Communications to the Editor

Low-Temperature Carbon-13 Magnetic Resonance in Solids. 2.[1a] Six π-Electron Ring Systems: $C_7H_7^+$, C_6H_6, and $C_5H_5^-$

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The seminal work of Spiesecke and Schneider[2] relating liquid ^{13}C chemical shifts to π-electron charge densities, q_π, has stimulated electronic structural correlations of chemical shifts for 2 decades. With the rapid emergence[3] in recent years of solid-state NMR techniques into chemistry, considerable attention is now being focused on the tensorial features of chemical shielding.[4] Using cryogenic techniques developed in this laboratory,[1,5] we report the principal values of the ^{13}C chemical shift tensor for tropylium cation (**1**), benzene (**2**), and the cyclopentadienide anion (**3**).

All sample handling was done under N_2 atmosphere. The tetrafluoroborate salt of **1** was run both neat and dissolved in liquid SO_2, and a solution of **3** in liquid NH_3 was made from freshly distilled cyclopentadiene and excess $NaNH_2$. The solutions were transferred into a Kel-F cell with a precooled syringe. The cell is attached to a sapphire rod which is part of the cold tip of a Displex closed-cycle helium cryostat. During transfer the cell was cooled by dry ice. After transfer the solution was frozen rapidly with liquid N_2. The frozen sample, Kel-F cell, and sapphire rod were rapidly enclosed in the glass vacuum shroud, evacuated, and cooled to ~20 K. The vacuum shroud enclosing the sample was kept immersed in liquid N_2 during the cooling process. This procedure brings the cold finger down to temperature rapidly enough to ensure that the solution does not melt and boil off in the vacuum. The spectrum was measured on our ν-80, a home-built spectrometer (20.12 MHz for ^{13}C). The three principal components of the chemical shielding tensor are extracted by computer simulation of the spectra.

The spectrum of **1** in SO_2 suffered from a poor signal to noise ratio. Therefore a singly ^{13}C labeled tropylium tetrafluoroborate was prepared from ^{13}C-enriched diazomethane and benzene.[6] Since it is known[7] that **1** freely rotates about its 7-fold symmetry axis at higher temperatures the spectrum of the neat salt was recorded at 298 and 77 K and at 10 K increments between 20 and 70 K. These spectra show no deviation from axial symmetry at any temperature, thus confirming that **1** as a neat salt freely rotates at all temperatures currently observable. Spectra of labeled **1** in SO_2 were also taken between 20 and 70 K. Figure 1 shows the spectra of neat **1** and **1** dissolved in SO_2 both at 20 K.

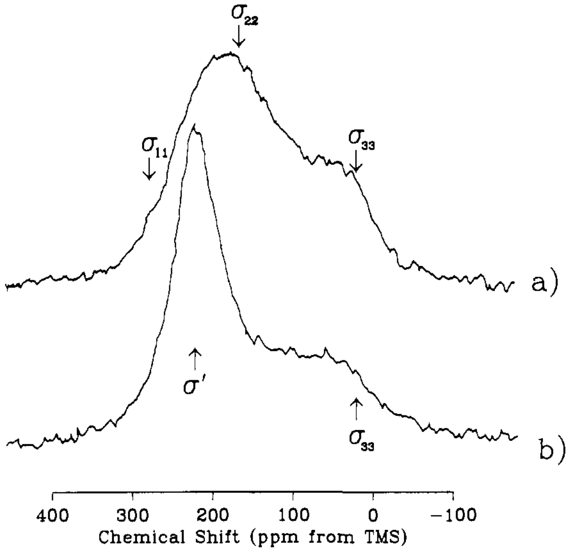

Figure 1. ^{13}C spectra at 20 K of tropylium tetrafluoroborate (a) dissolved in SO_2 and (b) neat. As spectrum (a) likely is still in an intermediate motional regime, the intensity of the anisotropic pattern is distorted between the σ_{11} shoulder and the prominent σ_{22} peak. For this reason the average of σ_{11} and σ_{22}, obtained directly from the neat salt, guides in the selection of σ_{11}, which is otherwise poorly defined due to the motional distortions.

Table I. Tensorial ^{13}C Chemical Shifts[a]

compd	σ_{11}	σ_{22}	σ_{33}	σ' (σ_{11} + σ_{22})/2	σ_{trace}	σ_{liq}[2]
$C_7H_7^+$ (1)	280	168	22	224	167	156.3
C_6H_6 (2)	234	146	9	190	130	128.7
$C_5H_5^-$ (3)	182	114	21	148	106	103.0

[a] Values in parts per million from Me_4Si. Error in referencing ±2 ppm. Overall errors due to referencing and fitting approach ±3 ppm.

Comparison of the line shapes observed in the SO_2 matrix vs. the neat sample for labeled **1** leads one to conclude that the rotation of **1** is slowed down in the SO_2 matrix such that the two in-plane components can be recognized in the spectrum. Even so the sample is in an intermediate motional regime[8] and some signal intensity is observed in the vicinity of σ', the average of σ_{11} and σ_{22}. The value for σ' can be determined accurately from the neat salt of **1**. Spectra of **2** and **3** in natural abundance were of sufficient quality that no enrichment was necessary and the tensorial shifts are given in Table I along with those for **1**.

The shielding results are plotted in Figure 2 along with the original isotropic results of Spiesecke and Schneider.[2] The σ_{11} value is identified with the C–H bond axis; the σ_{22} axis lies in the molecular plane perpendicular to the C–H bond; the σ_{33} axis is perpendicular to the molecular plane. These assignments are based on analogy to previous work using single crystal[9] methods. The

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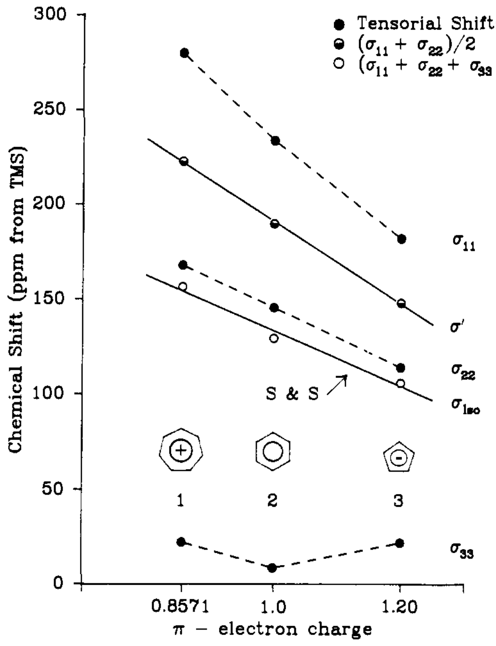

Figure 2. Tensorial chemical shifts for tropylium cation (**1**), benzene (**2**), and cyclopentadienide anion (**3**) as a function of π-electron charge.

values for **1** and **3** are reported here for the first time. Our values for **2** differ from those reported recently[10] by more than our experimental error of ±3 ppm. It is noted that our trace agrees within ±3 ppm with the isotropic liquid values as do the corresponding trace values for the two ions. Our referencing technique involves using an external sample of Me_4Si and therefore may introduce an error as large as ±3 ppm.

Figure 2 clearly indicates that σ_{11}, σ_{22}, σ', and to a reasonable degree σ_{iso} are dependent upon q_π. The plot of σ_{33}, however, shows no simple dependence upon q_π, and the relationship is not even monotonic. The negligible dependence upon q_π in σ_{33} compared with σ_{11} and σ_{22} makes the trace less sensitive to q_π than the two more responsive components.

Waugh and co-workers[4] have used charge-withdrawal arguments to rationalize the changes in tensorial shifts of alkylbenzenes complexes with $Cr(CO)_3$. Such arguments are even more jusitified in the present case. The variations in the tensorial components reflect primarily the behavior of electrons located in the p orbitals oriented perpendicular to the component axis.[5] The value of σ_{33} is characteristic of saturated carbon atoms, and this is reasonable considering that it is determined primarily by the properties of electrons in the σ bonds. Thus, σ_{33} is likely to be more sensitive to the strain in the C–C–C angle than to q_π, upon which the original correlation for σ_{iso} was based.[2] The q_π will affect σ_{33} only through second-order charge-polarization effects upon the σ-electron structure.

Both σ_{11} and σ_{22} are affected by changes in q_π directly as the axes of these components lie in the molecular plane. They differ only in the manner in which they sample the σ-electron distribution in the C–C and C–H bonds, respectively. Because both σ_{11} and σ_{22} depend directly upon q_π, the average, σ', of these two shifts was calculated and is plotted against q_π in Figure 2. A very linear relationship exists between σ' and q_π with a slope for −218 ppm/e compared with the −160 ppm/e slope found for the isotropic shift in ref 2. Thus, the curvature in the plot of the isotropic shift largely arises from the σ_{33} contribution.

This work supports the original premise that chemical shifts depend upon q_π but refines the proposal to focus on only those shift components that reflect the very anisotropic charge distributions associated with charged aromatic systems. As chemical shielding is very sensitive to charge effects, such three-dimensional information is of the utmost importance in understanding this relationship. This work also graphically emphasizes the importance of using the tensorial shifts over the traditional isotropic chemical shift obtained in liquids. Not only does one obtain three times more information but very important directional features also are obtainable. It is hoped that these results will contribute to a greater appreciation of the importance of three-dimensional chemical shift data among chemists interested in structurally selective chemical properties or processes. Furthermore, it should warn against overinterpretation of isotropic chemical shift parameters.

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Registry No. 1, 26811-28-9; **2**, 71-43-2; **3**, 12127-83-2.

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Biosynthesis of Mevinolin. Spectral Assignment by Double-Quantum Coherence NMR after High Carbon-13 Incorporation[†]

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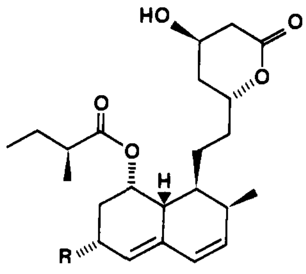
Mevinolin (**1**),[1,2a] compactin (**2**),[2b,c] and analogues such as the corresponding 4a,5-dihydro derivatives[2d,e] are fungal metabolites that block isoprenoid biosynthesis.[2,3] Competitive inhibition of the key enzyme in the pathway, 3-hydroxy-3-methylglutaryl coenzyme A reductase (HMG-CoA reductase; E.C. 1.1.1.34), by the lactone-opened forms of these compounds decreases availability of mevalonate and thereby lowers plasma cholesterol levels in various mammals, including man.[3,4] Since more than half of the



1 R=CH_3
2 R=H

[†] Dedicated to Professor Christoph Tamm, University of Basel, on the occasion of his 60th birthday.

[1] Mevinolin (**1**) from *Aspergillus terreus*[2a] and monacolin K from *Monascus ruber* (Endo, A. *J. Antibiot.* **1979**, *32*, 852–854. Endo, A. *Ibid.* **1980**, *33*, 334–336) appear to be the same compound;[2e] compactin (**2**) is also known as ML-236B.[2c]

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