

stearate-benzene system exhibited no optical activity, because of absence of any kind optical activity in the components.

Conclusion

Optically active *N*-acylamino acids formed a new type of lyotropic cholesteric liquid crystals when they were solvated without being dissolved and suspended as liquid crystals in solvents. These suspended liquid crystals showed some characteristics of lyotropic cholesteric liquid crystals.

These systems exhibited CD bands and the maximal wavelengths changed with variation of temperature or solvent compositions. Further, the appearance of LCICD bands due to achiral molecules intercalated into these systems and formation of a spherulite-like phase having an optically negative sign led to the conclusion that these suspended liquid crystals have cholesteric helical structures.

Although these suspended liquid crystals showed the iridescent color of typical cholesteric liquid crystals, the observed color is due to the "Christiansen effect" and not the cholesteric structure.

References and Notes

- (1) (a) Ajinomoto Co. Inc. (b) Tohoku University. (c) Ochanomizu University.
- (2) *N*-Acylglutamic acids can be obtained in crystalline or amorphous form depending on the preparation conditions. Crystalline and amorphous forms of *N*-acyl-L-glutamic acid have different spectral profiles in IR absorption or X-ray diffraction. We can obtain the suspended liquid crystals only in the case of amorphous powdered *N*-acylglutamic acid. These results will be reported elsewhere in the near future.

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Anisotropic Ring-Carbon Chemical Shifts in Arene Chromium Tricarbonyl Complexes

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Abstract: There is known to be a substantial upfield change in ¹³C chemical shifts in olefins and aromatics when they are incorporated into transition metal π complexes. Solid-state NMR studies of ArCr(CO)₃, with Ar = benzene, hexamethylbenzene, and hexaethylbenzene show that this is predominantly due to a very large (>50 ppm) specific increase in screening when the external magnetic field lies in the plane of the aromatic ring along the bonds to the substituents.

Introduction

¹³C chemical shifts in olefins and aromatic ring systems undergo characteristic and substantial changes in the direction of increased screening when these molecules undergo π complexation with metals.^{2a} The changes are of such large magnitude as to encourage some hope of qualitative theoretical interpretation in terms of the nature of chemical bonding in these substances. Indeed a bewildering variety of such interpretations have been made: the increased screening has been ascribed variously to (a) sp²-sp³ rehybridization,^{2b,3} (b) increased total electron density at the ¹³C nucleus,^{2b,3,4} (c) metal-ligand π* interaction,^{2b} (d) "nonbonded shielding terms",³ (e) enhanced σ character of the C-C bonds,⁵ (f) back-bonding,⁶ and (g) changes in effective excitation energy.^{2b,7,8} These explanations are neither independent nor precise; yet they contain the seeds of differing pictures of the bonding and its effect on the carbon shifts. Among other features, these pictures have differing consequences for the di-

rectional character of the shielding; for example, a simple appeal to total charge density or mean excitation energy envisions an essentially isotropic effect on shielding. More direct consideration of individual orbitals would inevitably predict characteristic anisotropies in the effect. It would clearly be helpful to have experimental knowledge of the effect of complexation on the ¹³C shielding tensor, rather than only its isotropic average.

While in some cases anisotropies can be experimentally elicited by use of liquid-crystalline solvents, it is in many ways advantageous and straightforward to embed the molecule of interest in the solid state so as to avoid as much as possible the complexities and uncertainties arising from partial averaging over molecular motion. By now a number of techniques are available for studying chemical shifts in solids, without obscuration by the dipolar broadening characteristic of ordinary "wide-line" spectroscopy.⁹ These methods provide the most complete and accurate information when samples are available

Table I. Principal Shielding Values (σ) in $\text{ArCr}(\text{CO})_3$, (ppm from Liquid Benzene) and Changes in These Values ($\Delta\sigma$) on Going from Free Ligand to the Corresponding Complex (All Values ± 5 ppm)^b Note two sets of values for $\text{C}_6(\text{C}_2\text{H}_5)_6$ (see text).

arene	σ_{\perp}	σ_t	σ_r	$\Delta\sigma_{\perp}$	$\Delta\sigma_t$	$\Delta\sigma_r$	$\Delta(\sigma_t + \sigma_r)/2$
C_6H_6	122	-9	-23	+2	<i>a</i>	<i>a</i>	+44
$\text{C}_6(\text{CH}_3)_6$	104	-9	-41	-6	+17	+57	+37
$\text{C}_6(\text{C}_2\text{H}_5)_6$	100	-32	-41	-7	+4	+50	+27
$\text{C}_6(\text{C}_2\text{H}_5)_6$	107	-17	-39	0	+19	+52	+36

^a σ_t and σ_r in benzene are not known individually because of averaging over rapid C_6 rotation. ^b Note two sets of values for $\text{C}_6(\text{C}_2\text{H}_5)_6$ (see text).

as single crystals. When they are not, the resulting powder patterns still yield the principal elements (though not the eigenvectors) of the shielding tensor. A difficulty is that in many cases powder patterns arising from chemically inequivalent spins overlap and prevent analysis. (A case in point is hexaethylbenzenechromium tricarbonyl, to be discussed below, which contains seven inequivalent carbon types.) Accordingly in the present study we have employed a new procedure which accomplishes the separation and individual analysis of such overlapping powder patterns.

The principles of this method have been described previously but will be outlined briefly here for completeness. We begin by applying proton-enhanced NMR⁹ to improve the detectability of the natural-abundance ^{13}C resonance and to remove dipolar broadening by surrounding protons. At the same time the sample is rotated about the "magic axis" making an angle of 54.7° with the external field, producing averaging of the chemical shielding anisotropy and extraction of the isotropic resonance position.¹⁰ However, in the present case the rotation is made deliberately not very fast, so that the spectrum does not collapse completely to the isotropic one; instead each resonance develops a prominent set of spinning sidebands whose intensities are governed by the anisotropy of the chemical shift.¹¹ A theoretical analysis of this intensity profile permits the extraction of the individual shielding tensor elements.

Experimental Section

The NMR experiments were conducted with a double-resonance spectrometer employing a wide-bore superconducting magnet at a field strength of 3.90 T, corresponding to 166 MHz for protons and 41.8 MHz for ^{13}C . The single-coil probe incorporates a magic-angle turbine/rotor system of the Beams configuration,¹⁰ containing an active sample volume of approximately 0.3 cm^3 , into which the powdered samples were packed. Samples were typically rotated at 1–2 kHz, which is considerably less than the roughly 7 kHz frequency widths of the aromatic carbon powder patterns. The free induction decay (rotational echo train)¹¹ was sampled in some cases in the normal way and in other cases synchronously with the sample rotation, triggered by a signal from a photoelectric tachometer incorporated in a phase-locked-loop harmonic generator. Sideband envelopes arising from each resolved inequivalent species were subjected to a moment analysis¹² to extract principal shielding tensor elements. A statistical error analysis and comparison with results for test compounds obtained in other ways indicate an accuracy of the order of ± 5 ppm, which is comparable to what we achieve by direct examination of patterns in stationary samples.

The samples of $\text{ArCr}(\text{CO})_3$, were prepared by standard methods¹³ and purified by repeated vacuum sublimations.

Results and Discussion

The first feature to emerge from a magic angle spinning experiment is the isotropic chemical shift spectrum. The shifts observed (see Table I) are essentially the same in the solid state as in solution—a result consistent with many previous findings that intermolecular (solvent) effects on ^{13}C shifts are relatively slight. An interesting feature not seen in the liquid state, however, appears in the hexaethylbenzene (HEB) complex; the ring carbon resonance, as well as the methylene and methyl resonances, is split into two components of equal intensity. The

conclusion is that the sixfold symmetry of the ring is broken to C_3 , making three alternating ring positions inequivalent to the intervening ones. This result is rationalizable on the basis of an internally eclipsed conformation whereby the carbonyl groups impose a threefold symmetry on the molecule. HEB itself is known to adopt D_{3d} symmetry¹⁴ in which the ethyl groups project alternately above and below the plane of the ring. The conformational preference of the $\text{Cr}(\text{CO})_3$ group with respect to the complexed ring has been attributed to the stereoelectronic effects of the ring substituents.¹⁵ A ^{13}C study¹⁶ of alkylated arene complexes where the substituents have a gradation of steric requirements, but little electronic disparity, has shown that, in cases where the eclipsed rotamer predominates, the eclipsed ring carbons exhibit a smaller complexation shift (δ free – δ complex) than when they do not lie directly above the carbonyl groups. In the case of $(\text{HEB})\text{Cr}(\text{CO})_3$, the molecule apparently adopts a C_{3v} configuration in the solid state and the isotropic ring carbon shifts, obtained in each case by averaging the appropriate tensor elements, differ by 8 ppm. It is thus tempting to assign the ring carbons such that those with the higher field isotropic shift are bonded to the ethyl groups proximate to the $\text{Cr}(\text{CO})_3$ moiety.

In an apparently close analogue, viz., hexaethylborazine, $\text{B}_3\text{N}_3\text{Et}_6$, the free ligand has D_{3d} symmetry¹⁷ and the X-ray structure of $\text{Cr}(\text{CO})_3$ complex shows it to be eclipsed with the eclipsing ethyl groups projecting above the plane of the ring, i.e., away from the metal.¹⁸

The detection of two different methylene and methyl environments in $(\text{HEB})\text{Cr}(\text{CO})_3$ is not entirely unexpected since the use of $\text{Cr}(\text{CO})_3$ to differentiate between faces of an arene ring is the basis of a number of asymmetric syntheses.¹⁹ However, one concludes that in solution rapid intramolecular conformation exchange averages the two spectra observed in the solid state.

The principal tensor elements for the ring carbons, obtained from a moment analysis, are presented in Table I. Since the experiments were performed in powdered samples, there is no way to assign these elements to particular principal axis directions in the molecular framework. However, previous measurements on the parent uncomplexed aromatic molecules in single crystals have yielded both shielding eigenvalues and eigenvectors.¹⁴ In an isolated molecule such as benzene, the carbon site symmetry demands that the principal directions be (a) perpendicular to the plane of the ring (σ_{\perp}), (b) in the plane of the ring and radially outward from the carbon toward its attached hydrogen or other substituent (σ_r), and (c) perpendicular to that bond in the plane of the ring, i.e., "tangential" to the ring (σ_t). In uncomplexed aromatic molecules the principal shielding values decrease in the order $\sigma_{\perp} > \sigma_t > \sigma_r$. The shielding elements observed in the chromium complexes do not differ from those characteristic of the parent molecules so greatly as to prevent assignment by comparison. It is on that basis that the assignments appearing in Table I have been made. Of course one must remember that the removal of a mirror plane in the complexes allows a rotation of the eigenvectors away from directions mentioned above: in particular the tangential eigenvector remains unchanged, but the per-

pendicular and radial ones may be rotated together toward or away from the ring axis.

On the basis of these assignments and with the reservation just made, we may examine the shielding elements one by one to determine the effects of complexation by comparison with previously published anisotropic shieldings in the parent molecules. The increases in shielding are denoted by $\Delta\sigma_i$ in Table I. The results of the comparison are striking: the perpendicular element is unchanged by complexation and the tangential one only moderately. The change in liquid state chemical shifts observed in complexation is almost entirely accounted for by a very large change (>50 ppm) in the shielding when the external field is in the radial direction. The very specificity of the change means that arguments based on gross electron density must be incomplete. If an "average excitation energy" picture is to be used, it must consider specifically the energies of excited states of appropriate symmetry. It is noteworthy that the lowest energy electronic spectral band in $(C_6H_6)Cr(CO)_3$ has been calculated to be a $5e \rightarrow 6e$ transition and to be xy polarized.²⁰ One might thus naively have anticipated that the in-plane elements would be more affected upon complexation than the perpendicular element. It is interesting that in the free arenes the radial element is almost insensitive to the identity of the substituent but this suffers the predominant change on π complexation. One could view this shielding, when the external field is directed radially, as requiring greatly enhanced circulation about an axis parallel to the C-H bond, and as a corollary the marked upfield shift of the aromatic protons upon complexation can also be rationalized. Hitherto, this latter result has been attributed solely to a quenching of the aromatic ring current.²¹ A number of molecular orbital calculations on sandwich and half-sandwich compounds have used a Mulliken population analysis approach, although this has been criticized.²² Clearly a detailed picture of the electron density distribution in the arene chromium tricarbonyls would be very valuable. However, not being experts in the field, we defer to our more knowledgeable colleagues for further exegesis.

Finally, one would hope that, as more data become available, theories relating substituent parameters to isotropic shifts of fluorine or carbon nuclei in free²³ or π -complexed^{24,25} aromatic systems will be superseded by correlations with appropriate tensor elements.

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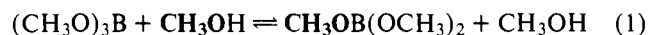
Solvent Isotope Effect on the Rate of Methoxyl Exchange between Methyl Borate and Methanol

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Abstract: NMR studies of methyl borate in methanol solution indicate fast methoxyl exchange with a large deuterium solvent isotope effect: $k_{CH_3OH}/k_{CH_3OD} = 11.0$ at 25 °C. The temperature dependence of the first-order rate constants (s^{-1}) is given by $k_{CH_3OH} = 5.7 \times 10^3 e^{-2360/RT}$ and $k_{CH_3OD} = 9.1 \times 10^3 e^{-4060/RT}$. These constants refer to a pH-independent phase of the exchange. Catalysis by lyonium and lyate ions occurs with approximate rate constants ($M^{-1} s^{-1}$) $k_{CH_3OH_2^+} = 1.4 \times 10^5$, $k_{CH_3OD_2^+} = 1.0 \times 10^5$, and $k_{CH_3O^-} = 7 \times 10^{10}$.

Alkyl transfer between borate esters and alcohols, a moderately fast reaction with secondary alkyl borates at room temperature, is too fast for conventional measurements at room temperature in the case of primary borates.¹ We have found the rate of the symmetrical exchange reaction (1) to be accessible by NMR line broadening and report rate constants and solvent isotope effects for the reaction.



Results

Reaction 1 was observed in methanol solutions² of trimethyl borate (MB) sufficiently concentrated (4.4 M) to give equal concentrations of borate and alcohol methyl groups. The 100-MHz methyl proton resonance of such a solution is a broad singlet over the temperature range -23 to $+91$ °C. When CH_3OD is used, however, the methyl signal is a doublet. At 91 °C, this doublet is approaching coalescence. Below -23 °C,