as first approximation, to represent the difference in coordination bond lengths between Co^{III} and Co^{II} complexes. The change in volume of the Co^{III} complexes within the van der Waals region on going to Co^{II} species is estimated to be +19.7 and +29.8 cm^3 mol^{-1}, for reactions 1 and 2, respectively. These values are regarded as maximum, since the bond distances at the transition state should be somewhere between those of Co^{III} and Co^{II}. The observed values are close to the above values, suggesting that the transition state would be closer to Co^{II} than to Co^{III} with respect to the bond distances.

Registry No. [Ir^{IV}Cl$_6$]$^{2-}$, 16918-91-5; [Co^{III}(edta)]$^-$, 15136-66-0; [Fe^{II}(CN)$_6$]$^{4-}$, 13408-63-4; [Co$_2$^{III}(μ-O$_2$$^{(-)}$)($\mu$-NH$_2$)(en)$_4$]$^{4+}$, 12387-59-6; [Co^{III}(NH$_3$)$_5$Py]$^{3+}$, 31011-67-3; [Co$_2$^{III}(μ-O$_2$$^{(2-)}$)(en)$_4$(NH$_3$)$_2$]$^{4+}$, 47178-28-9; [Co$_2$^{III}($\mu$-O$_2$$^{(2-)}$)(dien)$_2(en)_2$]$^{4+}$, 22386-10-3; [Co$_2$^{III}($\mu$-O$_2$$^{(2-)}$)(dien)$_2$($R$-pn)$_2$]$^{4+}$, 86561-36-6.

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Carbon-13 NMR Study on Liquid Crystal Solutions. Chemical Shift Tensors in Benzonitrile

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Carbon-13 chemical shifts have been widely used in the study of molecular structure, motion, and properties. The components of the chemical shift tensor are a more sensitive probe into molecular structure than the trace alone.[1] The most straightforward way of determining the chemical shift tensor is to perform a line-shape analysis of the proton-decoupled carbon-13 NMR spectrum of a polycrystalline solid. When there are overlapping signals, they can be resolved by using magic angle spinning, and the anisotropic patterns of individual signals can be reconstructed from the spinning sidebands[2-4] or by using pulses synchronized with the rotation of the spinner.[5-7] Chemical shift tensors for individual carbons can also be obtained by analyzing the spectra obtained from single crystals oriented at various angles.[8-10]

Another approach to measuring the chemical shift tensor is to study the NMR spectra of molecules in liquid crystal solutions.[11,12] In the past, this has been limited to the investigation of very simple molecules, and compounds with carbon-13 enrichment were often used for carbon-13 NMR study. This is mainly due to problems

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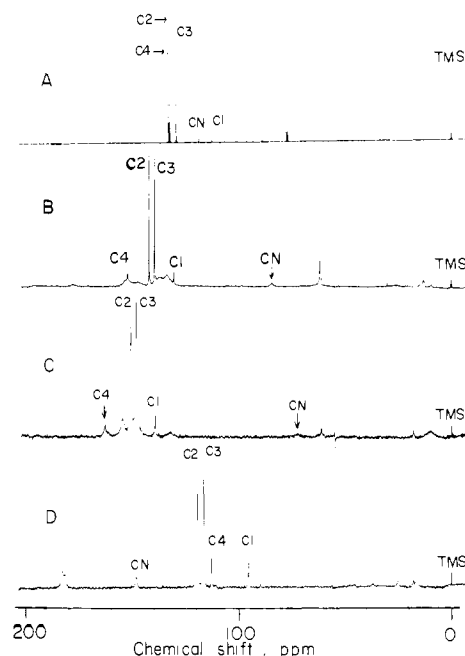
Figure 1. Carbon-13 NMR spectra at 75.43 MHz and 298 K of benzonitrile (ca. 7%) and tetramethylsilane (ca. 1%) in (A) CDCl$_3$, (B) EBBA, (C) NP 1565 TNC, and (D) ZLI 1167. The unmarked peaks in the spectra of the liquid crystal solutions are residual solvent peaks and were identified by comparing these spectra with those with other solutes. The spectra were obtained with a Varian XL-300 spectrometer. A 90°–τ–180°–2τ–180°–τ–acquisition pulse sequence with τ = 0.3 ms and a phase alternated broad-band decoupling scheme (MLEV-64, ref 15) were used in obtaining spectra B–D, with 1000 scans in 33 min for each spectrum.

Table I. Ordering Factors of Benzonitrile (ca. 7% with ca. 1% Me$_4$Si) in Three Liquid Crystal Solutions at 298 K[a]

solvent	S_{zz}	$S_{xx} - S_{yy}$	$S_{zz}/$ $(S_{xx} - S_{yy})$
EBBA	0.1696 ± 0.0002	0.0592 ± 0.0005	2.865
NP 1565 TNC	0.2313 ± 0.0001	0.1614 ± 0.0004	1.433
ZLI 1167	−0.1494 ± 0.0003	−0.1078 ± 0.0007	1.386

[a] The z axis is the CN-bond axis, and the y axis is perpendicular to the ring.

in solvent interference and insufficient decoupling power in spectrometers designed for studying liquid samples. We have recently shown[13] that the first problem can be solved by using a simple spin–echo sequence of 90°–τ–180°–2τ–180°–τ– acquisition, and the second problem can be solved or at least reduced by using phase-alternated broad-band decoupling.[14-21] Here we report the determination of carbon-13 chemical shift tensors of all carbon atoms in benzonitrile by this approach.

The proton-decoupled ^{13}C spectra of benzonitrile in deuteriochloroform and in three liquid crystal solutions are shown in Figure 1. The assignment of the peaks in the isotropic spectrum is straightforward.[22,23] The assignment of the peaks in the spectra

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of the liquid crystal solutions was made by the following consideration. The optic axes of EBBA (from American Liquid Crystals, Kent, OH) and NP 1565 TNC (from EM Chemicals, Hawthorne, NY) orient parallel to the magnetic field, and the solute molecules are partially oriented accordingly. The aromatic carbon signals move downfield and the cyano signal moves upfield (Figure 1, B and C) compared to the corresponding signals in liquid (Figure 1, A). The liquid crystal ZLI 1167 (from EM Chemicals) has a negative magnetic anisotropy, and the optic axes of the solvent molecules orient perpendicular to the magnetic field.[24,25] The ^{13}C signals of benzonitrile in this solvent move to the opposite directions (Figure 1, D). Taking advantage of these differences in the changes in the chemical shifts, the assignment was readily made (Figure 1, B–D). It can be seen that the CN peaks are considerably broader than the other peaks because of dipolar and quadrupolar interactions of nitrogen-14. The chemical shift tensors were determined from these spectra in the following way.

The isotropic chemical shift in a liquid is the trace of the tensor:

$$\delta_{iso} = \frac{1}{3}(\delta_{xx} + \delta_{yy} + \delta_{zz}) \quad (1)$$

and the chemical shift in a liquid crystal solution is

$$\delta_{aniso} =$$
$$\delta_{iso} + \frac{2}{3}S_{zz}[\delta_{zz} - \frac{1}{2}(\delta_{xx} + \delta_{yy})] + \frac{1}{3}(S_{xx} - S_{yy})(\delta_{xx} - \delta_{yy}) \quad (2)$$

for a solute molecule with C_{2v}, D_2, or D_{2h} symmetry.[11] In eq 2, S_{zz} and $S_{xx} - S_{yy}$ are ordering factors of the molecule and can be obtained by analyzing the proton NMR spectrum of the solution at the same temperature. The values of the ordering factors determined for benzonitrile in the three liquid crystal solutions discussed above are given in Table I. The computer program PANIC in an IBM NR/80 spectrometer and the structure carefully determined by Diehl et al.[26] were used in the calculation. In principle, one only needs δ_{iso} and the values of δ_{aniso}, S_{zz}, and $S_{xx} - S_{yy}$ for two liquid crystal solutions to determine the three components of the chemical shift tensor. In practice, this would yield considerable errors because of uncertainties in the experimental data. This is especially true if the ratios of $S_{zz}/(S_{xx} - S_{yy})$ for the two solutions do not differ appreciably, as in the case of NP 1565 TNC and ZLI 1167 (Table I). The errors are reduced as the number of available experimental data sets is increased. Therefore, in addition to the three liquid crystal solutions discussed here, we studied the ^1H and ^{13}C spectra of seven other solutions with binary mixtures of these liquid crystals as solvents. δ_{iso} from the CDCl$_3$ solution and δ_{aniso}, S_{zz}, and $S_{xx} - S_{yy}$ for all ten sets of liquid crystal solutions were used in a least-squares calculation to obtain δ_{xx}, δ_{yy}, and δ_{zz} for each carbon atom. In the calculation, each datum for the isotropic chemical shift was given a weight equal to the total number of anisotropic data, because the former is more accurate, does not depend on the ordering factors, and appears in every equation used in the analysis. The results only differ slightly from those using a unit weighing factor for the isotropic data.

In the calculation, it was assumed that the isotropic shifts in the liquid crystal solutions are the same as those in CDCl$_3$. This is justifiable because the solvent dependence of carbon-13 chemical shifts is appreciably only for strongly hydrogen-bonded systems.[22] Another assumption made in the calculation is that the contribution of the anisotropic chemical shift of the reference compound, Me$_4$Si, was negligible. This is also justified within experimental error, because Me$_4$Si has an extremely small ordering factor in all the solvents used, the anisotropic shift of the methyl group is small, and the changes in the carbon-13 chemical shifts in benzonitrile are large. On the other hand, the changes in the proton

Table II. C-13 Chemical Shift Tensors of the Cyano Group in Three Compounds (in ppm with Me$_4$Si as Reference)[a]

δ	HCN[b]	CH$_3$CN[b,c]	C$_6$H$_5$CN[d]
iso	117.4 ± 0.2	117.2 ± 0.2	118.7 ± 0.2
aa	−71 ± 13	−90 ± 4	−88 ± 5
bb	211 ± 13	221 ± 4	231 ± 14
cc	211 ± 13	221 ± 4	213 ± 9

[a] The *a* axis is the CN-bond axis, and the *c* axis is perpendicular to the ring for benzonitrile. [b] Reference 12. [c] Reference 30. [d] This work.

Table III. C-13 Chemical Shift Tensors of Aromatic Carbons in Benzene and Benzonitrile (in ppm with Me$_4$Si as Reference)[a]

δ	benzene[b]	benzonitrile[c]			
		C1	C2	C3	C4
iso	128.5 ± 0.2	112.5 ± 0.2	132.7 ± 0.2	129.0 ± 0.2	132.8 ± 0.2
aa	234 ± 3	211 ± 2	202 ± 4	195 ± 3	232 ± 4
bb	146 ± 3	104 ± 7	180 ± 2	178 ± 2	158 ± 11
cc	9 ± 3	23 ± 4	14 ± 4	14 ± 3	9 ± 7

[a] The *a* axis is the CH axis (CC≡N axis for C1), and the *c* axis is perpendicular to the ring. [b] References 29 and 31. The tensor was determined at 20 K. [c] This work.

chemical shifts are not as large and cannot be directly measured. They can be obtained from computer simulation of the spectra, but the uncertainties in their values are sometimes comparable to the changes themselves. Therefore, it is not justifiable to use the present method to calculate the proton chemical shift tensors.

The calculated values of the carbon-13 chemical shift tensors in benzonitrile are given in Tables II and III. In Table III, the axis system for individual carbon atoms rather than that for the whole molecule (Table I) was used to present the components of the chemical shift tensors, because they are mainly determined by local electron distributions. The two axis systems are related to each other simply by[27,28]

$$\delta_{aa} = \sin^2 \theta \cdot \delta_{xx} + \cos^2 \theta \cdot \delta_{zz} \quad (3)$$

$$\delta_{bb} = \cos^2 \theta \cdot \delta_{xx} + \sin^2 \theta \cdot \delta_{zz} \quad (4)$$

$$\delta_{cc} = \delta_{yy} \quad (5)$$

where θ is the angle between the *a* and the *z* axes. The axes *a*, *b*, and *c* do not necessarily coincide with the principal axes of the chemical shift tensors for carbons 2 and 3 because of the lack of symmetry about the corresponding C–H bonds. However, the respective angles between the two sets of axes may be quite small,[8–10] and the molecular axes do form a reasonable axis system for the purpose of comparing the data of all carbons.

The errors in the components of the chemical shift tensor of the cyano group (Table II) are larger than those of the ring carbons (Table III) because the cyano group has larger line widths and uncertainties in δ_{aniso}. For this group, neither the tensor components nor the trace were greatly affected by the atom or group that it is attached to (Table II). Moreover, it does not seem to have a very strong π-conjugation with the benzene ring, as δ_{xx} and δ_{yy} only differ slightly. For the aromatic carbons, the effect of substituent-induced changes in their chemical shifts is complicated.[23] This effect on the chemical shift tensors of other benzene derivatives is being investigated. The study of tensorial chemical shifts may be important in the understanding of structurally selective chemical properties or processes.[29]

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