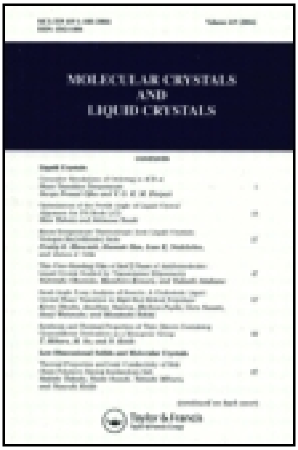

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NMR Investigations on (Benzene) Chromium Tricarbonyl Oriented in a Nematic Phase

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NMR Investigations on (Benzene) Chromium Tricarbonyl Oriented in a Nematic Phase

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Abstract—The NMR spectrum of (benzene) chromium tricarbonyl oriented in the nematic phase of a mixture of 50% 4-methoxybenzylidene 4-amino-α-methyl cinnamic acid-*n*-propyl ester and 50% anisole-*p*-azophenyl-*n*-capronate has been investigated.

It has been shown that the complex has a structure in which the $Cr(CO)_3$ group is bonded to the delocalised π-electron cloud such that the effective symmetry is 6-fold. Ratios of the interproton distances are determined.

Contrary to other aromatics, the molecule is shown to orient preferentially with the benzene plane perpendicular to the direction of the magnetic field, under the assumption that the indirect *H–H* couplings in the complex have the same sign as in benzene.

The proton chemical shift anisotropy in the compound is determined.

1. Introduction

NMR spectra of small organic molecules dissolved in the nematic phase of liquid crystals have been extensively investigated(1) in order to obtain information about the molecular structure. However, the application of this method to inorganic complexes has so far been restricted to a single compound.(2) In this case, it was not possible to obtain the absolute sign of the molecular orientation and hence of the chemical shift anisotropy. Investigations on (benzene) chromium tricarbonyl were undertaken in order to get a deeper insight into the orientation and the chemical shift anisotropy of such compounds as well as their molecular geometry. The results are presented in this communication.

2. Experimental

The (benzene) chromium tricarbonyl complex was commercially available. An 11 mole percent solution of the complex was made in a mixture of 50% 4-methoxybenzylidene 4-amino-α-methyl cinnamic acid-*n*-propyl ester (I) and 50% anisole-*p*-azophenyl-*n*-capronate (II). The proton spectrum was recorded at room temperature (28 °C) on a Varian HR-spectrometer operated at 56.445 MHz. Several traces were taken and the statistical error in the measurement of line positions was ± 1.0 Hz. The average line width was 17 Hz.

Tetramethylsilane was used as an internal standard for the measurement of the chemical shift anisotropy.

3. Results and Discussion

3.1. Analysis of the Spectrum

The spectrum of the compound is shown in Figure 1. The symmetry of the spectrum with respect to the centre indicates that there is no chemical shift between the various protons.

The chromium tricarbonyl group may be coordinated (a) to a double bond (C_2-symmetry) or (b) to the overall *pi* electron cloud of the benzene ring (effective C_6-symmetry).(3,4) A structure in which the benzene ring is rotating rapidly will also have an effective C_6-symmetry.

The analysis of the spectrum was carried out with the help of the LAOCOONOR programme(5) on a CDC-3600 computer using C_2 as well as C_6-symmetries of the molecule. It was found that it is not possible to analyse the spectrum iteratively unless information about the 6-fold symmetry is included. In order to find out the extent to which it would have been possible to detect C_2-symmetry, a forward analysis of the spectrum was carried out with the help of part I of the LAOCOONOR programme. It was concluded that the observed spectrum corresponds to the 6-fold symmetry of the molecule within limits of experimental accuracy and resolution. Hence, the molecule has a structure in which either the $Cr(CO)_3$ group is coordinated to the overall *pi* electron cloud of the benzene ring or the " rotating structure " as discussed earlier.

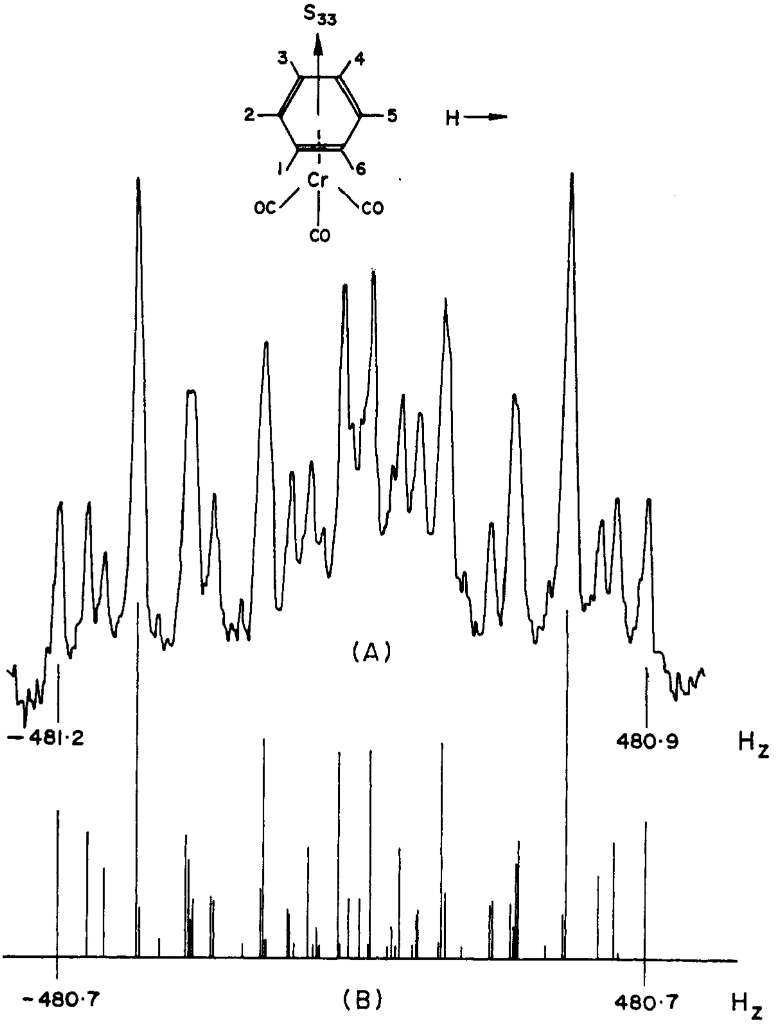

Figure 1. NMR spectrum of (benzene) chromium tricarbonyl oriented in the nematic phase of 50% (I) + 50% (II). Concentration of the solute = 11 mole %. Temperature = 28 °C. Spectrometer frequency = 56.445 MHz.

The analysis of the spectrum was performed using known values of the indirect couplings for benzene.(6) The corresponding couplings in the complex may be slightly smaller but are not known. Iterative calculations were carried out with both possible sign combinations of the direct couplings relative to the indirect ones. A root mean square error of 2.5 Hz was obtained between the observed and the calculated line positions with opposite signs of the direct (D) and the indirect (J) coupling and 0.7 Hz with similar signs. This indicates that the signs are the same in this case. Expressions for transition frequencies and intensities in terms of the parameters derived(7) for a six-fold symmetry case were also used to verify this result. Since the major H–H indirect couplings in benzenes are known to be of positive sign, the direct couplings must also be positive. Values of the parameters derived are reproduced in Table 1. Errors of the various parameters (Table 1) were obtained as described earlier.(8)

TABLE 1 Results of spectral analysis for (benzene) chromium tricarbonyl oriented in the nematic phase of a mixture of 50% (I) and 50% (II). The numbering of the protons is given in Fig. 1.

Parameter	Value		
$D_{ortho}(D_{12} = D_{23} = D_{34} = D_{45} = D_{56} = D_{16})$	127.6	±0.2	Hz
$D_{meta}(D_{13} = D_{35} = D_{24} = D_{46} = D_{15} = D_{26})$	24.7	±0.1	Hz
$D_{para}(D_{14} = D_{25} = D_{36})$	15.9	±0.1	Hz
S_{33}	0.0325	±0.0002	
r_{13}/r_{12}	1.729	±0.003	
r_{14}/r_{13}	2.002	±0.003	
$\Delta\sigma$	−14.9	±2.0	ppm.

3.2. GEOMETRY OF THE PROTON SKELETON

The proton skeleton of (benzene) chromium tricarbonyl has an effective 6-fold symmetry. The ratios of the direct couplings D_{meta}/D_{ortho} and D_{para}/D_{ortho} in this case are 0.1936 ± 0.0010 and 0.1246 ± 0.0010 respectively. They agree with the corresponding values (0.1929 and 0.1247)(7) for benzene within experimental accuracy (the values for a regular hexagonal geometry are 0.1925 and 0.1250). The two distance-ratios derived from the ratios of the dipolar couplings are included in Table 1.

3.3 MOLECULAR ORIENTATION

It has been pointed out in section 3.1 that the sign of the direct couplings is positive. This indicates that the molecule orients preferentially with its benzene plane perpendicular to the direction of the magnetic field. This is in contrast to benzene and other aromatics, which under similar conditions orient with their planes along the direction of the magnetic field.(1)

The only independent orientation parameter S_{33} along the symmetry axis can be obtained if one of the *H–H* distances in the molecule is known. The value reported in Table 1 has been obtained with $r_{H-H}^{\text{ortho}} = 2.481 \pm 0.005$Å.(9)

3.4. CHEMICAL SHIFT ANISOTROPY

The proton chemical shift anisotropy $\Delta\sigma (= \sigma_{\parallel} - \sigma_{\perp}$ where $\sigma_{\parallel}$ is measured along the symmetry axis) in this case can be determined by a measurement of the shift ($\Delta\delta$) between the centre of the spectrum in the nematic and isotropic phases with the help of Eq. (1).(1)

$$\Delta\delta = \tfrac{2}{3} S_{33} \cdot \Delta\sigma \qquad (1)$$

The centre of the spectrum in the nematic phase is 18.2 ± 2.4 Hz downfield from its position in the isotropic medium. The chemical shift anisotropy thus obtained is included in Table 1. It differs significantly from the value for benzene(7) but is of the magnitude observed for (cyclobutadiene) iron tricarbonyl.(2) This indicates that a contribution to the shift anisotropy from the chromium tricarbonyl group is quite important.

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