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The Effect of Ring Substitution on the Manganese-55 Nuclear Quadrupole Resonance Spectra in π-Cyclopentadienylmanganese Tricarbonyl

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The room-temperature ^{55}Mn nuclear quadrupole resonance spectra in fourteen different monosubstituted and one disubstituted cyclopentadienylmanganese tricarbonyl compounds have been recorded. An attempt is made to correlate the manganese resonance frequencies with ir, nmr, and uv data which measure variations in the ring π-electron density. It is evident that the manganese atom monitors the variations in π-electron density about as well as the other techniques do. The effect of virtually all the substituents on the nqr frequencies is interpretable in terms of elementary arguments. An attempt has been made to complement the previous nqr data in these systems reported by Nesmeyanov, *et al.*

Introduction

The question of the extent to which the π system of an aromatic compound is affected by monosubstitution has been the subject of extensive well-known research. Hammett[2] used linear free energy relationships and developed σ functions for various groups. Taft[3] used ^{19}F nmr in substituted fluorobenzene compounds to study the substituent effects. Doub and Vandenbelt[4] studied the effect of monosubstitution on the primary absorption uv band in benzene.

Manganese-55 nqr spectroscopy can be used to study the electronic effects of substitution in the cyclopentadienyl ring in cyclopentadienylmanganese tricarbonyl. This parent compound (Figure 1) is particularly attractive because the manganese atom interacts with the cyclopentadienyl ring through its π system and thus can be used to reflect the extent of π-density variation as the substituent is changed. It would seem worthwhile to compare the nqr data with other techniques which can be used to correlate variations in π-electron density. Nmr studies of the ring protons in most of these compounds have been published[5] and the extent of their shielding or deshielding with respect to C_5H_5-$Mn(CO)_3$ is related to changes in ring currents. In addition, some correlations can be made with ir and uv data taken from the benzene systems.

Nesmeyanov, *et al.*,[6] have recorded ^{55}Mn signals in this particular class of compounds at 77°K. In nearly all of the compounds presented here, the R substituent is different from those previously recorded by those workers. We have, however, recorded at room temperature several signals reported at 77°K by Nesmeyanov, *et al.*, in cases where we felt these data would complement our own. We have also attempted to extend the type of substituent beyond those previously reported. For example, in previous work,[6] carbon, iodine, and highly oxidized sulfur were bonded to the ring. In the present study, nitrogen, mercury, and reduced sulfur were investigated as well. Several trends in the frequencies are evident, and it is possible to propose sources of the direction of the shifts.

Experimental Section

Compounds.—The cyclopentadienylmanganese tricarbonyl was obtained from the Ethyl Corp. Preparation of the derivatives of $C_5H_5Mn(CO)_3$ have been described.[5] The sodium and ammonium salts of carboxycyclopentadienylmanganese tricarbonyl were prepared by adding the appropriate base (0.5 *N*) to a suspension of the acid in water until the pH was slightly basic and all the acid had dissolved. Water was removed under vacuum until crystals of the carboxylate salt formed. These were filtered and dried over P_2O_5.

Nqr Spectra.—The nqr data reported in Table I were obtained with a Wilks Scientific NQR-1A spectrometer.[7] Frequency measurements were carried out with a Hewlett-Packard 5245L electronic counter. Since the resonance frequencies appear as a multiplet of lines, an error of about the magnitude of the quench frequency may be incurred if the wrong line is chosen. The quench frequency was about 0.020 MHz. Otherwise, the error in the frequency is about 0.005 MHz.

Results and Discussion

Nuclear quadrupole resonance spectroscopy measures the coupling between a component electric field gradient tensor, $\mathbf{q}$, and the nuclear quadrupole moment, Q, in a crystalline lattice. Manganese-55 has a nuclear spin of $^5/_2$ so that two transitions, $\nu(\pm{}^5/_2 \leftrightarrow \pm{}^3/_2)$ and $\nu(\pm{}^3/_2 \leftrightarrow \pm{}^1/_2)$, may be observed. From these two experimental frequencies, one can compute the two chemically interesting parameters e^2Qq/h and η directly from the spectrum. e^2Qq/h is the nuclear quadrupole coupling constant, and η is the electric field gradient asymmetry parameter.

In cyclopentadienylmanganese tricarbonyl, the manganese atom sits in a nearly axially symmetric environment. Except for the electrostatic crystal lattice effect and slight distortions of the molecule due to the lattice, η should be close to zero. The manganese resonance in

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[2] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1940.

[3] R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **74**, 2729, 3120 (1952); **75**, 2167 (1963).

[4] L. Doub and J. M. Vandenbelt, *ibid.*, **69**, 2714 (1947).

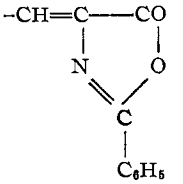
[5] L. M. C. Shen, G. G. Long, and C. G. Moreland, *J. Organometal. Chem.*, **5**, 362 (1966).

[6] A. N. Nesmeyanov, G. K. Semin, E. V. Bryuchova, T. A. Babushkina, K. N. Anisimov, N. E. Kolobova, and Yu. V. Makarov, *Tetrahedron Lett.*, **37**, 3987 (1968).

[7] We have succeeded in gathering data for one addition compound, α-aminoethylcyclopentadienylmanganese tricarbonyl hydrochloride: $\nu(\pm{}^5/_2 \leftrightarrow \pm{}^3/_2) = 19.47$ (40), $\nu(\pm{}^3/_2 \leftrightarrow \pm{}^1/_2) = 9.88$ (10), $e^2Qq/h = 65.05$ MHz, and $\eta = 0.108$.

Table I

Nqr Data for ^{55}Mn in $RC_5H_4Mn(CO)_3$ Compounds in Megahertz at 298°K

		ν					
Compd	R	$\pm ^5/_2 \rightleftarrows \pm ^3/_2$	$\pm ^3/_2 \rightleftarrows \pm ^1/_2$	e^2Qq/h	η	$\nu(^{35}Cl)$	$\nu(^{37}Cl)$
a	$-NHCOOCH_2C_6H_5$	19.86 (8)	10.17 (2)	66.45	0.138		
b	$-H^{a,b}$	19.28 (70)	9.65 (10)	64.29	0.0		
c	$-HgCl$	19.15 (35)	9.61 (6)	63.86	0.056	17.37 (6)	13.69 (2)
		18.96 (35)	9.59 (6)	63.32	0.096		
d	$-CNOHCH_3$	19.06 (40)	9.65 (5)	63.72	0.102		
e	$-CO_2^-NH_4^+$	18.88 (30)	9.47 (4)	62.97	0.046		
f	$-SS-$	18.84 (15)	9.59 (2)	62.97	0.119		
g	$-SO_2H$	18.77 (22)	9.43 (5)	62.61	0.061		
		18.51 (10)	9.30 (2)	61.74	0.063		
h	$-CO_2H^a$	18.38 (20)	9.20 (4)	61.28	0.034		
i	$-CHO$	18.23 (70)	9.24 (50)	60.89	0.102		
j	$-COCH_3^a$	18.20 (40)	9.17 (8)	60.73	0.076		
k	$-CH_3^c$	19.61 (3)	...	...	...		
	$-SO_3^-NH_3C_6H_4CH_3^+$						
l	$-CO_2^-Na^+$	19.30 (5)	...	...	...		
m	$-CONH_2$	18.57 (7)	...	...	...		
n		17.83 (4)	...	...	...		
o	$-CH_3^{a,d}$	*Ca.* 19.2	...	...	...		

[a] Reported in ref 6 at 77°K. [b] Reported in ref 8 and 9. [c] Disubstituted compound but the specific isomer is unknown. [d] A liquid at 298°K so the estimated approximate transition frequency was computed from the 77°K value and $(\partial\nu/\partial T)_P$ in Table II.

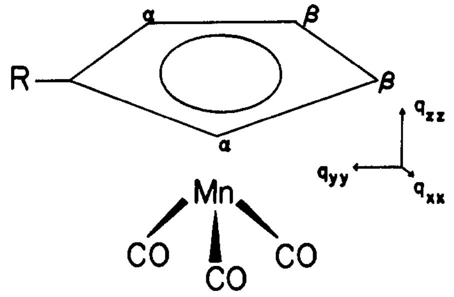


Figure 1.—The geometry of atoms and probable orientation of the electric field gradient principal axes in π-cyclopentadienylmanganese tricarbonyl.

Table II

Temperature Coefficients for Several $RC_5H_4Mn(CO)_3$ Compounds

	$\nu(\pm ^5/_2 \leftrightarrows \pm ^3/_2)$		
R	77°K[a]	298°K	$(\partial\nu/\partial T)_P$
$-H$	19.57[b]	19.28[b]	−0.0013[b]
$-COOH$	18.68	18.38	−0.0014
$-COCH_3$	18.47	18.20	−0.0012

[a] Reported in ref 6. [b] Reported in ref 8.

this compound has been reported at 77°K[6,8,9] and at 300°K[6] by a number of investigators and was recorded again here for the purpose of comparison. In the R-substituted derivatives of this parent compound, the axial symmetry is destroyed either by the presence of the R group and ensuing distortions of the ring or by ring slippage or by both. Evidence for ring slippage has been presented by Fayer and Harris[8] based on ^{55}Mn temperature-dependence data in pyrrolenylmanganese tricarbonyl.

Several of the resonances reported by Nesmeyanov, *et al.*, at 77°K were recorded again in this work at room temperature so that we could compare these compounds to our own. The coupling constants and asymmetry parameters for these compounds are shown in Table II at the two temperatures. Although it was not our goal to determine temperature coefficients, the value of $(\partial\nu/\partial T)_P$ for all the compounds studied is roughly the same. This $(\partial\nu/\partial T)_P$ was used to compute an approximate $\nu(\pm ^5/_2 \leftrightarrow \pm ^3/_2)$ for compound o. Since the manganese electric field gradient is predominently determined by its orbital characteristics, it is necessary to comment on the mode of bonding in these compounds. Mn(I) is d^6 and diamagnetic.[10] In the simplest description the d_{z^2} orbital is perpendicular to the plane of the cyclopentadienyl ring and, along with the $d_{x^2-y^2}$ and d_{xy} orbitals, contains the six electrons. This leaves the d_{xz} and d_{yz} orbitals as the important d orbitals involved in the manganese–cyclopentadienyl bonding. The d_{xz} and d_{yz} orbitals can, therefore, be used as a gauge for the extent of π-electron variation in the ring. The molecular electric field gradient, q_{mol}, due to d-orbital occupations is related to the atomic value, q_{at}, according to

$$q_{mol} = q_{at}\left[N_{d_{z^2}} + \frac{N_{d_{xz}} + N_{d_{yz}}}{2} - N_{d_{x^2-y^2}} - N_{d_{xy}}\right] \quad (1)$$

providing d_{z^2} is taken along the symmetry axis. An estimate of q_{at} for manganese has been made,[11] but we will restrict this discussion to relative trends since the

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(8) M. D. Fayer and C. B. Harris, *Inorg. Chem.*, **8**, 2792 (1969).

(9) J. Voitlander, H. Klocke, R. Longino, and H. Thieme, *Naturwissenschaften*, **49**, 491 (1962).

(10) T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).

(11) C. B. Harris, *Inorg. Chem.*, **7**, 1517 (1968).

effects are small. If the d_{xz} and d_{yz} orbitals contain very little electron density, then the bracketed quantity is negative. Since these orbitals are involved in bonding and are partially occupied, this situation is not realistic and it is not immediately certain whether the positive or negative terms predominate. Substitution of electron-donating or -withdrawing groups onto the ring will change the d_{xz} and d_{yz} populations, and, by the direction of the frequency shift, it is clear which terms should be larger. For example, with the carbonyl substituents, $N_{d_{yz}}$ and $N_{d_{yz}}$ would be expected to be smaller than most noncarbonyl groups (*vide infra*). If the positive terms in (1) predominate, then e^2Qq_{mol}/h should be in general smaller for the carbonyl compounds than for the other substituents. This is precisely what is observed in the present work and also in the work of Nesmeyanov, *et al.* We must conclude that the sum of the orbital populations of the d_{z^2}, d_{xz}, and d_{yz} orbitals is greater than that of $d_{x^2-y^2}$ and d_{xy} in these compounds.

In the long run it is more useful to know how well these results compare with the data obtained from other experimental techniques which are considered to measure π-electron density in rings. Comparison is, of course, complicated by crystal lattice effects which can lead to small shifts in the nqr frequency. These shifts alone can be important enough to be the sole source of discrepancy. On the other hand, the techniques to which we compared our data were taken from solution studies and these may be complicated by solvent effects. We have chosen to plot $\nu(\pm{}^5/_2 \leftrightarrow \pm{}^3/_2)$ for manganese rather than e^2Qq_{mol}/h because, in cases where the $\nu(\pm{}^3/_2 \leftrightarrow \pm{}^1/_2)$ transition was not observed, the coupling constant cannot be computed with certainty. The $(\pm{}^5/_2 \leftrightarrow \pm{}^3/_2)$ frequency will vary slightly for different values of η. Since the values of η are quite small in Table I, the points are shifted negligibly by this effect.

The nmr spectra of the α and β protons have been reported for most of these compounds.[5] The shielding and deshielding of the protons with respect to $C_5H_5Mn(CO)_3$ are related to the disturbance of the π-electron density by the substituent group. The most deshielded protons are associated with the most electron-withdrawing substituents. Figure 2 represents a least-squares fit of the τ value for the α and β protons and the ^{55}Mn $(\pm{}^5/_2 \leftrightarrow \pm{}^3/_2)$ transition. Two facts are immediately obvious. First, the β protons are less sensitive to the substituent than the α protons and, second, the points tend to be less scattered with the β protons than with α. Since inductive effects diminish quickly as the number of bonds are increased between the inductive source and the site of observation, the β protons might be expected to be less affected by R than the α protons. The second observation may be an example of the "through space" electrostatic effect of R which should be more important at the α positions.[12] Naturally, the "through space" effects should also be important at the manganese site and this may be a further source of discrepancy between the nmr and nqr results.

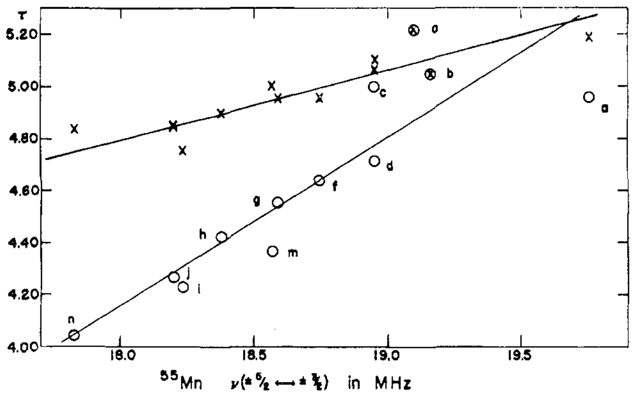

Figure 2.—A plot of the correlation between the nmr chemical shift of the α (○) and β (×) ring protons and the ^{55}Mn transition frequency.

Considerable work on substituent effects has been carried out on benzene systems. Little difficulty should be encountered in transferring these data to the cyclopentadienyl ring because the systems are quite similar.[13] Taft[3] proposed a σ_R function to represent the disturbance of the π system in monosubstituted benzene. The value is proportional to total charge transfer, and the intensity of the ν_{16} in-plane vibration has been shown to correlate with the electron-donating properites of R.[14] From these vibrational data, $\sigma_R{}^0$ values have been proposed.[15] There is only rough qualitative correlation between $\nu(\pm{}^5/_2 \leftrightarrow \pm{}^3/_2)$ and $\sigma_R{}^0$, but comparison is hampered by the lack of R groups common to the two studies. The ir spectrum of the monosubstituted nucleus $-C_5H_4Mn(CO)_3$ has been found[5] not to differ markedly from the parent compound $C_5H_5Mn(CO)_3$. Little information can therefore be gained from these latter spectra.

The above comparisons involve solely ground-state techniques, and it might be informative to extend the comparison to an experimental method, such as uv spectroscopy, which involves excited states as well. Doub and Vandenbelt[4] studied the $^1B_{1u} \leftrightarrow {}^1A_{1g}$ transition of monosubstituted benzenes as a function of the substituents. Figure 3 shows the correlation between $\nu(\pm{}^5/_2 \leftrightarrow \pm{}^3/_2)$ and the electronic transition frequency. The correlation is again qualitatively acceptable but suffers from a lack of common substituents. In summarizing the above comparisons, the ^{55}Mn frequencies correlate with information from other techniques about as well as the other techniques correlate with one another. It is, therefore, reasonably certain that ^{55}Mn monitors variations in ring density as well as the other techniques do.

Turning to a closer look at the effects of specific groups on the ^{55}Mn resonance frequencies, in general, carbonyl compounds exhibit lower frequencies than do

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(12) J. N. Murrell, S. F. A. Kettle, and J. M. Tedder, "Valence Theory," Wiley, New York, N. Y., 1965; K. Bowden and D. C. Parkin, *Can. J. Chem.*, **47**, 185 (1969).

(13) H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, p 247.

(14) R. T. C. Brownlee, A. R. Katritzky, and R. D. Topsom, *J. Amer. Chem. Soc.*, **87**, 3260 (1965); **88**, 1413 (1966); R. T. C. Brownlee, R. E. J. Hutchinson, A. R. Katritzky, T. T. Tidwell, and R. D. Thompson, *ibid.*, **90**, 1757 (1968).

(15) A. R. Katritzky and R. D. Topsom, *Angew. Chem., Int. Ed. Engl.*, **9**, 87 (1970).

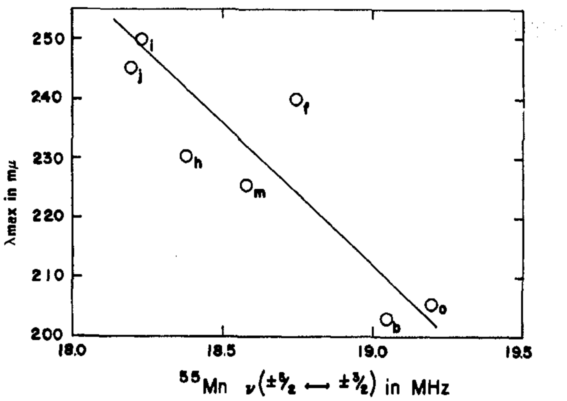
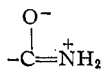
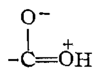


Figure 3.—The correlation between the primary uv absorption frequency in benzene and the ^{55}Mn resonance frequency.

most of the other substituents. This is consistent with their electron-withdrawing substituent effect. The acetyl compound (j) should be more favorable to the resonance effect than its oxime (d). The fact that the ^{55}Mn frequency in the oxime is considerably greater than in the acetyl system is evidence of this. Further, α-benzamido-β-(cyclopentadienylmanganese tricarbonyl)acrylic azlactone (compound n) is also expected to be conjugated with the ring, and indeed the ^{55}Mn frequency is the lowest of all those reported here. A very informative sequence of compounds is the isoelectronic series acetyl-, amido-, and carboxycyclopentadienylmanganese tricarbonyl. The frequencies follow the trend $-CONH_2 > -COOH > -COCH_3$, and each successive frequency differs by about 0.2 MHz. Unhindered resonance with the ring causes the acetyl compound to exhibit the lowest frequency. With the amido and carboxyl groups, a second resonance effect, which is internal to the substituent, becomes important and inhibits resonance with the ring. I is much more favorable than II and it is easily predicted that carbonyl resonance with the ring is more inhibited with the amide than with the carboxyl group. The observed frequency trend is consistent with this elementary reasoning. As expected, the aldehyde derivative (compound i) gives rise to a ^{55}Mn resonance which is very close to that of the acetyl compound.


$$-\overset{\overset{O^-}{|}}{C}=\overset{+}{N}H_2$$
I


$$-\overset{\overset{O^-}{|}}{C}=\overset{+}{O}H$$
II

The carboxylate salts represent examples of the effects of charged substituents. In both cases, carboxylate salts have higher ^{55}Mn frequencies than does carboxycyclopentadienylmanganese tricarbonyl because a negatively charged substituent is more nucleophilic than a neutral one. There is also a significant dependence of the resonance frequencies upon the cation counterpart. Since the lattice now contains ions, electrostatic contributions to the electric field gradient become more important.

It was hoped that sulfur could be used to demonstrate the effect on the ^{55}Mn frequency of different oxidation states in the substituent. The compound, bis(cyclopentadienylmanganese tricarbonyl) disulfide, (compound f) contains sulfur in the −I oxidation state gives a comparable ^{55}Mn frequency to sulfur in the +IV state (*cf.* sulfinocyclopentadienylmanganese tricarbonyl). Nesmeyanov, *et al.*, found the $\nu(\pm 5/2 \leftrightarrow \pm 3/2)$ transition in $(CO)_3MnC_5H_4SO_3C_2H_5$ which contains S(VI), and it is not markedly different from either S(−I) or S(IV). It appears to make little difference to the manganese atom what the oxidation state of sulfur in the substituent is. $(CO)_3MnC_5H_4SO_2H$ does not appear to be isostructural with $(CO)_3MnC_5H_4CO_2H$. The expected trend in nucleophilicity of S(IV) > C(IV) is supported by the nqr data, but the result may be fortuitous in view of the different crystal structures.

Mercury is expected to be a soft σ donor and does give rise to a reasonably high ^{55}Mn frequency. There may also be some π repulsion between the ring and the mercury atom because there exists a considerable amount of electron density on mercury in a plane perpendicular to the C–Hg–Cl bond.[16] The lattice contains two crystallographically different manganese atoms which are present in a 1:1 ratio. On the other hand, only a single type of chlorine atom appears to be present and this may indicate that there is some type of association between molecules, perhaps as chlorine bridges between mercury atoms. The chlorine atoms could conceivably become crystallographically equivalent whereas the manganese may not. The ^{35}Cl resonance frequency is about 5 MHz less than that in pure mercuric chloride.[17] This is consistent with the fact that the cyclopentadienyl ring is much more nucleophilic than chlorine so that the Hg–Cl bond becomes more ionic in the organometallic bond.

Benzyl *N*-(cyclopentadienylmanganese tricarbonyl)-carbamate (compound a) represents the only compound with a nitrogen atom bonded to the ring for which an nqr spectrum has been recorded. Of the compounds presented here, it also exhibits the highest ^{55}Mn frequency. The reasons for this may be either resonance effects of the lone-pair electrons on nitrogen with the ring or nonbonded repulsions between ring π electrons and the lone pair or both.

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(16) L. E. Orgel, *J. Chem. Soc.*, 4187 (1958).

(17) H. G. Robinson, H. G. Dehmelt, and W. Gordy, *Phys. Rev.*, **93**, 408 (1954).