

## AN NMR STUDY OF ARENECHROMIUM TRICARBONYL COMPLEXES

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## INTRODUCTION

Since its discovery in 1955 by Fischer and Hafner<sup>1</sup>, dibenzenechromium,  $(C_6H_6)_2Cr$ , has aroused considerable interest because of the possibility that bonding to the chromium atom might destroy the aromaticity of the benzene rings and produce an alternation of the lengths of the carbon-carbon bonds. This idea was supported by an X-ray investigation<sup>2</sup> which showed alternate C-C bonds to have lengths of 1.439 and 1.353 Å, but other workers<sup>3</sup> failed to observe the effect. Spectral<sup>4,5</sup> and theoretical<sup>6,7,8</sup> studies have proven similarly inconclusive, although a recent electron diffraction investigation<sup>9</sup> of gaseous  $(C_6H_6)_2Cr$  has shown that any difference in the C-C bond lengths in the benzene rings is probably less than 0.02 Å.

The same problem exists for the arenechromium tricarbonyl complexes,  $ArCr(CO)_3$ , although in them the organic ligand has been shown to display aromatic<sup>10</sup> behavior and an X-ray investigation<sup>11</sup> of biphenylchromium tricarbonyl has shown no significant alternation in C-C bond length. The present study was undertaken in the hope that proton magnetic resonance measurements could provide information about the distribution of electronic charge in the benzene ring in these compounds. The complexes of various methoxybenzenes were selected because electron-donating power of the methoxy group helps to increase the stability of the complexes, and a recent PMR study<sup>12</sup> of the methoxybenzenes themselves has shown that the resonances of the ring protons are spread over a reasonably wide range, thus simplifying interpretation of the spectra.

## EXPERIMENTAL

Infrared spectra (Table 2) were recorded on an Infracord model IR 5 equipped with sodium chloride optics, using concentrated solutions of the compounds in carbon tetrachloride and carbon disulphide. Absorptions in the range 2000-1850  $cm^{-1}$  were also examined on a Perkin-Elmer model 421 with diffraction grating optics, using 0.0025 *M* solutions of the compounds in carbon tetrachloride, and are thought to be accurate to better than 1  $cm^{-1}$ .

Proton magnetic resonance spectra (Table 3) were measured in 5 mm o.d. spinning pyrex tubes at 56.4 mc/s on a Varian Associates Model DP-60 spectrometer fitted with field homogeneity coils. Approximately 0.5 *M* solutions of the compounds in deuteriochloroform containing a small amount of tetramethylsilane as an internal reference were used, and line positions were determined by conventional side-band techniques.

Micro-analyses were performed by Dr. F. KASLER of this department, and melting points are uncorrected. Chromium hexacarbonyl was prepared by the high pressure reaction between carbon monoxide, magnesium, and chromium acetylacetonate in pyridine<sup>13</sup>, and was vacuum-sublimed before use. 1,2,3-Trimethoxybenzene was made from pyrogallol and dimethyl sulphate<sup>14</sup> and was recrystallized from light petroleum; other starting materials were obtained commercially.

The complexes were prepared by maintaining a mixture of chromium hexacarbonyl (10 mmol) and the methoxybenzene (*ca.* 20 mmol) at 150° under nitrogen; chromium carbonyl which sublimed from the reaction vessel being returned mechanically from time to time. The ligands containing the greatest number of methoxy groups required the longest reaction time, and after 5–20 h the mixture was cooled and dissolved in 30 ml chloroform. The solution was filtered, and the filtrate was evaporated at 25°/20 mm and then maintained at 60°/0.01 mm overnight to remove unreacted starting materials. Finally, sublimation at 100°/0.01 mm gave the complex. Yields, melting points, reaction times, and analytical data are given in Table 1. The com-

TABLE 1  
PREPARATIVE DATA

Compound	Yield (%)	M.p. (°C)	Reaction time (h)	Analysis			
				Calcd.		Found	
				% C	% H	% C	% H
1,2-(CH <sub>3</sub> O) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Cr(CO) <sub>3</sub>	49	116	8	48.17	3.67	48.28	3.93
1,3-(CH <sub>3</sub> O) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Cr(CO) <sub>3</sub>	45	122	10	48.17	3.67	48.33	3.80
1,4-(CH <sub>3</sub> O) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Cr(CO) <sub>3</sub>	58	101	12	48.17	3.67	48.11	3.85
1,2,3-(CH <sub>3</sub> O) <sub>3</sub> C <sub>6</sub> H <sub>3</sub> Cr(CO) <sub>3</sub>	22	95	12	47.37	3.98	47.56	4.20
1,2,4-(CH <sub>3</sub> O) <sub>3</sub> C <sub>6</sub> H <sub>3</sub> Cr(CO) <sub>3</sub>	29	114	15	47.37	3.98	47.66	4.25
1,3,5-(CH <sub>3</sub> O) <sub>3</sub> C <sub>6</sub> H <sub>3</sub> Cr(CO) <sub>3</sub>	5	157	20	47.37	3.98	48.00	3.88

TABLE 2  
INFRARED SPECTRA

The bold-printed numbers are the carbonyl stretching frequencies, and were determined with special care.

CH <sub>3</sub> OC <sub>6</sub> H <sub>5</sub> Cr(CO) <sub>3</sub>	2880 w, 2850 w, 2780 w, <b>1975 vs. 1903 vs. 1450 s. 1420 m, 1235 vs. 1170 m, 1146 w, 1137 w, 1048 m, 1027 s, 988 m, 801 m, 780 m, 668 vs. 653 s cm<sup>-1</sup></b>
1,2-(CH <sub>3</sub> O) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Cr(CO) <sub>3</sub>	2870 w, 2760 w, <b>1969.5 vs. 1894.5 vs. 1460 m, 1415 m, 1250 s, 1210 m, 1172 w, 1143 w, 1092 w, 1023 m, 993 w, 806 w, 750 w, 662 s cm<sup>-1</sup></b>
1,3-(CH <sub>3</sub> O) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Cr(CO) <sub>3</sub>	2920 w, 2870 w, 2760 w, <b>1970.5 vs. 1895 vs. 1435 m, 1408 w, 1388 w, 1268 m, 1200 s, 1156 m, 1142 m, 1138 sh, 1053 w, 1032 w, 1025 w, 986 w, 911 w, 892 w, 809 m, 726 w, 672 s, 653 m cm<sup>-1</sup></b>
1,4-(CH <sub>3</sub> O) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Cr(CO) <sub>3</sub>	2920 w, 2870 w, 2800 sh, 2700 w, <b>1971 vs. 1898 vs. 1465 s, 1448 w, 1416 w, 1240 sh, 1222 vs. 1171 m, 1141 sh, 1135 w, 1078 w, 1068 s, 1010 m, 825 w, 805 m, 714 s, 662 vs cm<sup>-1</sup></b>
1,2,3-(CH <sub>3</sub> O) <sub>3</sub> C <sub>6</sub> H <sub>3</sub> Cr(CO) <sub>3</sub>	2900 sh, 2860 w, 2750 w, <b>1965 vs. 1888 vs. 1488 w, 1460 m, 1440 m, 1422 sh, 1402 m, 1273 m, 1228 m, 1150 w, 1093 s, 1024 w, 999 w, 804 w, 711 w, 678 w, 662 s cm<sup>-1</sup></b>
1,2,4-(CH <sub>3</sub> O) <sub>3</sub> C <sub>6</sub> H <sub>3</sub> Cr(CO) <sub>3</sub>	2900 sh, 2850 w, 2760 w, <b>1966 vs. 1889 vs. 1465 s, 1423 w, 1407 m, 1358 w, 1270 m, 1250 m, 1208 sh, 1198 s, 1170 w, 1150 m, 1110 w, 1028 m, 910 w, 762 w, 710 w, 663 s cm<sup>-1</sup></b>
1,3,5-(CH <sub>3</sub> O) <sub>3</sub> C <sub>6</sub> H <sub>3</sub> Cr(CO) <sub>3</sub>	2870 w, <b>1965.5 vs. 1888.5 vs. 1494 w, 1460 sh, 1445 w, 1430 w, 1396 w, 1318 m, 1242 w, 1206 sh, 1195 m, 1145 s, 1040 m, 980 w, 902 m, 733 s, 673 m cm<sup>-1</sup></b>

pounds are bright yellow solids [except for 1,3,5-(CH<sub>3</sub>O)<sub>3</sub>C<sub>6</sub>H<sub>3</sub>Cr(CO)<sub>3</sub> which is somewhat paler] and are stable in air, although their solutions in some organic solvents (carbon tetrachloride in particular) are rather vulnerable to atmospheric oxidation. This sensitivity decreases as the number of methoxy groups present in the compound increases.

TABLE 3

CHEMICAL SHIFTS OF RING PROTONS OF THE COMPLEXES AT 56.4 MC/S

See text for explanation of symbols used in columns 5, 6, and 7.

Compound	Type of spectrum	Proton No.	$\tau$ -Value in complex	$\Delta$	$\delta_2$ complex	$\delta_1$ ligand	Point no. in Fig. 1 and 2
C <sub>6</sub> H <sub>6</sub> Cr(CO) <sub>3</sub>	A <sub>6</sub>	All	4.63	1.91	0.00	0.00	0
CH <sub>3</sub> OC <sub>6</sub> H <sub>5</sub> Cr(CO) <sub>3</sub>	(AB) <sub>2</sub> X	2, 6	4.86	1.60	+0.23	+0.54	1
		3, 5	4.42	1.62	-0.21	+0.08	2
1,2-(CH <sub>3</sub> O) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Cr(CO) <sub>3</sub>	A <sub>2</sub> B <sub>2</sub>	4	5.10	1.84	+0.47	+0.54	3
		3, 6 <sup>a</sup>	4.64	1.39	+0.01	+0.53	4
		4, 5 <sup>a</sup>	4.87	1.62	+0.24	+0.53	5
1,3-(CH <sub>3</sub> O) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Cr(CO) <sub>3</sub>	AB <sub>2</sub> X	2	4.7 <sup>8</sup>	1.06	+0.15	+1.00	6
		4, 6	5.12	1.51	+0.49	+0.89	7
		5	4.38	1.43	-0.25	+0.23	8
1,4-(CH <sub>3</sub> O) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Cr(CO) <sub>3</sub>	A <sub>4</sub>	2, 3, 5, 6	4.68	1.37	+0.05	+0.59	9
1,2,3-(CH <sub>3</sub> O) <sub>3</sub> C <sub>6</sub> H <sub>3</sub> Cr(CO) <sub>3</sub>	AB <sub>2</sub>	4, 6	5.15	1.59	+0.52	+0.84	10
		5	4.50	1.32	-0.13	+0.46	11
1,2,4-(CH <sub>3</sub> O) <sub>3</sub> C <sub>6</sub> H <sub>3</sub> Cr(CO) <sub>3</sub>	ABX	3	4.68	1.03	+0.05	+0.93	12
		5	5.25	1.47	+0.62	+1.06	13
		6	4.45	1.09	-0.18	+0.64	14
1,3,5-(CH <sub>3</sub> O) <sub>3</sub> C <sub>6</sub> H <sub>3</sub> Cr(CO) <sub>3</sub>	A <sub>3</sub>	2, 4, 6	5.00	0.91	+0.37	+1.37	15

<sup>a</sup> Tentative assignment.

## RESULTS

The chromium tricarbonyl complexes of the di- and trimethoxybenzenes have been obtained, and their PMR and IR spectra measured, and in addition the spectra of C<sub>6</sub>H<sub>6</sub>Cr(CO)<sub>3</sub> and CH<sub>3</sub>OC<sub>6</sub>H<sub>5</sub>Cr(CO)<sub>3</sub> have been measured. The results are given in Tables 3-5, which also give some data derived from the free ligands for comparison. The parts of the spectra given by the ring protons were analysed by standard methods<sup>15</sup>, and the treatment used in each case is indicated in column 2 of Table 3.  $\Delta$  (column 5) is the change in chemical shift experienced by a particular proton on formation of the complex, but since this will depend upon a number of factors, including the change in ring current brought about by complex formation, the quantity  $\delta$  is also calculated.  $\delta_2$  is the chemical shift of ring proton in complex *minus* chemical shift of C<sub>6</sub>H<sub>6</sub>Cr(CO)<sub>3</sub>, and is thus a measure of the influence of the methoxy groups upon the chemical shift of aromatic protons in the complex.  $\delta_1$  is the corresponding quantity for the free ligand.

In all of the complexes the coupling constant between the methoxy and the ring protons, which is more than 1 cps in some of the free ligands, is less than 0.8 cps and was not measured accurately.

While this work was in progress Strohmeier and Hellmann<sup>16</sup> reported values for the chemical shifts of the ring protons of C<sub>6</sub>H<sub>6</sub>Cr(CO)<sub>3</sub> ( $\tau = 5.57$ ) and 1,4-(CH<sub>3</sub>O)<sub>2</sub>-

$C_6H_4Cr(CO)_3$  ( $\tau = 5.43$ ) which differ substantially from those found in this work. Their result for  $1,4-(CH_3O)_2C_6H_4$  itself is also different from that given by Weiss *et al.*<sup>12</sup>, and these discrepancies appear to be due to the former workers' use of benzene as a solvent.

TABLE 4

CHEMICAL SHIFTS OF THE METHOXY PROTONS IN THE COMPLEXES

Compound	$-OCH_3$ group attached to carbon atom No.	$\tau$ -value	Change in $\tau$ -value on complex formation (ppm)
$CH_3OC_6H_5Cr(CO)_3$	1	6.28	$\pm 0.02$
$1,2-(CH_3O)_2C_6H_4Cr(CO)_3$	1, 2	6.19	-0.04
$1,3-(CH_3O)_2C_6H_4Cr(CO)_3$	1, 3	6.24	-0.04
$1,4-(CH_3O)_2C_6H_4Cr(CO)_3$	1, 4	6.33	$\pm 0.01$
$1,2,3-(CH_3O)_3C_6H_3Cr(CO)_3$	1, 3	6.15	-0.07
	2	6.07	-0.21
$1,2,4-(CH_3O)_3C_6H_3Cr(CO)_3$	a	6.30	
	b	6.26	
	c	6.14	
	mean	6.23	-0.05
$1,3,5-(CH_3O)_3C_6H_3Cr(CO)_3$	1, 3, 5	6.19	-0.11

TABLE 5

COUPLING CONSTANTS BETWEEN THE RING PROTONS IN THE COMPLEXES

Compound	Positions of protons	$J$ in cps in the complex	$J$ in cps in the ligand
$CH_3OC_6H_5Cr(CO)_3$	2-3 = 5-6	7.2	$\sim 8$
	3-4 = 4-5	5.7	$\sim 8$
	2-4 = 4-6	1.0	$\sim 2.5$
$1,2-(CH_3O)_2C_6H_4Cr(CO)_3$	3-4 = 5-6	6.9	?
	4-5	5.3	?
	3-5 = 4-6	1.3	?
$1,3-(CH_3O)_2C_6H_4Cr(CO)_3$	2-4 = 2-6	1.8	$\sim 2.5$
	4-5 = 5-6	6.7	8.0
$1,2,3-(CH_3O)_3C_6H_3Cr(CO)_3$	4-5 = 5-6	7.0	7.9
$1,2,4-(CH_3O)_3C_6H_3Cr(CO)_3$	3-5	2.4	2.6
	5-6	7.2	8.5

## DISCUSSION

The proton magnetic resonance spectrum of benzenechromium tricarbonyl is a single line, and this would be so irrespective of whether the benzene ring possesses three- or six-fold symmetry. However, the spectrum of a *para*-disubstituted benzene may depend upon the degree of delocalization of the  $\pi$ -electron system: if only one Kekulé structure is present two of the ring protons will have a double bond between them and be flanked by single bonds, and two will enclose a single bond and be flanked by double bonds. Thus in principle it should be possible to distinguish between the two possibilities for the structure of  $ArCr(CO)_3$  by an examination of the PMR spectrum of *p*- $X_2C_6H_4Cr(CO)_3$ , where X is chosen to have negligible spin coupling with the ring protons.

The resonance of the aromatic protons in  $1,4-(\text{CH}_3\text{O})_2\text{C}_6\text{H}_4\text{Cr}(\text{CO})_3$  is a single line with a width at half-height of 1.5 cps which displays poorly resolved fine structure arising from the coupling ( $J = 0.8$  cps) to the adjacent methoxy group. Although it is difficult to estimate with certainty the difference in chemical shift of the two kinds of proton associated with a single Kekulé structure, comparison with the PMR spectra of metal-olefin complexes<sup>17</sup> suggests that a value of 0.5–1.5 ppm is not unreasonable. In the present case the observed difference is less than 0.02 ppm so the PMR results provide no evidence of significant localization of the  $\pi$ -electronic charge. Taken in conjunction with the other evidence on this point, it appears that this is because the  $\pi$ -electronic charge is completely delocalized. It should be pointed out, however, the PMR results could arise in a number of other different ways. The two different kinds of proton to be expected in the case of localization could fortuitously have the same magnetic and different chemical environments. This effect is observed in the ligand  $1,2-(\text{CH}_3\text{O})_2\text{C}_6\text{H}_4$ <sup>12</sup>, but it is unlikely to occur in all of the complexes studied, and although in most cases the spectra are more complicated as a result of spin-spin coupling among the ring protons, in no case has it been necessary to invoke localized double bonds to produce a satisfactory interpretation.

Free rotation of the rings with respect to the  $\text{Cr}(\text{CO})_3$  moiety at a reasonably rapid rate (similar to the dynamic process believed to be responsible for the magnetic equivalence of the protons in cyclo-octatetraene iron tricarbonyl<sup>18</sup>) has also been proposed as a mechanism whereby magnetic equivalence of the ring protons might be achieved.

As can be seen from Table 4 the effect of complex formation upon the chemical shift of the methoxy protons is small, and the variation observed may well be due to solvent effects. This does not necessarily imply that the oxygen atoms play no part in the bonding to the metal atom, for in the complexes the methoxy protons will be exposed to a different ring current, and this might cancel out any effect which a change in the electron density on the oxygen atom would produce.

There is a small but definite decrease in the carbonyl stretching frequency which is found as the number of methoxy groups in the ligand increases from one to three; it appears, therefore, that there is an overall increase in the  $\pi$ -electron density on the aromatic ring as the number of methoxy groups increases which in turn enables the chromium atom to transfer electrons into the anti-bonding orbitals of the CO groups. The somewhat larger coupling constants between the ring protons found in the complexes which contain most methoxy groups support this view. The fact that the ring to methoxy-proton coupling constants are smaller in the complexes than in the free ligands indicates that the interaction between the ring and the methoxy groups is reduced by complex formation. In the free ligands maximum overlap between the aromatic nucleus and the  $p$ -orbitals of the oxygen atoms is achieved when the methyl group lies in the plane of the ring<sup>19</sup>, and it may well be that the metal atom forces the methyl group out of this plane, thus reducing the interaction between the ring and its substituents. It is significant that the greatest change in chemical shift on complex formation is experienced by the central methoxy group in  $1,2,3-(\text{CH}_3\text{O})_3\text{C}_6\text{H}_3$ . It is believed<sup>19</sup> that in the free ligand this group is forced out of the plane of the ring by the steric requirements of its neighbors, so that on complex formation its position relative to the ring might remain unaltered, and the full effect of a change in electron density on the oxygen atom would be displayed.

It has been shown by HMO calculation that the chemical shifts of the ring protons in the methoxybenzenes have a linear dependence on the electron densities at the carbon atoms to which they are attached<sup>12</sup>. For the present purpose it is more convenient to adopt a simpler approach (*cf. e.g. ref. 20*) and assume that the chemical shift of a particular proton is an additive function of the number of methoxy groups which are *o*-, *m*-, and *p*- to it.

TABLE 6

ADDITIVE CONTRIBUTION OF A METHOXY GROUP TO THE CHEMICAL SHIFT OF A RING PROTON IN THE FREE AND COMPLEXED LIGANDS

Position of group	Free ligand	Complex
<i>ortho</i> -	+0.48 ppm	+0.20 ppm
<i>meta</i> -	+0.10 ppm	-0.20 ppm
<i>para</i> -	+0.45 ppm	+0.45 ppm

The best agreement between the calculated and observed values is obtained when the constants listed in Table 6 are used: the calculated value is the sum of the appropriate constants for a particular proton, and the observed value is  $\delta_2$  (in the complex) or  $\delta_1$  (in the free ligand) of Table 3. The success of this approach can be judged from Figs. 1 and 2; the deviation shown by points 10 and 11 of Fig. 1 is proba-

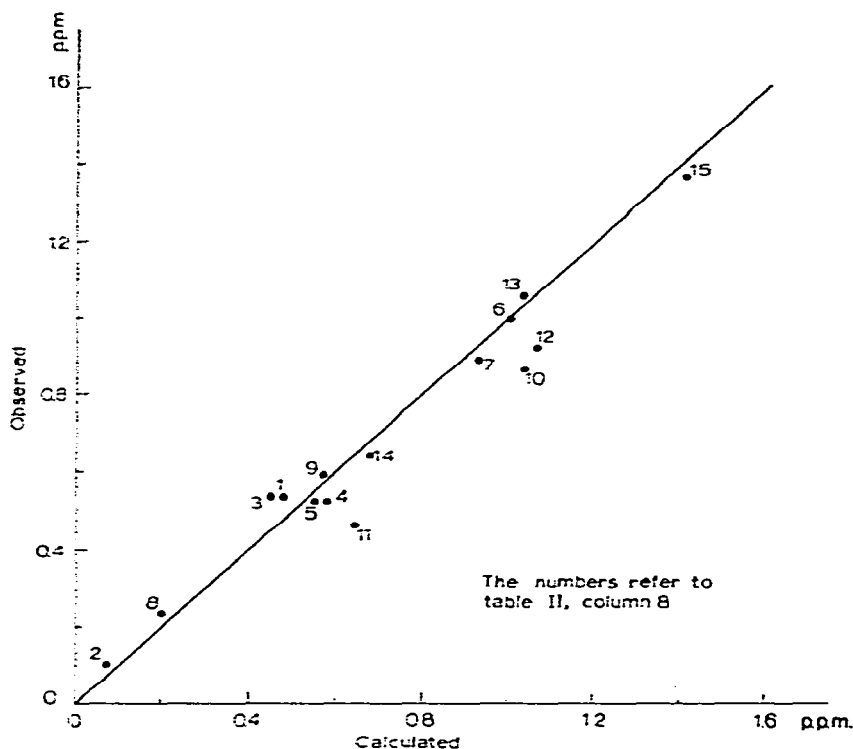


Fig. 1. Observed vs. calculated change in chemical shift of ring protons on adding  $-\text{OCH}_3$  groups to an aromatic nucleus.

bly due to the steric overcrowding in 1,2,3-(CH<sub>3</sub>O)<sub>3</sub>C<sub>6</sub>H<sub>3</sub>, and even so the agreement is as good as obtained by molecular orbital calculations. The spread of the points for the complexes is somewhat greater (Fig. 2), but the constants of Table 6 still give useful predictions.

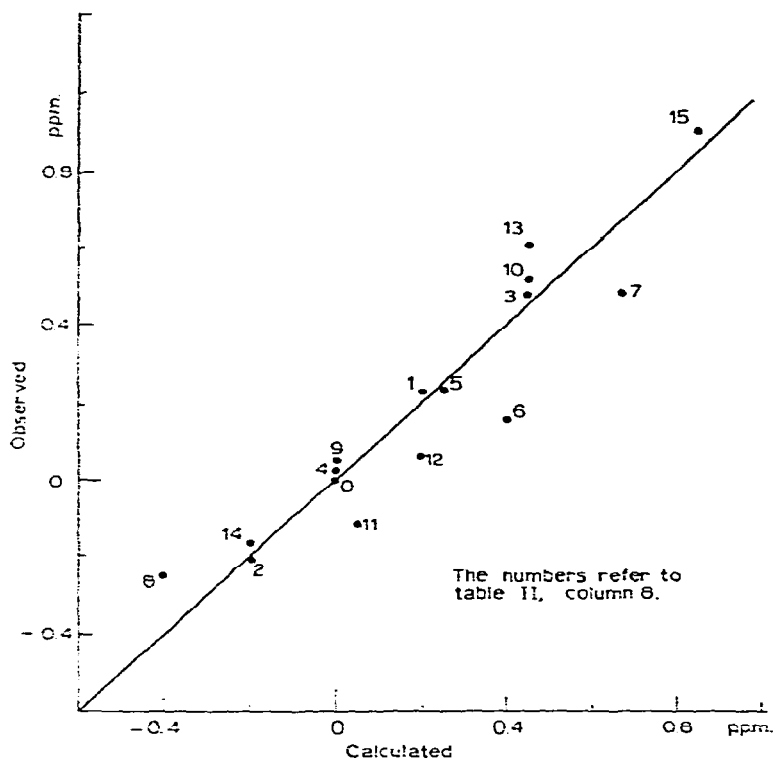


Fig. 2. Observed vs. calculated change in chemical shift of ring protons on adding -OCH<sub>3</sub> groups to an aromatic nucleus bound to Cr(CO)<sub>3</sub>.

It is often supposed that the influence of a *meta*-substituent in an aromatic nucleus depends mainly on the inductive effect<sup>21</sup>, whereas mesomerism plays an important part in determining the effects of *ortho*- and *para*-substituents. The figures in Table 6 would then suggest that the ability of an aromatic nucleus to transmit mesomeric effects is little affected by association with a Cr(CO)<sub>3</sub> moiety, whereas there is a considerable change in inductive effects. Clearly a wide range of complexes in which the aromatic ring carries a variety of substituents must be studied before definite conclusions can be drawn; it may be significant that the methoxy group is one of the few groups for which the Hammett constants,  $\sigma_m$  and  $\sigma_p$  are of opposite sign.

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#### SUMMARY

The high resolution proton magnetic resonance spectrum of 1,4-dimethoxybenzenechromium tricarbonyl furnishes no evidence for a trigonal distortion of the aromatic nucleus in this complex. The PMR and infrared spectra of benzene- and anisole-chromium tricarbonyl and five previously unreported polymethoxybenzenechromium tricarbonyl complexes are also reported and discussed. A simple method for predicting the chemical shifts of the ring protons in both ligands and complexes is presented.

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