^2)} \simeq 3P_{CX}I_X r^{-6} \qquad (1)$$

The distance r between the observed carbon and the dipole center as well as the first ionization potential I_X of the heteroatom can be regarded as approximately solvent independent. The change of C-X bond polarizability with the dielectric constant ϵ of the solvent can be described by[11,12]

$$P_{CX} = 1 - \mathrm{const}(0.333 - k_i)\frac{\epsilon - 1}{\epsilon + 2} \qquad (2)$$

The expected deshielding with increasing solvent polarity, linear in $(\epsilon - 1)/(\epsilon + 2)$, has in fact been observed[13] for the functional carbon shifts (C_α) of nonsymmetrical molecules (anisotropy factor $k_i < 0.333$). It should be noted, that a very similar function, like $(\epsilon - 1)/(2\epsilon + 1)$,[14] would account for the increasing polarity of a C_α-X bond with ϵ, which would lead to deshielding by lowering the electron density at C_α.

Measurements with ethyl bromide in neat liquid as well as in pentane, for which solvents ϵ is known at different temperatures,[15] show indeed the predicted linear dependence of C_α shifts on $(\epsilon - 1)/(\epsilon + 2)$[13] (Figure 1).

Table II. ^{13}C Shift Temperature Gradients[a] for Polar Compounds

$C{-}Br_4$	$Me{-}I$	$\mathrm{Me_3{-}C{-}\overset{I}{C}{-}Me_2}$[e]
−118 ±4[b]	−200 ±10[c]	19 −15 −194 15 ±3 ±5 ±9 ±3
$Me{-}CH_2{-}Br$[c]	$Me{-}CH_2{-}Br$[d]	
−17 −122 ±1 ±3	−7 −70 ±3 ±4	

[a] See footnotes to Table I. [b] 5 mol % in pentane. [c] Neat liquid. [d] 3 mol % in pentane. [e] 40 wt % in a 1:1 mixture of $CFCl_3$ and CH_2Cl_2.

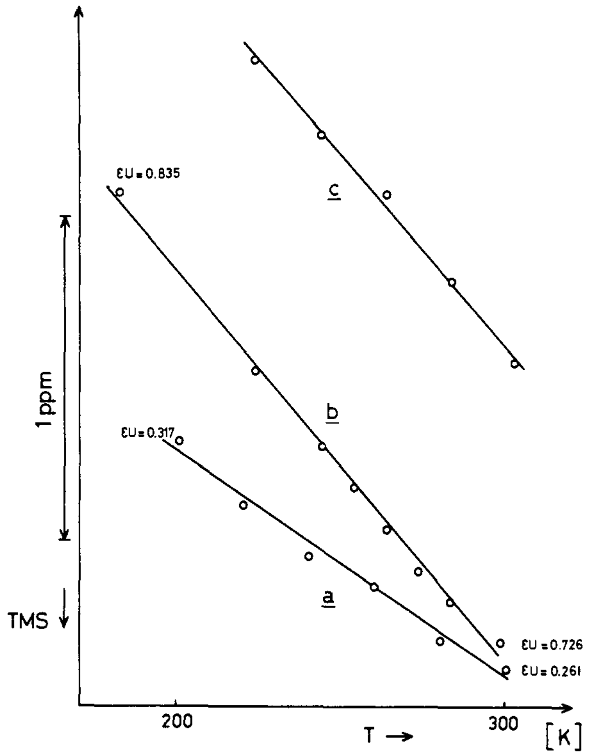


Figure 1. $^{13}C_\alpha$ shift dependence on temperature T and on ϵ units for: (a) ethyl bromide, 3 mol % in pentane; (b) ethyl bromide, neat; and (c) carbon tetrabromide, 5 mol % in pentane.

There is, however, a major contradiction to results of measurements of ethyl bromide carbon shifts in solvents of varying dielectric constants, which have been extrapolated to zero concentration of the solute.[13] Here we have observed for C_α a sensitivity of 6 ppm per $(\epsilon - 1)/(\epsilon + 2)$ unit (= ϵu), while the slopes of the temperature plots (Figure 1) are 13.2 ppm/ϵu in neat ethyl bromide and 14 ppm/ϵu in pentane. In addition, carbon tetrabromide shifts depend even more strongly on temperature (Figure 1, −0.012 ppm/K), although this spherically symmetrical molecule (k_i = 0.333) should be rather insensitive to solvent ϵ changes. There must be another factor besides solvent effects which contributes substantially to the observed C_α shielding with increasing temperature. An increasing population of higher vibrational ground states will lenghthen the C_α-X bond to some extent, which in view of the square electric field effect dependence on r^{-6} (eq 1) will produce an upfield shift. This effect is dominating at C_α and levels off at C_β by the counteracting deshielding observed for hydrocarbons. The latter effect becomes dominant at carbon atoms remote to the C_α-X substitution site (Table II).

The temperature dependence of ^{13}C signals of compounds undergoing rapid chemical exchange can be used as a sensitive probe for the equilibrium, provided one can estimate the chemical shift temperature dependence of the participating species. With conformationally inhomogenous hydrocarbons, we find, as usual, linear deshielding with in-

Table III. Temperature Dependence of ^{13}C Shifts for Linear Alkanes[a]

	C1				C2				C3				C4			
	$\Sigma\gamma$	S	A	B	$\Sigma\gamma$	S	A	B	$\Sigma\gamma$	S	A	B	$\Sigma\gamma$	S	A	B
n-Butane	1	55	7.9	1.119	0	20	2.6	1.395								
n-Pentane	1	45	5.8	1.376	1	40	3.7	1.351	0	12	1.0	1.540				
n-Hexane	1	45	6.7	1.1335	1	40	3.4	1.356	1	45	3.2	1.500				
n-Heptane	1	40	6.6	1.134	1	40	3.6	1.355	1	45	2.9	1.503	2	95	6.0	1.453

[a] $S = d\delta/dT$ at 230 K in 10^4 ppm deg units; for other explanations, see text.

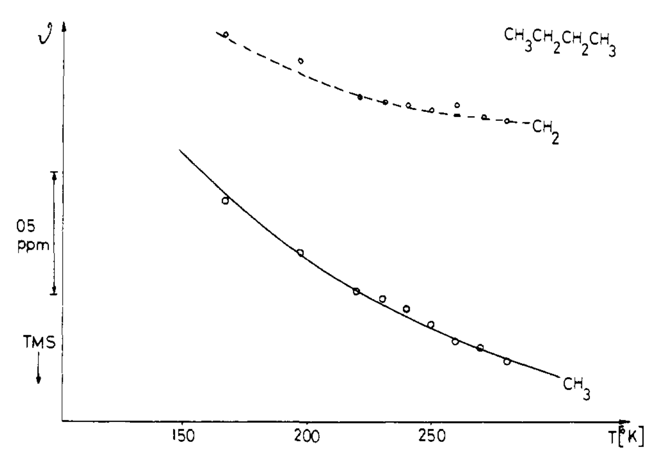


Figure 2. Temperature dependence of ^{13}C shifts in *n*-butane. Experimental points and computer-simulated curve (solid line). For measuring conditions see footnotes to Table I and Experimental Section.

creasing temperature for all carbon atoms not involved in rotational equilibria, but a marked and *non*linear upfield shift for those carbon atoms which participate in gauche/trans conformational equilibria. At elevated temperature the gauche conformations become more populated, leading to upfield shifts particularly for those carbons changing from an antiperiplanar to a syn clinal position. In methylcyclohexanes, e.g., such a change is accompanied by an upfield shift for the methyl carbon of 5-6 ppm.[16]

The temperature dependence of methyl signals in fixed conformations (see Figure 1 and ref 17 for axial CH_3 groups) is much smaller than the observed gradients (δ_{exp}) in *n*-butane (Figure 2). One can thus analyze the corresponding equilibrium between gauche and trans conformers, characterized by an enthalpy difference $\Delta H°$, with mole fractions and (unknown) rotamer shifts n_g, n_t and δ_g, δ_t, respectively:[18]

$$\delta_{exp} = 2n_g\delta_g + (1 - 2n_g)\delta_t$$

$$n_g = (1 + 2\exp(-\Delta H°/RT))^{-1}$$

Compaison of experimental and calculated shifts with the aid of a least-squares minimization computer program furnishes solutions within ±0.01 ppm standard deviation for $300 < \Delta H° < 700$ cal/mol with $11.0 < \delta_g < 12.1$ ppm and $13.5 < \delta_t < 16.8$ ppm (relative to Me_4Si). Since the experimental line is only weakly curved, the computed minima are rather flat, but the shift values and the enthalpy difference are found to be in general agreement with literature data.[19]

Other linear hydrocarbons also show a temperature dependence which is shielding and nonlinear for carbons affected by conformational equilibria. The slope of the curves $d\delta/dT$ is approximately proportional to the number $\Sigma\gamma$ of gauche conformations possible for a specific carbon atom (Table III). These shifts can be represented by eq 3 with ±0.02 ppm accuracy.

$$\log \delta = AT^{-1} + B \qquad (3)$$

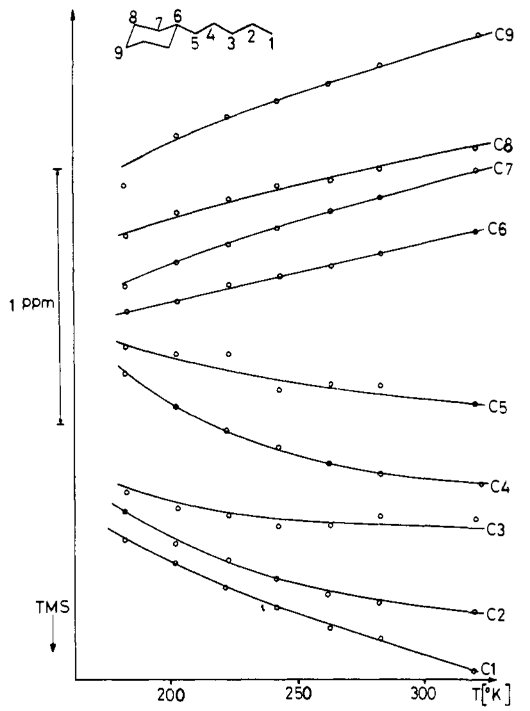


Figure 3. Temperature dependence of ^{13}C shifts in *n*-pentylcyclohexane. For measuring conditions, see footnotes to Table 1 and Experimental Section.

The use of temperature shift gradients for the assignment of mobile parts in a molecule which are present in mixed conformations is illustrated in Figure 3. In *n*-pentylcyclohexane there are gauche rotamers only around the C2-C3 and C3-C4 bonds since the branching at C6 prevents the formation of other gauche conformations. Correspondingly, one finds upfield shifts for C1, C2, and C4, and downfield shifts for C6 to C9, whereas C5 and C3 exhibit the same behavior as the CH_2 signal in *n*-butane.

Experimental Section

^{13}CMR spectra were run in PFT mode at 21.14 kG under proton noise decoupling on a Bruker HX90/Nicolet 1080 system using 8K data points at 3000-Hz spectrum width corresponding to ±0.015 ppm digital resolution. $CFCl_3$ (10-20%) was added as internal ^{19}F lock, except in solvent effect studies, where C_6F_6 or D_2O contained in a capillary tube was used as lock. Me_4Si (2-5%) served as internal reference; for other conditions, see footnotes to tables. The temperature was controlled to ±0.5 °C by a Bruker BST 100/700 unit and calibrated with the aid of chemical shift "^{13}CMR thermometer",[4] which was again calibrated with a thermocouple and the standard methanol ^{1}H NMR temperature probe and showed the same temperature with and without ^{1}H noise decoupling.

2-Iodo-2,3,3-trimethylbutane. 2,3,3-Trimethyl-2-butanol (3 g, 0.034 mol) was stirred with a fourfold excess of hydroiodic acid for 1 h. The product was filtered, washed with water, and found to contain 80% iodide (by ^{1}H NMR). The residual alcohol was removed by recrystallization and sublimation; the iodide was then obtained in 40% yield at 98% purity (by ^{1}H NMR): ^{1}H NMR (CCl_4) 1.15 (*t*-Bu singlet), 2.05 (β-Me singlet).

Other materials were commercially available compounds and purified prior to use, if necessary, by destillation or sublimation.

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Supplementary Material Available. A listing of ^{13}C shifts for all measured compounds at various temperatures (3 pages). Ordering information is given on any current masthead page.

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Resonance Raman Study of the Thermochromic Phase Transition of a Polydiacetylene

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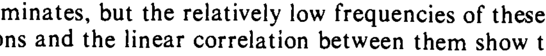
Abstract: Polymers of the type $[{=}C(R){-}C{\equiv}C{-}(R)C{=}]_n$, obtained by the solid-state polymerization of the corresponding diacetylene, have substantial π-electron delocalization along the chain, forming a pseudo-one-dimensional electronic system. The polymer poly-ETCD, of this form, where R is $-(CH_2)_4OCONHC_2H_5$, has a nearly reversible (green-red) thermochromic phase transition in the 117-137°C range. Its Raman spectra reveal dramatic changes in the frequency and intensity of $\nu(C{=}C)$ and $\nu(C{\equiv}C)$ bands as a function of source frequency and of temperature, as it is raised through the transition. The changes result from the thermal transition and from selective resonance enhancement of vibrations for domains with whose electronic transitions the source is in resonance. The π-electron delocalization is thus shown by resonance Raman spectroscopy to occur over segments, or domains, along the polymer backbone. The distribution of the "delocalization lengths" is peaked at three values at 25°C but at one value above the transition, for poly-ETCD samples prepared by 100 Mrad γ-ray irradiation. Energy level calculations are consistent with a delocalization-length distribution peaked around 3.0–8.0 nm, and above 20.0 nm at 25°C and at about 8.0 nm above the transition.

Crystalline materials formed by the solid-state polymerization of diacetylene monomers, of the form $RC{\equiv}CC{\equiv}CR$, are under investigation because π-electron density can be delocalized extensively along the polymeric chains.[2-7] This extended, conjugated, π-bond structure can be described by two resonance forms:



Intense $\nu(C{=}C)$ and $\nu(C{\equiv}C)$ vibrational bands observed in the Raman spectra indicate that the acetylenic structure predominates, but the relatively low frequencies of these vibrations and the linear correlation between them show that there is a substantial "resonance admixture" of the butatriene structure.[2,3]

Electron delocalization can be over a distance as long as the chain length of a polymer molecule, but it can be over shorter distances if continuity of "conjugation" is broken by configurational or chemical (functional group) defects. The chain lengths of the molecules are limited only by breaks which represent crystal defects. These defects are responsible for a distribution of chain lengths. There can be a distribution of configurations of the individual polymer molecules as well, so overall we may expect that in general there will be many "delocalization lengths" over which π-electron delocalization is uninterrupted.

Since the extent of π-electron delocalization along the backbone of the linear polymer chains should affect the optical properties of these materials strongly, optical absorbance and Raman scattering experiments should yield information about the distribution of π-electron delocalization lengths in a polydiacetylene.

In earlier Raman spectral studies of polydiacetylenes[2] it was found that the strong Raman bands appear in the $\nu(C{=}C)$ and $\nu(C{\equiv}C)$ regions and are at relatively low