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Liquid Crystals Composed of *N*-Acylamino Acids. 1. Circular Dichroism and Selective Light Transmission in Cholesteric Liquid Crystals Composed of *N*-Acylamino Acids and Organic Solvents

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Abstract: Optically active *N*-acylamino acids formed a new type of lyotropic cholesteric liquid crystals when they were swelled and dispersed as a suspension in solvents such as benzene, chlorobenzene, chloroform, and *n*-hexane. An appropriate solvating ability to swell but not to dissolve any given *N*-acylamino acid may be a necessary condition for a solvent to form the liquid crystalline phase which appears as a suspension. These suspended liquid crystals showed some characteristics of lyotropic cholesteric liquid crystals: (1) circular dichroism (CD) bands with a single sign, (2) the liquid-crystal-induced CD (LCICD) bands due to achiral molecules added to these systems, and (3) a spherulite-like phase having an optically negative sign. These suspended liquid crystals showed the iridescent color typical of cholesteric liquid crystals. These colors were found to originate from the difference of the refractive indices of the solvents from those of suspended liquid crystals, the so-called "Christiansen effect", and not from the chiral structure in the liquid crystals.

We reported recently that the amorphous powdered *N*-lauroyl-L-glutamic acid (L-LGA),² which was soaked into aromatic solvents such as benzene or toluene, showed not only birefringence under a polarized microscope but also a positive circular dichroism (CD) band around 300–400 nm.³ An achiral dye such as azulene or anthracene dissolved in this system exhibited also a type of liquid-crystal-induced circular dichroism (LCICD) in the wavelength region of the absorption bands. From these phenomena, the L-LGA–aromatic solvent system was assumed to form a liquid crystal with the cholesteric helical structure.

The L-LGA–aromatic solvent systems, being a suspension of liquid crystals, exhibited an iridescent color like typical thermotropic cholesteric liquid crystals. This color varied reversibly with temperature change, and the color of the scattered light was complementary to the transmitted light through the system.

Robinson et al.⁴ found a cholesteric color for the poly- γ -ethyl-L-glutamate (PELG) solution in ethyl acetate, where the cholesteric pitch is comparable to the wavelength of the visible light. They demonstrated that the origin of this cholesteric color is the selective reflection of the circularly polarized light of one sense by the cholesteric pitch.⁵ Hatano et al. found recently a brilliant iridescent color and a CD band due to the selective reflection in the cholesteric structure for the PELG solution in vinyl acetate.⁶ Furthermore, they found that achiral dye molecules became optically active when they were dissolved into the liquid crystalline phase of poly(γ -benzyl L-glutamate) (PBLG) and that definite CD bands appeared in the wavelength region where absorption bands of the dyes exist.⁶

These results indicate some similarities on the optical properties between the lyotropic liquid crystals of polyglutamate solution and the *N*-acylglutamic acid–aromatic solvent systems such as (1) the appearance of an iridescent color, (2) the existence of the CD bands due to the cholesteric helical structures, and (3) the spectral profile of the LCICD bands of achiral molecules intercalated into the systems.

In this paper, we report the properties of the new liquid crystals composed of optically active *N*-acylamino acids and organic solvents comparing with the polyglutamate solutions on the ground of these similarities.

Experimental Section

Liquid crystalline phase was analyzed with a Nikon PH-10 polarized microscope. The wavelength-dependent spectrum of the transmitted light travelling through the L-LGA–benzene system was measured on a Hitachi 200 spectrophotometer using a 10-mm quartz cell. Refractive indices and optical dispersive powers⁷ of the mixed-solvent systems were measured with an Abbe-type refractometer at 21 °C. The CD measurements of the L-LGA–aromatic solvent systems were made on a JASCO J-20A spectropolarimeter, where the samples were inserted slowly into quartz cells having a 0.1–0.5-mm path length. Powdered *N*-acylamino acid and any given solvent were suspended in a cell, and the optical measurements were conducted with the sediment formed in the cell kept at 15–60 °C.

No appreciable change could be detected when the cell was rotated around the light beam,⁸ and so it was concluded that no linear dichroism contribution to the CD bands could be observed.

N-Acylglutamic acids used here are the same ones as in the preceding papers.^{9–14} Dialuminum stearate was purchased from Wako Pure Chemical Industries, Ltd., and was used without further purification. The solvents used were of spectral grade and were used

Table I. Liquid Crystal Formation in L-LGA-Solvent Systems^a

solvent	refractive index of solvent, $n_D^{20.0}$	appearance	existence of liquid crystals ^b	color of transmitted light ^a
benzene	1.5014	suspension	+	violet
toluene	1.4964	suspension	+	violet
chlorobenzene	1.5248	suspension	+	yellow
methyl iodide	1.5293	suspension	+	colorless
chloroform	1.4464	suspension	+	colorless
<i>n</i> -hexane	1.3754	suspension	+	colorless
acetone	1.3589 ^d	solution	-	colorless
ethyl alcohol	1.3624 ^e	solution	-	colorless
methyl alcohol	1.3312 ^f	solution	-	colorless
water	1.3330	gelationous	-	colorless

^a LGA (0.1 g) and solvent (2 mL) are mixed, respectively. ^b Observation of birefringence under a polarizing microscope. ^c The color was observed at room temperature. ^d 19.4 °C. ^e 18.4 °C. ^f 14.5 °C.

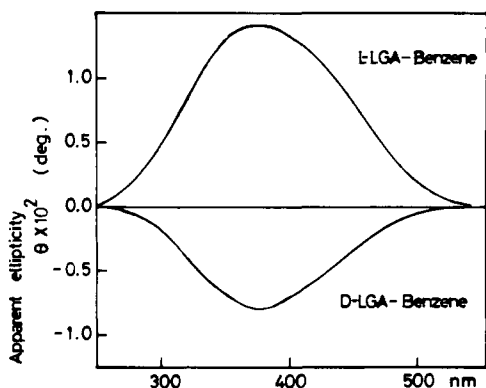


Figure 1. CD spectra of L- and D-LGA-benzene systems at 15 °C with 0.5-mm light path length.

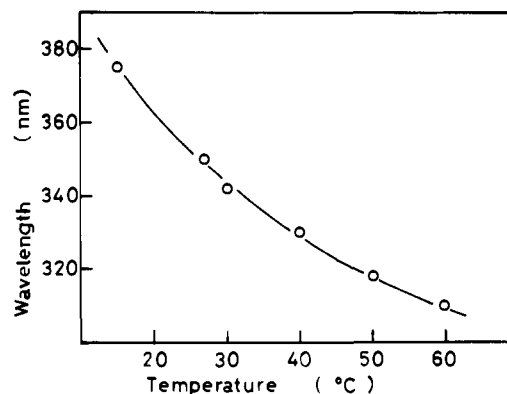


Figure 2. Temperature dependency of CD maxima in the L-LGA-benzene system; 0.5-mm light path length.

without further purification. Azulene and anthracene were purified by the method described elsewhere,¹⁵ and their purity was confirmed by thin-layer chromatography.

Results and Discussion

Formation of Liquid Crystal. Amorphous powdered L-LGA soaked in benzene, toluene, chlorobenzene, methyl iodide, or *n*-hexane behaved as a liquid crystal. In these solvents L-LGA was solvated to swell but not to be dissolved. This solvated powder of L-LGA suspended in the solvent showed birefringence due to the formation of a liquid crystalline phase under a polarized microscope (Table I). When solvents having refractive indices of ca. 1.50–1.53 were used, the systems with L-LGA exhibited a characteristic iridescent color.

On the other hand, when L-LGA was dissolved in such solvents as methanol, ethanol, or acetone, we could not observe the formation of liquid crystals.

Similar results were also obtained for other *N*-acylamino acids, e.g., *N*^α-palmitoyl-L-lysine in benzene. *N*-Lauroyl-L-valine or *N*-lauroyl-L-phenylalanine were dissolved in benzene without the formation of a liquid crystalline phase. Thus, an appropriate solvating ability to swell but not to dissolve the *N*-acylamino acid may be necessary for a given solvent to form the liquid crystalline phase which appeared as a suspension.

When the L-LGA-benzene system, which was an iridescent suspension of liquid crystal at room temperature, was heated above 80 °C, the L-LGA was completely dissolved in benzene to form an isotropic clear solution. Thereafter, by cooling to an ambient temperature, the L-LGA-benzene system became a gel showing birefringence. This gel was less colored than the original suspension, but shaking recovered the suspension with the iridescent color.

Structure of the L-LGA-Solvent Systems. The optically active LGA and benzene system showed a CD band around 300–400 nm with a positive sign for L-LGA and with a nega-

tive sign for D-LGA (Figure 1). In the racemic LGA-benzene system, no CD band could be detected. The observed CD bands should be inherent to the optically active LGA-benzene system, because both components per se have no absorption in this spectral region. Since the signs of CD bands for L-LGA and for D-LGA were opposite each other, it is concluded that the CD bands originate from the chiral configuration of LGA itself. Similar positive CD bands were obtained for suspensions of L-LGA in other solvents such as toluene, chlorobenzene, dimethyl phthalate, or chloroform (Table I). The CD maxima were shifted to the blue side with an increase in the fraction of the solvent species having the lower refractive index (Figure 3). Furthermore, similar CD bands were found for *N*-(2-ethylhexanoyl)-, *N*-myristoyl-, *N*-palmitoyl-, and *N*-stearoyl-L-glutamic acids suspended in benzene.

The maximum wavelengths of these CD bands were dependent on temperature (Figure 2). The temperature dependency of the CD maxima in the L-LGA-solvent systems were quite similar to that of thermotropic cholesteric liquid crystals reported by Ferguson.¹⁶ In both cases the CD maximum shifted to the blue side with increasing temperature.

We found another similarity for the suspended liquid crystals to the thermotropic cholesteric liquid crystals. *N*-Stearoyl-L-glutamic acid suspended in dimethyl phthalate showed a similar texture to the L-LGA-benzene system under a polarized microscope at first; however, after a long time, the *N*-stearoyl-L-glutamic acid-dimethyl phthalate system indicated the formation of a spherulite-like phase. This spherulite-like phase exhibited not only a CD band similar to that in the L-LGA-benzene system but also birefringence with an optically negative sign, which is characteristic of cholesteric liquid crystals. From these results, it was deduced that the L-LGA-benzene system is in a liquid crystalline phase, which has a nature similar to cholesteric liquid crystals.

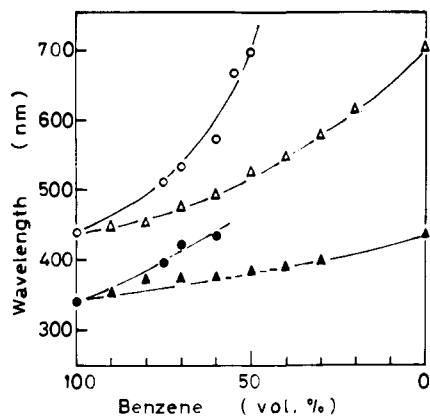


Figure 3. Relation between selective transmission or CD maxima and solvent compositions in the L-LGA-solvent systems at 22 °C with 1.0-cm light path length. Wavelengths of maximum transmission are as follows: O, benzene and chlorobenzene systems; Δ , benzene and dimethyl phthalate systems. Wavelengths of CD maxima are as follows: \bullet , benzene and chlorobenzene systems; \blacktriangle , benzene and dimethyl phthalate systems.

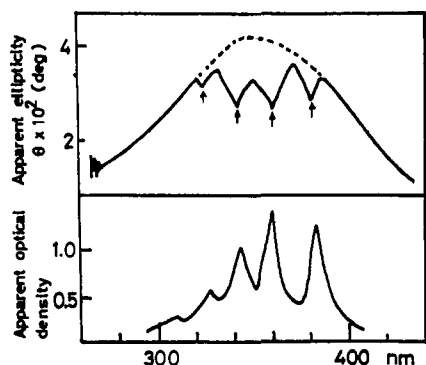


Figure 4. ICD and absorption spectra of anthracene intercalated into the L-LGA-benzene system at 24 °C, with 0.5-mm light path length, and with [anthracene] = 2×10^{-2} M. Arrows show the LCICD and the dotted line shows the CD band by the selective reflection.

In order to confirm further the twisted structure in the L-LGA-benzene system, the so-called liquid crystal induced circular dichroism (LCICD) technique¹⁷⁻²¹ was applied to the L-LGA-benzene system. LCICD was detected for achiral molecules such as azulene or anthracene, which were intercalated into the L-LGA-benzene system (Figures 4 and 5). The LCICD bands showed a single positive sign only, and the spectral profiles of the CD spectra were nearly identical with those of the absorption spectra. The LCICD bands in the D-LGA-solvent systems were opposite in sign to those in the L-LGA-solvent systems. However, the LCICD could not be observed in the racemic LGA-solvent systems.

Experimental results on the similar single-signed LCICD were reported by Saeva and Olin²² and Hatano et al.⁶ for anthracene and *N*-ethylcarbazole intercalated into lyotropic cholesteric liquid crystals of polyglutamates. But, when anthracene was dissolved in thermotropic cholesteric liquid crystals, the signs of LCICD bands were not single and were dependent on the polarization directions of the transition dipoles of anthracene.²²

The LCICD spectral results for the L-LGA-solvent systems, which were single signed as in polyglutamate solutions, support the assumption that each L-LGA-solvent system is a type of lyotropic cholesteric liquid crystal with a supramolecular helical structure. The sign of the CD band in the L-LGA-solvent systems, corresponding to the supramolecular helical sense, did not vary with solvent species or their compositions. Thus, the cholesteric helical sense in the LGA-solvent systems is determined only by the configuration (*R* or *S*) of the LGA

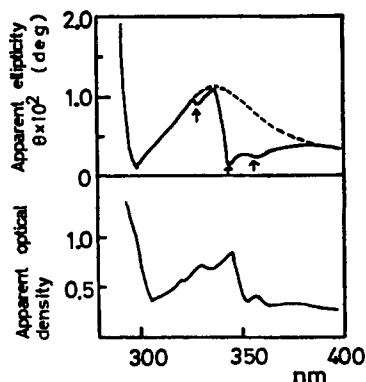


Figure 5. ICD and absorption spectra of azulene intercalated into the L-LGA-benzene system at 24 °C, with 0.2-mm light path length, and with [azulene] = 1×10^{-2} M. Arrows show the LCICD and the dotted line shows the CD band due to the selective reflection.

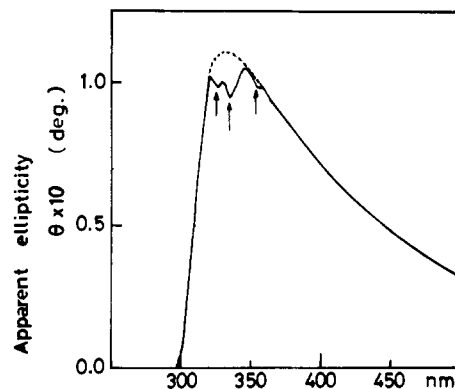


Figure 6. LCICD spectrum of azulene intercalated into the *N* ^{α} -palmitoyl-L-lysine and benzene system at 40 °C, with 0.1-mm light path length, and with [azulene] = 2×10^{-2} M. Arrows show the LCICD and the dotted line shows the CD band due to the selective reflection.

molecule itself, as in the case of thermotropic cholesteric liquid crystals. This is in contrast with the fact that, in the polyglutamate cholesteric liquid crystals, the cholesteric helical sense is determined not only by the steric isomerism of polyglutamate in the solution but also by the mode of the interaction of polyglutamate with the solvent. The chiral structure in the cholesteric liquid crystals of the optically active LGA-benzene system seems to be an intermediate one between thermotropic cholesteric liquid crystals and polyglutamate lyotropic cholesteric liquid crystals. Generally, it is reasonably considered that thermotropic cholesteric liquid crystals are more rigid in the helical structure than in lyotropic cholesteric liquid crystals. Therefore, the observed results suggest that the helical structure of L- or D-LGA-solvent systems are more rigid than that of polyglutamate liquid crystals.

Similar CD and LCICD results were obtained also for the suspended *N* ^{α} -palmitoyl-L-lysine in benzene (Figure 6). *N*-Lauroyl-L-valine, however, which is soluble in benzene, exhibits no CD and LCICD due to the cholesteric chiral structure.²³

Origin of Iridescent Color. The typical spectral profiles of the transmitted light through the LGA-benzene and the LGA-toluene systems are shown in Figure 7. The wavelengths of the maximum transmission of the LGA-solvent systems varied with changes of temperature, solvent compositions, and the length of the acyl groups. For example, the iridescent color of the transmitted light through the LGA-benzene system varied in the order of red, yellow, green, blue, and violet, when the temperature was raised from -5 °C to room temperature. And the wavelength of the maximum transmission shifted to red with an increase in the fraction of the solvent species having

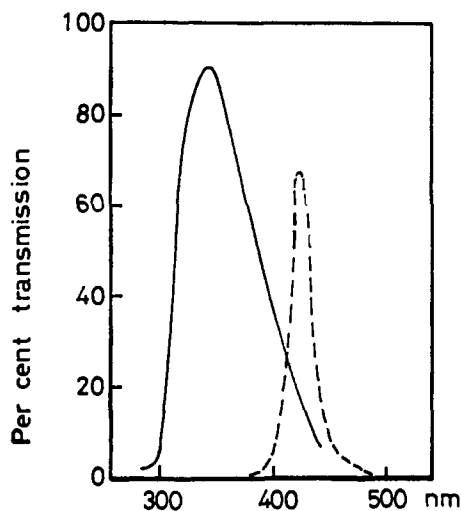


Figure 7. Selective transmission of L-LGA and benzene or toluene system: ---, benzene; —, toluene. Amorphous powdered L-LGA was suspended in a cell and the measurement was conducted with the sediment formed in the cell; at 22 °C, 10-mm light path length.

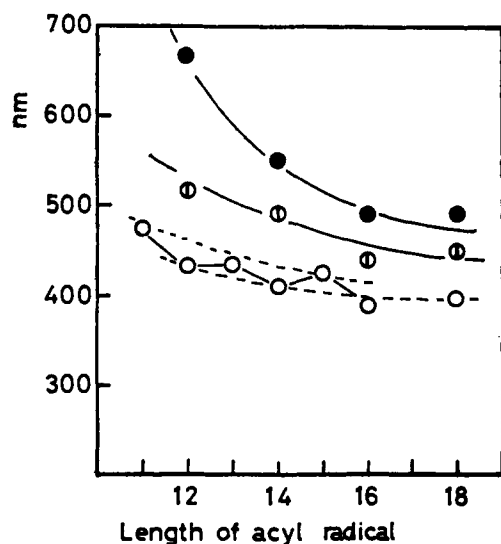


Figure 8. Relation between the selective transmission and the lengths of the acyl group at 22 °C and with 10-mm light path length: ○, benzene; ◐, benzene and chlorobenzene, 7/3 in volume ratio; ●, benzene and chlorobenzene, 5.5/4.5 in volume ratio.

higher refractive indices in the mixed-solvent systems (Figure 3). Figure 8 shows a relation between the selective transmission and the lengths of the acyl groups in the *N*-acyl-L-glutamic acids. This figure indicates that the wavelength of the maximum transmission shifted to the blue side with an increase in the length of the acyl groups. On the other hand, the maximum wavelengths of the observed CD bands in the suspended liquid crystals were different from those of the maximum transmission, and the variation of CD maxima with change of solvent species or temperature was smaller than that of the transmission maxima (Figures 2 and 3). Thus CD maxima variation was not consistent with the maximum transmission variation. Similar iridescent color was observed for the suspension of DL-LGA in benzene. From these experimental results, it is concluded that the iridescent color and the observed CD band result from different origins.

Optical dispersion curves for the benzene–chlorobenzene and benzene–dimethyl phthalate systems with various compositions are shown in Figures 9 and 10 as dotted lines;⁷ the wavelengths of the selective transmission of the light travelling through the LGA systems with the corresponding solvent

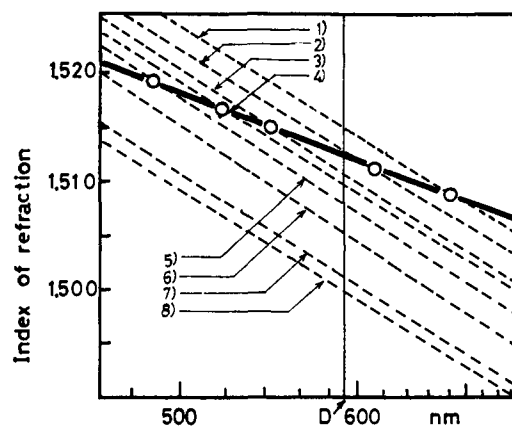


Figure 9. Dispersion of indices in mixtures of benzene and dimethyl phthalate and in L-LGA liquid crystals at 21 °C. Dotted lines show the optical dispersion of the solvents. Solvent compositions for benzene/dimethyl phthalate (in volume ratio) are (1) 0/10, (2) 2/8, (3) 4/6, (4) 5/5, (5) 6/4, (6) 8/2, (7) 9/1, (8) 10/0. Open circles show the wavelengths of selective transmission of the LGA–solvent systems. D means the Na-D-line wavelength.

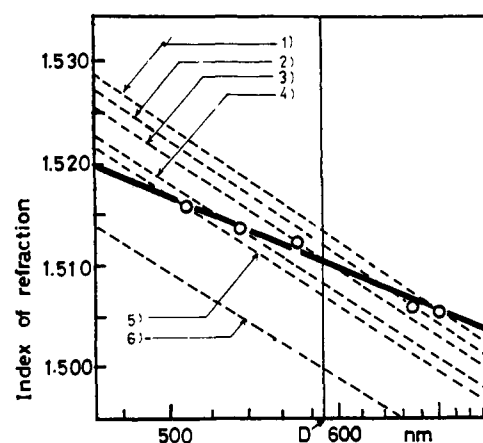


Figure 10. Dispersion of indices in mixture of benzene and chlorobenzene and in L-LGA liquid crystals at 21 °C. Dotted lines show the optical dispersion of solvent. Solvent compositions for benzene/chlorobenzene (in volume ratio) are (1) 5/5, (2) 5.5/4.5, (3) 6/4, (4) 7/3, (5) 7.5/2.5, (6) 10/0. Open circles show the wavelengths of selective transmission of the LGA–solvent systems.

mixtures are shown as open circles over the dotted lines. Each group of these open-circle points give a nearly straight line, as shown in Figures 9 and 10. If we assume that the maximum transmission can be expected when the two phases, i.e., solvent and liquid crystalline phases, have the same value of refractive index, the line connected with the open-circle points will indicate the optical dispersion of the corresponding LGA–solvent system. This phenomenon has been called the “Christiansen effect”.²⁴

Consequently, the iridescent color observed for the LGA–solvent systems results from the difference of the optical dispersion between the solvent and the suspended liquid crystalline phase, the so-called “Christiansen effect”, and does not originate from the selective reflection due to the twisted structure in the liquid crystals. The LGA–solvent systems can be grouped into an intermediate group between chromatic suspensions (solid–liquid systems)^{24,25} and chromatic emulsions (liquid–liquid systems).^{26,27}

Chromatic suspension of liquid crystals similar to the LGA–solvent systems could be obtained, when dialuminum stearate was suspended in benzene or the solvent mixture of methyl iodide and chloroform. Of course, the dialuminum

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