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NMR Spectra of π-Cyclopentadienyl Manganese Tricarbonyl in Nematic and Isotropic Solvents†

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^{1}H—NMR spectra including ^{13}C—H satellites in the natural abundance of ^{13}C in π-cyclopentadienyl manganese tricarbonyl dissolved in a nematic solvent are reported. In addition, the ^{13}C—NMR spectrum of the compound in the natural abundance of ^{13}C, in an isotropic medium is studied. Values of the direct and the indirect HH and ^{13}CH couplings are given. Information on the molecular geometry of the ring skeleton thus obtained is discussed. Contributions of the molecular vibrations to the observed dipolar couplings are estimated. The direct dipolar coupling between the carbonyl ^{13}C and the ring protons are used to derive the distance between the planes containing these carbons and the cyclopentadienyl ring.

I INTRODUCTION

We have earlier reported[1] PMR investigations on π-cyclopentadienyl manganese tricarbonyl (Figure 1) oriented in a nematic solvent. The spectrum of the molecule including the ^{13}C-satellites in the natural abundance was later studied[2] but (i) the satellites arising from the direct dipolar interactions of the ^{13}C nuclei of the carbonyl groups and the ring protons were not observed and hence no structural information on this part of the molecule could be derived and (ii) the indirect ^{13}CH couplings were assumed zero except for the directly bonded ^{13}C and ^{1}H. In recent studies,[3] the direct

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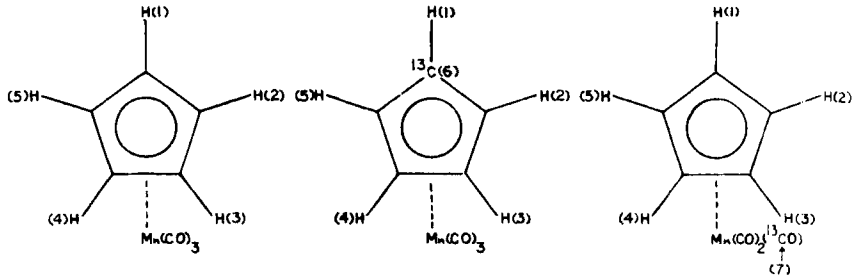

FIGURE 1 The structure of π-cyclopentadienyl manganese tricarbonyl and numbering of the nuclei.

dipolar coupling between ^{13}C nuclei of the carbonyl group and the ring protons have been observed in the ^{13}C-enriched compound.

In our present studies, we could observe all the ^{13}CH couplings in the natural abundance of ^{13}C using "time averaging." All the indirect ^{13}CH couplings have been determined from the ^{13}C—NMR spectrum in an isotropic solution. Such studies allow a more reliable determination of molecular geometry. "Vibrational corrections" to the direct dipolar couplings between the ring nuclei have also been considered and the results are discussed.

II EXPERIMENTAL

A 10 mole percent solution of commercially available π-cyclopentadienyl manganese tricarbonyl in the nematic phase of a mixture of 80% (by weight) 4-ethoxybenzylidene-4-*n*-butylaniline (a) and 20% (by weight) O-carbobutoxy-4-oxybenzoic acid ethoxyphenyl ester (b) was studied with a Varian XL-100 spectrometer†. The solution was stored horizontally in the NMR sample tube for a few days before the spectra were recorded at 30°C. The average line-width was 5 Hz. The spectrum due to the $^{12}C_5H_5Mn(^{12}CO)_3$ species is shown in Figure 2. The central line (in Figure 2) was used as the "lock-signal." The sweep time and sweep width were 2500s and 2500 Hz respectively.

Spectra due to the molecules containing a ^{13}C nucleus (Figure 1) were obtained on either side of the "lock-signal" by accumulating about 800 spectra on a Varian C-1024 computer. A spectrum on the high frequency side of the "lock-signal" is shown in Figure 3.

† Funds for the equipment were obtained partly from the National Science Foundation under Grant No. GP-10481.

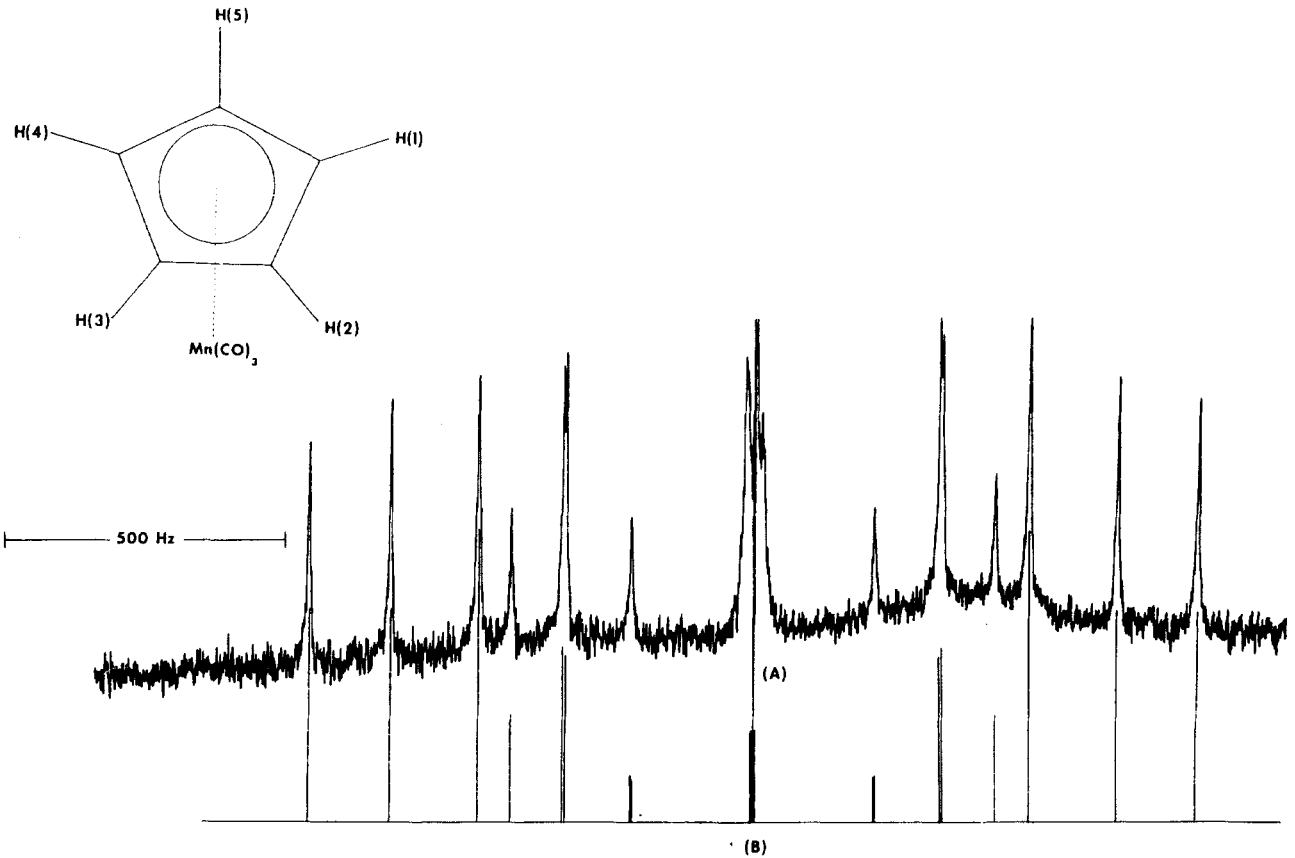

FIGURE 2 (A) Observed, and (B) Calculated PMR spectra of $^{12}C_5H_5Mn(^{12}CO)_3$ oriented in the nematic phase of 80% (a) and 20% (b). Solute concentration: 10 mole percent. Temperature: 30°C. Spectrometer frequency: 100 MHz.

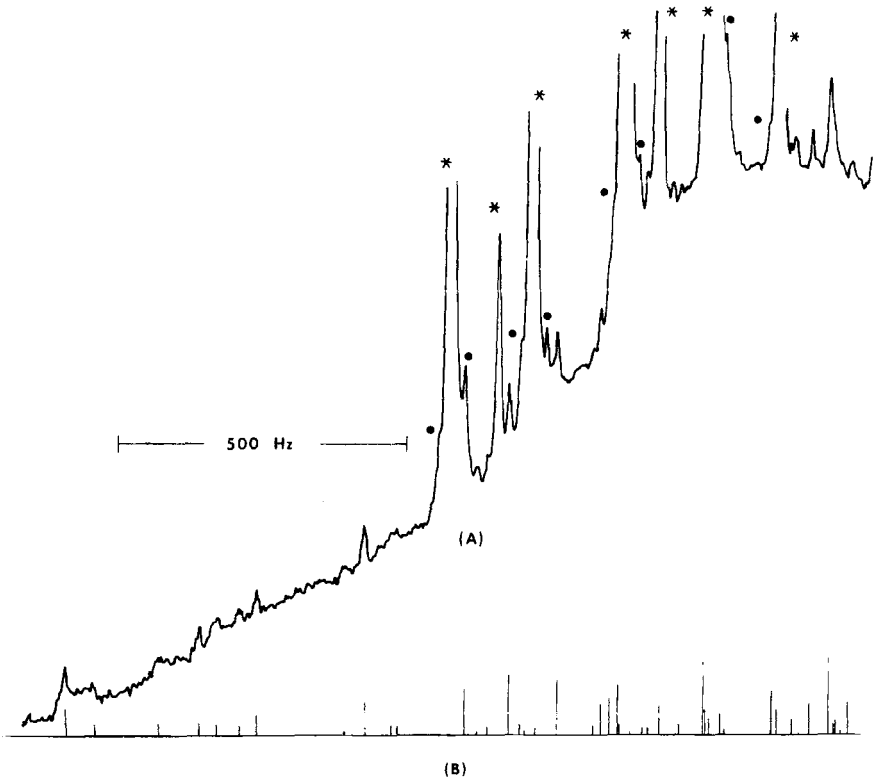

FIGURE 3 High frequency part of 800 accumulations of the PMR spectra of cyclopentadienyl manganese tricarbonyl. (A) Observed spectra due to (i) $^{12}C_5H_5Mn(^{12}CO)_3$ species for which the lines are marked with (*), (ii) species containing one ^{13}C in the carbonyl group for which the lines are marked with (•), and (iii) molecules containing a ^{13}C in the ring which constitute the remaining lines. (B) Calculated spectrum due to the molecules containing a ^{13}C in the ring. Experimental conditions are the same as given in Figure 2.

The ^{13}C—NMR spectra of the compound dissolved in acetone-d_6 were recorded with "deuterium-lock" of the solvent and with the help of a Varian C-1024 computer. The average width of the ^{13}C-lines was around 0.3 Hz. The operating frequency was 25 MHz.

III RESULTS AND DISCUSSION

A Analysis of the spectra

The indirect ^{13}CH *couplings* The proton NMR spectrum in the isotropic medium provides conveniently, only $J_{^{13}CH}$ between ^{13}C and the ^{1}H-directly bonded to it since the lines arising from the interactions with the non-

directly bonded protons are masked by the intense central line due to the species containing ^{12}C nuclei. Values of all the ^{13}CH indirect couplings can, however, be determined from the ^{13}C—NMR spectra. They are given in Table I together with the ^{13}C-chemical shifts. The value (179.9 ± 0.1 Hz) of $J_{^{13}CH}$ between ^{13}C and the directly bonded proton was also confirmed from the ^{1}H-spectrum in the isotropic medium. $J_{^{13}CH}$ is known to be positive. Signs of the other ^{13}CH indirect couplings (J_{26} and J_{36}) are also positive as will be shown.

TABLE I

Value of the indirect ^{13}CH couplings and the ^{13}C-chemical shifts in π-cyclopentadienyl manganese tricarbonyl dissolved in acetone-d_6.

Parameter	Value
$J_{^{13}CH}(J_{16})^b$	179.9 ± 0.1 Hz
$J_{^{13}C-C-H}(J_{26})^b$	6.8 ± 0.5 Hz
$J_{^{13}C-C-C-H}(J_{36})^b$	6.8 ± 0.5 Hz
$J_{(^{13}C=O)H}(J_{17})^b$	0.0 Hz
$\nu_{^{13}C}$ (for ring carbons)	−50.7 ppm[a]
$\nu_{^{13}C}$ (for carbonyl carbons	−180.5 ppm[a]

[a] Relative to $^{13}CD_3$ of the solvent.
[b] Numbering refers to Figure 1.

Analysis of the spectra in the nematic phase Spectra in the nematic phase (Figures 2 and 3) were analyzed iteratively with the help of the LAOCOONOR program[4] on a CDC-3600 computer. Errors of the parameters were derived as reported in the literature.[4]

The spectrum due to ^{12}C-species The direct as well as the indirect HH couplings could be derived from the analysis of the spectrum due to the ^{12}C-species (Figure 2). They are given in Table II. The r.m.s. error between the observed and the calculated line positions was 0.5 Hz with no line deviating by more than 1 Hz from its experimental position. D_{HH} and J_{HH} were all found to have the same sign as also found earlier.[1-3]

Spectrum due to species containing a ^{13}C-nucleus in the ring In this case, the spectra in the nematic phase are influenced by the sum $(J_{^{13}CH} + 2D_{^{13}CH})$ of the indirect couplings and twice the corresponding direct couplings. Therefore, in order to obtain $D_{^{13}CH}$, $J_{^{13}CH}$ values reported in Table I were introduced into the analysis and were not iterated upon. J_{HH} values were taken to be the same as given in Table II. In case of a noticeable isotopic

TABLE II

HH couplings and the ^{13}CH direct couplings obtained for π-cyclopentadienyl manganese tricarbonyl dissolved in (a). Numbering of nuclei refers to Figure 1.

Parameter	Value (Hz)
$D_{12} = D_{23} = D_{34} = D_{45} = D_{15}$	211.58 ± 0.4
$D_{13} = D_{14} = D_{35} = D_{24} = D_{25}$	51.25 ± 0.5
D_{16}	807.0 ± 1.0
$D_{26} = D_{56}$	94.8 ± 1.0
$D_{36} = D_{46}$	28.3 ± 1.0
D_{17}	−22.5 ± 0.5
$J_{12} = J_{23} = J_{34} = J_{45} = J_{15}$	3.4 ± 0.4
$J_{13} = J_{14} = J_{35} = J_{24} = J_{25}$	1.2 ± 0.3

effect on the geometry or orientation, the symmetry of the proton part of the effective Hamiltonian is reduced from D_5 to C_{2v}. For testing this point, an iterative analysis of the spectrum was carried out using $D_{12} = D_{15}$, $D_{13} = D_{14}$, $D_{23} = D_{45}$, $D_{24} = D_{35}$, $D_{26} = D_{56}$, $D_{36} = D_{46}$. Chemical shifts between the various protons were assumed zero. It was found that the values of the HH direct couplings thus obtained do not differ from those of the ^{12}C-species by more than the errors given in Table II. The results thus confirm the 5-fold symmetry of the ring.

Spectrum due to species containing a ^{13}C-nucleus in the carbonyl group The spectrum due to such species consists of doublets (Figure 3, lines marked with •) centered on the lines of the ^{12}C-species. The doublet splittings are equal to $|J_{17} + 2D_{17}|$, where D_{17} is the direct dipolar coupling between the ^{17}C of the carbonyl group and the protons and J_{17} is the corresponding indirect coupling. Since the indirect coupling J_{17} was found to be zero, the doublet separation provides $|D_{17}|$. The value is included in Table II.

B Geometry and the influence of molecular vibrations

The ring skeleton For a 5-fold symmetry of the proton skeleton $D_{13}/D_{12} = (r_{12}/r_{13})$.[3] A value of 1.604 ± 0.006 for (r_{13}/r_{12}) is thus obtained. This deviates slightly from the value (1.618) for a regular pentagon. Deviations of similar magnitude have been reported earlier also[1,3] for this molecule. It is not clear how they really arise. They have been attributed to non-rigidity of the cyclopentadienyl ring.[3,5] In an attempt to explain these deviations, we have tried to introduce a bend about a CC diagonal and averaged over five equivalent conformations so as to maintain an effective C_5 symmetry.

However, a bend of about 18° (with reasonable values of the CH and the CC bond lengths) is needed to explain the results. The deviations cannot be readily attributed to the neglect of the influence of molecular vibrations either, as shown in the following discussion.

If we assume a regular pentagonal geometry for the proton skeleton, the "best-fit" values for the two coupling constants are $D_{12} = 212.63$ Hz and $D_{13} = 50.20$ Hz. In order to study the problem further, we use only these values of D_{12} and D_{13}. Our following results are based on the assumption of the regular pentagonal geometry of the proton and the carbon skeletons.

The problem of the influence of molecular vibrations on the structural parameters derived from NMR studies in nematic solvents has been a subject of considerable interest[6-13] particularly for the direct C—H bonds. Since the estimation of the anharmonic contributions is in general not practicable, the problem has been discussed in terms of an "average structure" (r_α-structure) which can be derived using only the harmonic corrections, as suggested by Lucas.[6-8] We assume that the carbon ring can be considered as rigid and that the protons vibrate independently. For a system with a high symmetry like the cyclopentadienyl moiety, the vibrational effect on the dipolar coupling (D_{ij}) under these assumptions is given by

$$D_{ij} = -\frac{h\gamma_i\gamma_j}{4\pi^2}\frac{S_{11}}{(\bar{r}_{ij})^3}\left(\frac{6\langle\Delta x^2\rangle}{(\bar{r}_{ij})^2} - \frac{3}{2}\frac{\langle\Delta y^2\rangle}{(\bar{r}_{ij})^2} - \frac{9}{2}\frac{\langle\Delta z^2\rangle}{(\bar{r}_{ij})^2}\right)$$

where $\bar{r}_{ij}$ is the distance between the average nuclear positions. The $\langle\Delta x_{ij}^2\rangle$ etc. are the mean square vibrational amplitudes in a Cartesian coordinate system for which the x-axis is the internuclear axis and the z-axis is perpendicular to the ring. For a C—H bond Δx means stretching, Δy in-plane bending and Δz out-of-plane bending. S_{11} is the order parameter in the ring plane and all other symbols have their usual meaning. Using the C—H stretching, in-plane and out-of-plane bending frequencies as 3100 cm^{-1}, 1000 cm^{-1} and 800 cm^{-1} respectively,[15] the above equation allows one to calculate the relative vibrational corrections $[\Delta D_{ij}/D_{ij(\text{exp})}]$. They are given in Table III together with the average dipolar couplings $D_{ij}^{(\alpha)} = D_{ij(\text{exp})} - \Delta D_{ij}$.

The table shows that the vibrational corrections are largest for directly bonded ^{13}C—H nuclei (7.2%). This is in agreement with the results obtained for several other compounds.[10,12] All other relative corrections are in the vicinity of 1%. The relative corrections for D_{12} and D_{13} are about the same (less than 1% in each case) and hence the inclusion of the influence of molecular vibrations does not change the deviation of the calculated ratio r_{13}/r_{12} from the regular pentagon value. However, the errors introduced by the simplified model for the vibrations are probably of the same order of magnitude as these corrections. They are usually not of much importance for the calculation of internuclear distances.

TABLE III

$\Delta D_{ij}/D_{ij(\text{exp})}$ and the vibrationally corrected average D-values for the ring nuclei in π-cyclopentadienyl manganese tricarbonyl oriented in the nematic phase. Numbering of nuclei refers to Figure 1.

ij	$\frac{\Delta D_{ij}}{D_{ij(\text{exp})}}$	D_{ij} (average Hz)
12	-0.008_3	214.47
13	-0.008_7	50.63
16	-0.072	865.15
26	-0.013	96.03
36	-0.007_5	28.50

We have derived the C—C bond length and the order parameter in two different ways, namely: (1) by neglecting the influence of molecular vibrations and taking $r_{CH} = 1.105$ Å, and (2) by taking into consideration only the harmonic corrections with $\bar{r}_{CH} = 1.105$ Å and thus deriving the "average molecular structure" as described above. Both cases are discussed below:

The C—C bond distance and the only independent order parameter in the ring plane were determined from the 5 different internuclear dipolar couplings, with the help of the modified SHAPE[14] program adapted to an IBM 360/44 computer. They are included in Table IV for both cases together with the "best-fit" values of the direct couplings thus determined. It is seen from Table IV that the value of the C—C bond length obtained without applying the vibrational corrections 1.43 Å is in agreement with the x-ray value of 1.42 ± 0.03 Å.[17] The more reliable vibrationally corrected value is 1.48 Å. It is in agreement with the value estimated for π-methylcyclopentadienyl manganese tricarbonyl complex[16] from PMR studies. In view of the large error of the x-ray data and the assumptions involved in our calculations, the deviations may not be significant. The r.m.s. error between the "best-fit" and experimental D-values is less when the vibrational corrections are neglected than when they are applied. It indicates that the corrected dipolar couplings still deviate by about 1% from the $D_{ij}^{(\alpha)}$ values.

Calculations were also carried out by obtaining D_{26} and D_{36} under the assumptions of negative signs of J_{26} and J_{36}. These, however, give a C—C bond length which is too small (1.366 Å and 1.281 Å respectively). Therefore, the signs of J_{26} and J_{36} are positive as given in Table I.

The carbonyl carbons The coupling constant D_{17} can be used to provide the distance (Y) between the planes of the carbonyl carbons and the ring,

TABLE IV

The C—C bond distance, the order parameter and the "best-fit," D-values for π-cyclopentadienyl manganese tricarbonyl oriented in a nematic phase. Number of nuclei refers to Figure 1.

Parameter	Value	
	Without applying "vibrational corrections"	With application of vibrational corrections as described in the text
D_{12}	213.07 Hz (212.63)	215.35 Hz (214.47)
D_{13}	50.30 Hz (50.20)	50.84 Hz (50.63)
D_{16}	807.03 Hz (807.04)	865.12 Hz (865.15)
D_{26}	93.89 Hz (94.77)	94.29 Hz (96.03)
D_{36}	28.15 Hz (28.30)	27.96 Hz (28.50)
r.m.s. error	0.45 Hz	0.91 Hz
S_{11}	−0.0361	−0.0387
r_{CC}	1.43 Å	1.48 Å

Values within parentheses are observed values (Tables II and III). S_{11} is the order parameter in the ring plane.

using equations reported earlier[16] for π-methyl cyclopentadienyl manganese tricarbonyl. In this case, two quantities, namely (Y) and the distance between the carbons of the carbonyl group have to be determined and only one coupling constant (D_{17}) for these carbons is known. We, therefore, assumed the x-ray value[17] of 2.590 Å for the CC distance between the carbonyl carbons and computed (Y). It is found to be 2.78 ± 0.04 Å which agrees with the values determined from x-ray[17] and the recent NMR studies.[3] It also supports the negative sign for D_{17}.

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