Proton Magnetic Resonance Spectroscopy of Unsaturated Ring Systems. XI.[1a] Chromium Tricarbonyl Complexes of Cycloheptatriene and 1,6-Methano[10]annulene

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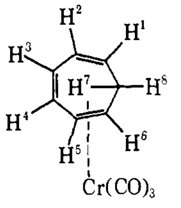
Abstract: The ^{1}H nmr spectra of π-cycloheptatriene- and π-1,6-methano[10]annulenechromium tricarbonyls (I and II) have been analyzed in terms of chemical shifts and coupling constants. The results are discussed with respect to the π-electronic structure of these compounds. The aromatic character of II is demonstrated. The chemical shifts of the protons in I and II are related to the orientation of the chromium tricarbonyl group.

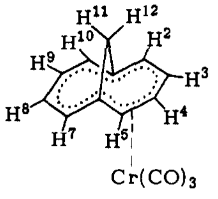
Despite the important contributions of nmr spectroscopy to the solution of structural problems in the field of transition metal complexes of cyclic π systems,[2] surprisingly little precise data for the H,H′ coupling constants in this class of compounds have been reported. Since spin–spin interactions yield information about the stereochemistry as well as the electronic structure of molecules, their knowledge seemed to us to be of interest mainly for two reasons. (1) For many complexes, structural data are available from X-ray analysis and their relationship to nmr parameters may be tested. (2) Information about the effect of complex formation on the coupling constants in a given π system may eventually lead to a better understanding of the nature of bonding in these compounds.

Following the analysis of the ^{1}H nmr spectrum of π-cycloheptatrienemolybdenum tricarbonyl,[3] we have analyzed the spectra of π-cycloheptatrienechromium tricarbonyl (I)[4] and π-1,6-methano[10]annulenechromium tricarbonyl (II).[5,6] In the present case, comparison of the nmr parameters obtained for I with those of the corresponding molybdenum compound[3] was of interest in connection with the question of how chemical shifts and coupling constants are influenced by the nature of the metal coordinated with the olefinic ligand. The analysis of the spectrum of II was believed to provide evidence for the structure of this new compound, especially with regard to the π-electron decet. Since the unsymmetrical arrangement of the $Cr(CO)_3$ group was evident from the spectrum and had been proposed earlier by Fischer, *et al.*,[5] three distinct alternatives concerning the π bonds seemed feasible: (a) a fully delocalized (aromatic) structure IIa, (b) a localized (olefinic) structure IIb, and (c) a delocalized (homoaromatic) π-electron sextet combined with an olefinic diene system (IIc). In addition, the chromium tricarbonyl group might take a position *syn* or *anti* to the methylene group.

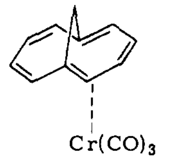
In connection with our work on the spectrum of the free ligand, 1,6-methano[10]annulene (III),[7] and a number of cyclohexadiene systems,[8] it was thought that the exact determination of the coupling constants would differentiate between IIa, b, and c. Furthermore, the assignment of the resonance frequencies of the bridge protons H_{11} and H_{12} should yield information about the relative position of the $Cr(CO)_3$ and the CH_2 group, since in case of a *syn* arrangement H_{12} should be shielded with respect to H_{11}.[9]



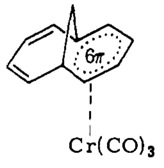
I



IIa



IIb



IIc

Results

The spectrum of I resembles closely that of the corresponding molybdenum complex, $C_7H_8Mo(CO)_3$-(IV), and has been described in qualitative terms by Bennett, *et al.*[4] The multiplet of the protons H_3 and H_4 shows the fine structure typical for the unsubstituted or 7-substituted cycloheptatrienes, possessing a plane of symmetry, as has been discussed in detail elsewhere.[3] The analysis, therefore, followed that outlined for IV.[3] The best parameters obtained by an iterative computer calculation with the program LAOCOON II[10] are given in Table I. Calculated and observed line positions agreed within 0.05 Hz. A zero value was assumed for the coupling constant $J_{1,5}$ ($=J_{3,6}$); $J_{1,6}$ could not be determined, but most probably is small. The relative signs of the coupling constants $J_{2,3}$, $J_{3,4}$, $J_{2,4}$, and $J_{2,5}$ are given by the analysis. As with IV, the best fit was obtained with like signs for these constants which are,

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(1) (a) Part X: H. Günther, *Z. Naturforsch.*, **24b**, in press; (b) to whom inquiries should be directed.

(2) (a) M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Advan. Organometal. Chem.*, 3, 1 (1965); (b) M. A. Bennett, *ibid.*, 4, 353 (1966).

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(4) M. A. Bennett, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 2037 (1961).

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(6) For a preliminary report see: H. Günther and W. Grimme, *ibid.*, 78, 1063 (1966).

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(8) H. Günther and H.-H. Hinrichs, *Ann. Chem.*, 706, 1 (1967).

(9) H. P. Fritz and H. J. Keller, *Chem. Ber.*, 96, 1676 (1963).

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Table I

1. Chemical Shifts[a]

	$\tau_1 = \tau_6$	$\tau_2 = \tau_5$	$\tau_3 = \tau_4$	$\tau_7 = \tau_{10}$	$\tau_8 = \tau_9$	τ_{11}	τ_{12}
I	7.329	5.815	4.703	8.918	7.830		
II		3.799	5.671	3.232	3.584	11.769	11.138

2. Coupling Constants[b]

	Geminal constants[c]		Vicinal constants						
	$J_{7,8}$	$J_{11,12}$	$J_{1,2} = J_{5,6}$	$J_{2,3} = J_{4,5}$	$J_{3,4}$	$J_{6,7} = J_{1,7}$	$J_{6,8} = J_{1,8}$	$J_{7,8} = J_{9,10}$	$J_{8,9}$
I	−14.05		8.2	6.97	8.45	3.17	8.90		
II		−8.90		7.05	7.31			8.16	9.22

Long-range Constants[d]

	$(J_{1,3} + J_{1,4}) = (J_{4,6} + J_{3,6})$	$J_{2,4} = J_{3,5}$	$J_{2,5}$	$J_{7,9} = J_{8,10}$	$J_{7,10}$	$J_{2,11} = J_{5,11}$	$J_{7,12} = J_{10,12}$
I	1.27	0.73	0.51				
II		0.37	1.18	0.24	1.56	0.91	1.08

	$J_{2,12} = J_{5,12}$	$J_{7,11} = J_{10,11}$	$J_{2,7} = J_{5,7}$	$J_{2,7} = J_{5,10}$	$J_{2,8} = J_{5,8}$	$J_{5,7} = J_{2,10}$
I			−1.07		0.92	
II	<0.4	<0.3		~0		0.49

[a] τ values in parts per million (ppm). [b] J values in hertz for I and II. [c] Sign assumed. [d] $J_{1,5} = J_{2,6} \sim J_{1,6} < 0.5$ for I (see text).

therefore, positive, since vicinal coupling constants have, according to current theory and experimental results, positive signs.[11,12] The positive sign of $J_{2,5}$ is further supported by spin-tickling experiments with 1,6-dicarbomethoxycycloheptatriene.[13] For $J_{2,7}$ and $J_{2,8}$ opposite signs have been determined by spin-tickling experiments in the case of IV,[14] and the same signs are assumed for I. A unique assignment of the resonance frequencies can be made on the basis of the observed spin–spin interactions.

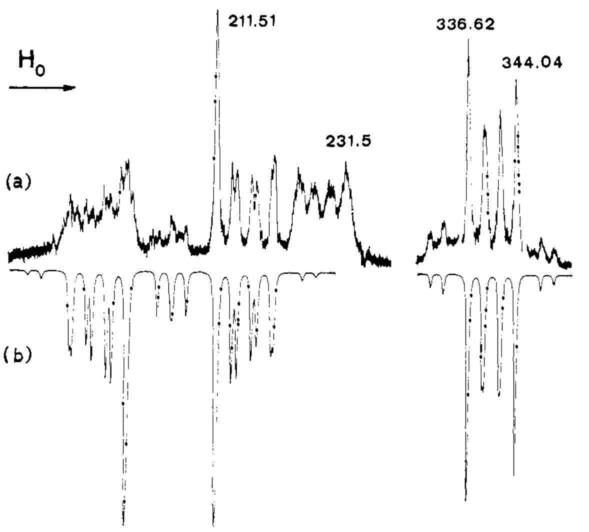

Figure 1. Experimental (a) and calculated (b) 60-MHz spectrum of the ring protons of II in benzene-d_6; line positions (in hertz) refer to internal tetramethylsilane at +600.00 Hz.

The spectrum of II consists of two overlapping four-spin systems of the AA′BB′ and AA′XX′ type, respectively, in the aromatic and olefinic region (Figure 1), and an AB system at high field from internal tetramethylsilane (Figure 2a). From the known effect of the metal carbonyl group on proton chemical shifts,[1] the AA′XX′ system can be assigned to the protons of the coordinated half-ring, whereas the AA′BB′ system corresponds to the protons of the uncoordinated half-ring. The assignment of the resonance frequencies for each system, which is not given by the analysis, is based on the long-range coupling with the bridge protons H$_{11}$ and H$_{12}$. The latter leads to additional fine structure in the half-spectrum of the ring protons in α position to the methylene bridge only. Accordingly,

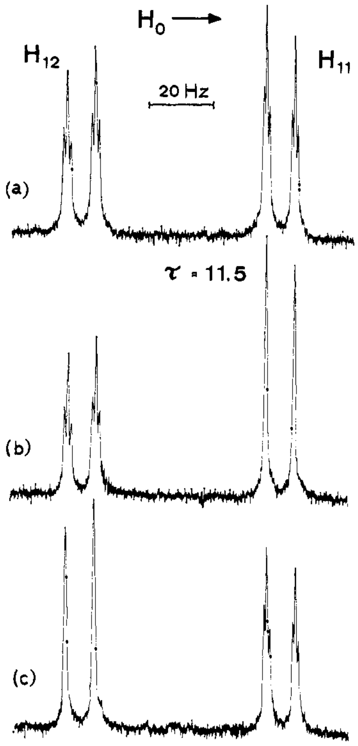

Figure 2. AB system of the protons H$_{11}$ and H$_{12}$ of II at 100 MHz in benzene-d_6: (a) undecoupled spectrum, (b) decoupled spectrum with simultaneous irradiation at the resonance frequency of H$_2$ and H$_5$, and (c) decoupled spectrum with simultaneous irradiation at the resonance frequency of H$_7$ nd H$_{10}$.

(11) P. C. Lauterbur and R. J. Kurland, *J. Am. Chem. Soc.*, **84**, 3405 (1962).

(12) G. Englert and A. Saupe, *Mol. Cryst.*, **1**, 503 (1966).

(13) H. Günther and M. Görlitz, unpublished results.

(14) H. Günther, to be published.

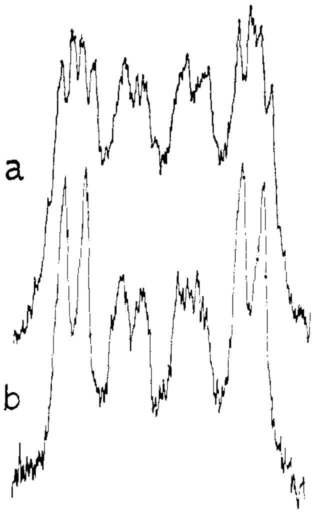

Figure 3. AA′ part (protons H_2, H_5) of the AA′XX′ system of II (see text): (a) undecoupled spectrum, (b) decoupled spectrum with simultaneous irradiation at the resonance frequency of H_7 and H_{10}.

a triplet splitting is observed in the AB system of H_{11} and H_{12} (Figure 2a). The two four-spin systems (due to H_2–H_5 and H_7–H_{10}, respectively) can be analyzed separately, since spin–spin interaction between protons at different half-rings is small. Based on the unperturbed lines of the β-protons (H_3,H_4 and H_8,H_9, respectively) the analysis is straightforward, using standard methods.[15] Computer-refined parameters obtained with LAOCOON II are collected in Table I. The spectrum calculated with these data is shown in Figure 1b. The spectrum recorded at 100 MHz agreed within experimental error with that calculated using the data of Table I with appropriate corrections for the chemical shifts. The errors in the coupling constants are approximately 0.1 Hz or smaller.

Owing to the nonequivalence of the α-protons in both half-rings of II it was possible to measure also the coupling constant $J_{5,7}$ ($=J_{2,10}$). Figure 3 shows the lines of protons H_2 and H_5 at 100-MHz field strength. For the two pairs of degenerate transitions of the AA′XX′ system, clearly four lines are resolved in each case. The magnitude of the splittings was found to be 0.86 and 0.49 Hz. Since a value of 0.91 Hz is obtained for $J_{2,11}$ from the triplet splitting in the lines of H_{11}, the remaining splitting must correspond to the interaction with H_7 and H_{10}. This is demonstrated by a decoupling experiment. Irradiation with a second radiofrequency field at $\nu_{7,10}$ leaves only the large splitting (0.87 Hz in this experiment, Figure 3b) unchanged. Since $J_{2,7}$ is most probably zero (see below), the splitting of 0.49 Hz is due to $J_{5,7}$.

The assignment of the Larmor frequencies of the bridge protons H_{11} and H_{12} is based on double-resonance experiments and the assumption that the *anti* coupling constant $J_{2,11}$ ($J_{7,12}$) is larger than the *syn* coupling constant $J_{2,12}$ ($J_{7,11}$). The latter is justified theoretically, since J_{anti} has a coupling path that resembles the M geometry, which is well known to lead to large σ coupling over four bonds.[16] Furthermore, it has been supported experimentally by the observation that α-disubstituted derivatives of the parent compound III show large splittings only for the bridge proton oriented above the substituted half-ring.[17] The results of the double-resonance experiments are shown in Figures 2b and 2c. A strong H_2 field located at the resonance frequency of protons H_2 and H_5 causes a collapse of the triplet splitting of the high-field doublet, whereas irradiation at $\nu_{7,10}$ causes the splitting of the low-field doublet to disappear. This demonstrates that $\nu_{11} > \nu_{12}$, indicating an *anti* arrangement of the methylene and chromium tricarbonyl group.

$J_{2,11}$ and $J_{7,12}$ are obtained directly from the spectrum (Figure 2a). Test calculations, treating the protons of one half-ring and the methylene bridge as AA′KK′XY system, show that indeed the triplet splitting visible in the lines of H_{11} and H_{12} corresponds to $J_{2,11}$ and $J_{7,12}$, respectively. The splitting due to the *syn* coupling constants $J_{2,12}$ and $J_{7,11}$ is not resolved. According to the observed line width, these constants are smaller than 0.4 and 0.3 Hz, respectively.

Discussion

a. Coupling Constants. The spin–spin interactions obtained for I are very similar to those found for IV.[3] A change of the metal within the same group of the periodic table apparently has no pronounced effect on these parameters. In addition, the molecular structure of I must be practically identical with the one established for IV by X-ray analysis,[18] as far as the olefinic part of the molecule is concerned. Compound I therefore has alternating double and single bonds. There are minor changes for the spin–spin interactions between olefinic and methylene protons in going from IV to I. In the light of the similarities for the other coupling constants discussed above, it seems unlikely that these differences are due to a direct substituent effect of the metal carbonyl group. They most probably indicate a small difference in the structural angle α between the planes defined by the C atoms 1, 2, 5, and 6 and 1, 6, and 7, respectively, for both compounds.

For II, a consideration of the vicinal coupling constants alone immediately enables one to decide that only structure IIa of the three alternatives discussed at the beginning is in accord with experiment. In the coordinated half-ring no appreciable alternation is observed for these parameters, in contrast to the findings for the olefinic compound I. On the other hand, the relative magnitude of the vicinal coupling constants in the uncoordinated half-ring excludes any possible diene-like structure for this part of the molecule, since it is well documented[8] that this would lead to a ratio $J_{7,8} > J_{8,9}$ instead of the observed $J_{7,8} < J_{8,9}$. Structures IIb and IIc can, therefore, be eliminated.

These conclusions are further supported by the observed magnitude of the long-range coupling constants $J_{7,9}$ and $J_{7,10}$, which is similar to that of the corresponding constants in the free ligand III[7] and differs from that found for ^4J and ^5J in cyclohexadienes.[8] The values obtained for the vicinal coupling constants $J_{7,8}$ and $J_{8,9}$ are also close to that observed for the corresponding parameters in III[7]. The slight reduction

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[15] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 140 ff; B. Dischler, *Z. Naturforsch.*, **20a**, 888 (1965).

[16] M. Barfield, *J. Chem. Phys.*, **41**, 3825 (1964).

[17] Unpublished work with W. Bremser.

[18] J. D. Dunitz and P. Pauling, *Helv. Chim. Acta*, 43, 2188 (1960).

found for $J_{7,8}$ might be caused by the shortening of the C_1–C_6 distance in II. Preliminary data on the X-ray analysis of II,[19] that are fully in accord with the conclusions regarding the structure of this compound drawn above, show this distance to be smaller by 0.12 Å as compared to the same distance in III. The consequence of this change could be a small twist around the C_7–C_8 and C_9–C_{10} bonds, accompanied by an increase in dihedral angle between the CH bonds in question, or an increase in the H–C–C bond angles. Both effects would lead to the observed change for $J_{7,8}$.[20]

Turning now to the coordinated half-ring of II, complex formation leads to a decrease of the magnitude of the vicinal coupling constants by about 2 Hz, which is somewhat less than the change observed for $J_{3,4}$ in going from cycloheptatriene to I (ΔJ = 2.72 Hz). The small difference in the sense $J_{2,3} < J_{3,4}$ observed for III is retained in II as well as the ratio of the long-range coupling constants ($J_{2,5} > J_{2,4}$). The latter is distinct from that in the olefinic systems I and IV, where $J_{2,5} < J_{2,4}$ is found.

The geminal coupling constant $J_{11,12}$ (^2J) is larger, that is to say more negative,[21] than the one found for III (6.97 Hz[7]). According to the X-ray results,[19] the C_1–C_{11}–C_6 bond angle is smaller in II than in III (92.4° against 99.6° [22]). The opposite would be expected using an empirical relationship between ^2J and C–CH_2–C bond angles proposed recently.[23] Other factors, therefore, dominate.[24] It is interesting to note that the ^{13}C–H coupling constant of the methylene bridge has also changed, but in the opposite direction. Its value [147.2 ± 1.0 Hz for $J(^{13}CH_{11})$] is slightly larger (more positive) than the one measured for III[7] (142 ± 2 Hz). This trend is expected on the basis of the C–C–C bond angle change.

From the coupling constants between the α-protons in the two half-rings of II only $J_{5,7}$ ($=J_{2,10}$) is believed to have a value >0. Spin–spin coupling between H_2 and H_7 would have to involve an interaction of the π orbitals at C_1 and C_6, since a pure σ mechanism seems unlikely due to unfavorable geometry, *i.e.*, nonplanar bonds. However, the overlap at C_1 and C_6, though very probably present in III,[25] is most certainly disturbed by complex formation. The observed splitting of 0.49 Hz, that corresponds to the sum of $J_{5,7}$ and $J_{2,7}$, is, therefore, assigned to $J_{5,7}$.

b. Chemical Shifts. Since both I and II as well as IV have been analyzed in benzene-d_6 as solvent at approximately the same concentrations, differences in the resonance frequencies may be discussed in terms of structural changes only. For further comparison, the resonance frequencies of the protons in III and in cycloheptatriene (V) have been determined under the same conditions and are given in Table II.

Table II. τ Values[a] for the Protons in 1,6-Methano[10]annulene (III) and Cycloheptatriene (V) in Benzene-d_6[b]

	$\tau_{1,6}$	$\tau_{2,5}$	$\tau_{3,4}$	$\tau_{7,8}$	$\tau_{11,12}$
III		2.79	3.08		10.40
V	4.82	3.91	3.52	7.88	

[a] In parts per million (ppm). [b] Numbering according to I and II.

In accordance with our findings for the coupling constants, the chemical shift data for I and IV are very similar. Whereas $\nu_{3,4}$ is virtually identical, small upfield shifts are obtained for $\nu_{2,5}$ (0.064 ppm), $\nu_{1,6}$ (0.259 ppm), and ν_8 (0.091 ppm). A somewhat stronger shielding effect is exerted on H_7 (0.717 ppm). Since these changes are connected primarily with the protons at C_1, C_6, and C_7, they support the assumption of different structural angles α in I and IV as discussed above. The observed trend suggests $\alpha_I > \alpha_{IV}$, since this would bring H_7 closer to the shielding region of the olefinic system in I.

In II, the resonance frequencies of the protons H_7–H_{10} are shifted slightly (by *ca.* 0.5 ppm) to higher field as compared with the results for the free ligand III (Table II). The protons H_2–H_5 show the usual upfield shift observed on complex formation.[1] It is interesting to note that, contrary to the olefinic compound I, the central protons H_3 and H_4 are affected most (+2.59 ppm), whereas H_2 and H_5 show an upfield shift of only 1.01 ppm. For I the corresponding values are 1.18 and 1.91 ppm, respectively. Recent data on ^{13}C and ^1H chemical shifts of cyclopentadienyl transition metal complexes[26] indicate that possibly the π-electron density at the C atoms bound to the metal plays a major role in determining the resonance positions of the protons attached to these carbon atoms. The failure of the ^1H resonances in complexes of olefinic systems, as for instance butadieneiron tricarbonyl, to obey the linear relationship[26,27]

$$\delta_C = 197.7 - 18.06\delta_H$$

has been partly explained by steric reasons.[27] However, as was pointed out by Lauterbur and King,[26] other observations stand against a simple electron density–chemical shift relation and the importance of shielding effects due to the C≡O and carbon–metal bonds also has to be considered.

In our case, the experimental results may be related to the different orientation of the chromium tricarbonyl group with respect to the carbon–carbon bonds. The X-ray data for II[19] show the three CrC≡O groupings bisecting the C_1–C_2, C_3–C_4, and C_5–C_6 bonds (a). For I no X-ray data are available, but in analogy to the observations made for IV[18] and 7-phenylcycloheptatrienechromium tricarbonyl[28] the $Cr(CO)_3$ group is

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(19) P. E. Baikie and O. S. Mills, *Chem. Commun.*, 683 (1966).

(20) M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963).

(21) J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, **42**, 1339 (1965).

(22) M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, **48**, 1429 (1965).

(23) R. C. Cookson, T. A. Crabb, J. J. Frankel, and J. Hudec, *Tetrahedron, Suppl.*, 7, 355 (1966).

(24) According to the Pople–Bothner-By theory of geminal coupling constants,[21] the parallel arrangement of the H_{11}–H_{12} line and the plane of the conjugating perimeter should lead to a positive shift for $J_{11,12}$ in III due to hyperconjugative interaction. The increase observed for $J_{11,12}$ in II would then suggest a perturbation of this interaction because of the formation of the carbon–chromium bonds. Valence bond calculations, however, predict a negative shift for $J_{11,12}$ in III (M. Barfield and D. M. Grant, *Advan. Magnetic Resonance*, **1**, 183 (1965).

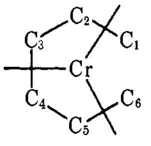
(25) H.-R. Blattmann, W. A. Böll, E. Heilbronner, G. Hohlneicher, E. Vogel, and J.-P. Weber, *Helv. Chim. Acta*, **49**, 2017 (1966).

(26) P. C. Lauterbur and R. B. King, *J. Am. Chem. Soc.*, **87**, 3266 (1965).

(27) H. L. Retcofsky, E. N. Frankel, and H. S. Gutowsky, *ibid.*, **88**, 2710 (1966).

(28) P. E. Baikie, O. S. Mills, P. L. Pauson, G. H. Smith, and J. Valentine, *Chem. Commun.*, 425 (1965); P. E. Baikie and O. S. Mills, *J. Chem. Soc., A*, 2704 (1968).

most probably rotated through 60°, the $CrC{\equiv}O$ axes then bisecting the C_2–C_3, C_4–C_5 bonds, and the C_1–C_6 distance (b). In solution, rapid rotation of the $Cr(CO)_3$ group seems possible,[29] but since the species a and b are certainly of different energy, only one will predominantly influence the chemical shifts in this case. The X-ray data suggest that the low-energy conformers are of type a for II and type b for I. This prevents an averaging out of the specific shielding effect associated with each conformer.



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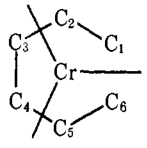

b

The above argument is supported by results published on the nmr spectra of chromium tricarbonyl complexes of naphthalenes, where the relative resonance position of the protons[30] and the orientation of the $Cr(CO)_3$ group[31] parallel the situation met with II. Model calculations[4] based on assumed anisotropies seem at present not justified, since nothing is known about the nature of the observed shielding. The upfield shift of the proton resonances due to the complexation in aromatic compounds, such as III, is evidently not caused mainly by a reduction of the ring current effect, as suggested by Fritz, *et al.*,[30] since the shielding effects found for complexes with olefinic ligands, such as I and IV, are of the same order of magnitude.

The over-all upfield shift obtained for the bridge protons in II, as compared to those of III (Table II), seems best explained by a long-range shielding effect of the $Cr(CO)_3$ group, which might also be responsible for the change of the resonance frequencies in the uncoordinated half-ring.

The possibility of an intramolecular exchange of the chromium tricarbonyl group between the two half-rings of II was tested. Thermal instability of the compound, however, prevented the observation of spectra at elevated temperatures (>+100°).

Experimental Section

Analytically pure samples of I and II, respectively, were transferred to 5 mm o.d. Pyrex tubes equipped with ground joints. The tubes were evacuated on the vacuum line and dry, pure benzene-d_6 was distilled into the tube to give *ca.* 1 *M* solutions. Tetramethylsilane (*ca.* 5% by volume) was added and the tubes were sealed under vacuum after degassing the solutions.

Spectra were recorded with a Varian A60-A nmr spectrometer equipped with a Hewlett-Packard audiooscillator Model 202 A and a Hewlett-Packard electronic counter Model 5212 A using standard side-band technique. Experimental line positions were determined by interpolation and averaging over ten spectra obtained in the two directions of the magnetic field. When completely resolved, the probable error was in the order of 0.05 Hz. Decoupling experiments were performed with a Varian HA-100 nmr spectrometer using frequency sweep mode and a Hewlett Packard audiooscillator Model 4204 A.

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Tetrahedral Structures of Unexpected Stability. On Distinguishing Randomization Mechanisms in the Mass Spectral Fragmentation of Substituted Cyclopentadienols

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Abstract: Pentaphenylcyclopentadienol molecular ions show partial hydrogen scrambling, as well as partial phenyl scrambling, before they fragment in the mass spectrometer. A major route for decomposition is the stepwise loss of the elements of aryl and CHO, to give a labeled $C_4Ph_4\cdot^+$. Labeling experiments suggest a tetrahedral symmetry for this species at some point before its further decomposition. The *p*-fluoro-labeling experiments suggest that the phenyl carbon skeleton remains intact, while deuterium labeling shows scrambling of hydrogens on the skeleton. The observation of this species after so unlikely a mode of formation, coupled with previous observations, offers the possibility that the tetraphenyltetrahedrane radical cation may possess unusual stability in mass spectral decompositions, like the tropylium ion in other systems.

The classic epitome of labeling experiments in mass spectrometry is the discovery of the symmetrical tropylium structure for $C_7H_7^+$.[1] Its observation in the spectrum of ethylbenzene was followed by studies of other aromatic systems and cycloheptatriene which showed the same result.[2] The spectra of many isomers of $C_7H_8\cdot^+$ have so many features in common with those of the spectrum of toluene that the tropylium structure has been postulated for the $C_7H_7^+$ ion in the

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