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SUBSTITUENT EFFECTS IN π-(TRICARBONYLCHROMIUM)ARENES

I. ^{1}H NMR SPECTROSCOPY OF ALKYLSUBSTITUTED π-(TRICARBONYLCHROMIUM)BENZENES

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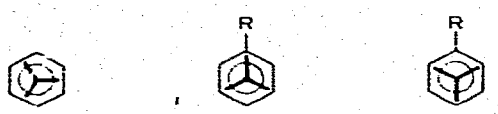
Summary

Some thirty substituted π-(tricarbonylchromium)benzenes, including some crowded alkylsubstituted complexes, e.g. (1′,1′-diethylpropyl)-, (1′-t-butyl-2′,2′-dimethylpropyl)-, 1,2-di-t-butyl- and 1,2,4-tri-t-butyl-π-(tricarbonylchromium)-benzenes, have been prepared. ^{1}H NMR spectra have been recorded from acetone solutions of the complexes. Using the chemical shift increments of the aromatic protons on complex formation of C_6H_5CH-t-Bu_2 as a reference for the eclipsed conformation with the substituent staggered with respect to the carbonyl ligands, the contribution of this conformer to the conformational equilibrium of the other monoalkylsubstituted complexes has been estimated. ^{1}H NMR spectroscopy turns out to be a useful probe in conformation analysis of π-(tricarbonylchromium)-arenes.

Introduction

The orientation of the $Cr(CO)_3$ group with respect to the arene ring in π-(tricarbonylchromium)benzene and its derivatives has been studied by X-ray and NMR techniques. The first technique showed a staggered conformation I for the benzene and the hexamethylbenzene complex, but eclipsed * conformations II or III for the monosubstituted derivatives [1]. The preference for II or III in the latter compounds seems to be governed by the effect of R on the charge distribution in the benzene ring (preference for II for R = OMe or alkyl, preference for III for R = COOMe). Furthermore, the molecular structure of some disubstituted π-(tricarbonylchromium)benzenes [3] is consistent with this view.

* Cf., however, the staggered conformation found in π-(tricarbonylchromium)acetophenone [2].



I II III

As to the conformation of these compounds in solution, the preference seems far from pronounced. Variable temperature ^1H [4,5] and ^{13}C [6,7] NMR spectra of monosubstituted π-(tricarbonylchromium)benzenes have been analysed in terms of a rapid equilibrium between the conformers II and III. For R = Me, Et, i-Pr or OMe enthalpy differences in favour of II (estimated to be less than 1 kcal mol^{-1}) are opposed by entropy differences in favour of III [4]. Here both conformers are present in solution in substantial amounts at room temperature. With increasing bulkiness of R conformation II is expected to become destabilised by steric interaction between R and the eclipsing carbonyl ligand. Accordingly, for R = t-Bu ^1H NMR spectra [4] indicate that the system prefers conformation III. The effect of steric interactions was further demonstrated by the conformation of 4-t-butyl-π-(tricarbonylchromium)benzoic acid in the solid phase [8].

In order to gain more insight into the directing effects of alkyl groups on the conformation of the π-tricarbonylchromium group with respect to the phenyl ring in alkyl-π-(tricarbonylchromium)benzenes we have measured ^1H NMR spectra of a series of complexes with R varying in size from Me to $CH\text{-}t\text{-}Bu_2$. In addition some di- and tri-alkylsubstituted benzene complexes have been included. Moreover, attention was paid to the effects on conformational preference of some other relatively large sized groups, i.e. the trimethylsilyl and the trifluoromethyl group, which differ substantially from the alkyl groups as to their electronic effect.

Experimental

Substituted benzenes were preparations of this laboratory or commercial products; purity was checked by GLC. Commercial hexacarbonylchromium (Strem Chemicals Inc.) was purified by sublimation in vacuo. Solvents were Baker analysed reagents; before use they were freed from oxygen by repeated degassing and saturation with nitrogen. All preparations were carried out under nitrogen.

Preparation of the π-tricarbonylchromium complexes. The complexes were prepared by thermal reaction of equimolar quantities of the benzene derivative and hexacarbonylchromium in boiling dibutyl ether at atmospheric pressure, using the apparatus described by Strohmeier [9]. The reaction was run until no more hexacarbonylchromium appeared in the cold regions of the system. The time required amounted to 6—15 h. After cooling, the solvent was removed by distillation in vacuo. The residu was extracted with hot petroleum ether (b.p. 60—80°C). The π-tricarbonylchromium complexes were crystallized from this solution. Recrystallization from light petroleum ether usually afforded analytically pure complexes. Analytical data and melting points are given in Table 1.

Spectral measurements. ^1H NMR spectra were obtained on Varian T-60, XL-100-15 and HR-300 spectrometers. Tetramethylsilane was used as internal

TABLE 1

ANALYTICAL RESULTS OF THE SUBSTITUTED π-(TRICARBONYLCHROMIUM)BENZENES

Substituent(s)	Melting point (°C)	Reference melting point(s) (°C)	Analyses found (calcd.) (%)	
			C	H
Me	81.0—82.5	80—81 [a,c]		
Et	48—49	48—49 [c]		
neoPent	122—123		59.3 (59.15)	5.8 (5.67)
i-Pr	62—63	63—64 [c] 61—62 [d]		
t-Bu	79—80	83.5—84.5 [b] 79.5—80.5 [c]		
CEt_3	103.5—104.0		61.6 (61.52)	6.7 (6.45)
$CH\text{-}t\text{-}Bu_2$	139—140		63.6 (63.51)	7.4 (7.11)
OMe	82.5—83.5	83—84 [a,c]		
$SiMe_3$	72.0—72.5		50.6 (50.34)	5.1 (4.93)
none	160—162	161.5—163.0 [a] 160—162 [c]		
COOMe	97.5—98.5	97.5—98.5 [b] 98—99 [e]		
CF_3	46.5—47.5		42.8 (42.57)	2.2 (1.79)
$1,2\text{-}Me_2$	90.0—90.5	98.5—99.0 [a]		
$1,2\text{-}Et_2$	26—27		57.6 (57.77)	5.4 (5.18)
$1,2\text{-}neoPent_2$	64.5—65.0		64.3 (64.39)	7.4 (7.39)
$1,2\text{-}i\text{-}Pr_2$	121.0—122.5		60.2 (60.39)	6.2 (6.08)
$1,2\text{-}t\text{-}Bu_2$	119—121		62.7 (62.56)	6.9 (6.80)
$1,2\text{-}(SiMe_3)_2$	82—82		50.4 (50.26)	6.4 (6.19)
$1,3\text{-}Me_2$	105—106	105—106 [b]		
$1,3\text{-}t\text{-}Bu_2$	136.5—139.0	136—138 [c]		
$1,3\text{-}(SiMe_3)_2$	104.5—106.0		50.3 (50.26)	6.5 (6.19)
$1,4\text{-}t\text{-}Bu_2$	140.5—142.0	139—141 [c] 140—141 [d]		
$1,4\text{-}(SiMe_3)_2$	125.0—125.5	123—124 [d]		
$1,3,5\text{-}Me_3$	172—173	172—174 [a]		
$1,3,5\text{-}Et_3$	96		60.5 (60.39)	6.3 (6.08)
$1,3,5\text{-}neo\text{-}Pent_3$	192 (dec.)		67.7 (67.89)	9.0 (8.55)
$1,3,5\text{-}i\text{-}Pr_3$	106.5—107.5		63.7 (63.51)	7.2 (7.10)
$1,3,5\text{-}t\text{-}Bu_3$	176—177	175—177 [c]		
$1,3\text{-}t\text{-}Bu_2\text{-}5\text{-}Me$	127—128		63.4 (63.51)	7.4 (7.10)
$1,2,4\text{-}t\text{-}Bu_3$	119—120		66.1 (65.94)	8.2 (7.91)

[a] Ref. 10. [b] Ref. 4. [c] Ref. 11. [d] Ref. 12. [e] Ref. 13.

reference. The data reported are for approximately 0.5 *M* solutions in acetone-d_6. All peak areas showed the correct relative intensities. The actual chemical shifts of the aromatic protons can be obtained by adding $\Delta\delta$ to the chemical shifts of benzene or π-(tricarbonylchromium)benzene protons. The $\Delta\delta$-values are considered to be better than ±0.02 ppm. Computations for spectrum simulation were performed on an IBM 370/158 computer, using the computer program LAME [14].

Results

Operating at 100 MHz, ^1H NMR spectra of the substituted π-(tricarbonylchromium)benzenes are easily interpretable. In monoalkylsubstituted benzenes

(continued on p. 346)

TABLE 2

PROTON NMR DATA [a] OF C_6H_5R AND THEIR π-$Cr(CO)_3$ COMPLEXES

R	Free ligand						Complex					
	$\Delta\delta(H_{2,6})$	$\Delta\delta(H_{3,5})$	$\Delta\delta(H_4)$	$\delta(CH_3)$	$\delta(CH_2)$	$\delta(CH)$	$\Delta\delta(H_{2,6})$	$\Delta\delta(H_{3,5})$	$\Delta\delta(H_4)$	$\delta(CH_3)$	$\delta(CH_2)$	$\delta(CH)$
H	0.00	0.00	0.00				0.00	0.00	0.00			
Me	−0.16 [b]	−0.08 [b]	−0.16 [b]	2.20			−0.19	+0.03	−0.25	2.19		
Et	−0.14 [b]	−0.05 [b]	−0.17 [b]	1.17	2.59		−0.15	−0.01	−0.19	1.21	2.46	
n-Pent	−0.28 [c]	−0.18 [c]	−0.25 [c]	0.93	2.53		−0.23	−0.01	−0.22	0.98	2.26	
i-Pr	−0.13 [b]	−0.08 [b]	−0.18 [b]	1.21		2.88	−0.06	−0.06	−0.06	1.27		2.68
t-Bu	+0.02 [b]	−0.10 [b]	−0.24 [b]	1.27			+0.15	−0.17	−0.02	1.32		
CEt_3	−0.10 [c]	−0.13 [c]	−0.29 [c]	0.67	1.73		+0.13	−0.21	+0.06	0.86	1.71	
CH-t-Bu_2	+0.15 [c]	−0.06 [c]	−0.15 [c]	1.04			+0.45	−0.25		0.97		2.16
	−0.28 [c]	−0.12 [c]				2.41	+0.12	−0.32	+0.26	1.33		
OMe	−0.45 [d]	−0.10 [d]	−0.42 [d]				−0.19	+0.21	−0.51	3.76		
$SiMe_3$	−0.10	−0.31	−0.30	0.25			+0.08	−0.20	+0.19	0.32		
COOMe	+0.72 [d]	+0.15 [d]	+0.26 [d]	3.93			+0.62	0.00	+0.27	3.86		
CF_3	+0.25 [c]	+0.13 [c]	+0.20 [c]				+0.40	+0.02	+0.25			

[a] Solvent, acetone-d_6; 100 MHz; $\Delta\delta$ is the chemical shift increment (in ppm) on substitution relative to C_6H_6 (δ 7.35 ppm) for the free ligands and relative to $C_6H_6Cr(CO)_3$ (δ 5.63 ppm) for the complexes; δ-values are given in ppm relative to tetramethylsilane as internal standard. [b] $\Delta\delta$-Values estimated from Bovey et al. [23]; 200 MHz; solvent, carbon tetrachloride. [c] From 300 MHz spectra. [d] $\Delta\delta$-Values taken from ref. 24; 60 MHz; solvent, acetone-d_6.

TABLE 3

PROTON NMR DATA [a] OF DI- AND TRI-SUBSTITUTED BENZENES AND THEIR π-$Cr(CO)_3$ COMPLEXES

Substituents	Type [b]	Δδ					δ(CH_3)	δ(CH_2)	δ(CH)
		H_2	H_3	H_4	H_5	H_6			
1,2-Me_2	L		−0.29	−0.29	−0.29	−0.29	2.19		
1,2-Me_2	C		−0.05	−0.17	−0.17	−0.05	2.19		
1,2-Et_2	L		−0.24	−0.24	−0.24	−0.24	1.17	2.64	
1,2-Et_2	C		−0.07	−0.07	−0.07	−0.07	1.23	2.41 [c], 2.64 [c]	
1,2-neoPent$_2$	L		−0.22	−0.22	−0.22	−0.22	0.87	2.69	
1,2-neoPent$_2$	C		+0.09	−0.07	−0.07	+0.09	1.10	2.23 [d], 2.37 [d]	
1,2-i-Pr_2	L		−0.13	−0.27	−0.27	−0.13	1.21		3.29
1,2-i-Pr_2	C		−0.06	−0.06	−0.06	−0.06	1.25, 1.27		3.09
1,2-t-Bu_2	L		+0.22	−0.25	−0.25	+0.22	1.52		
1,2-t-Bu_2	C		+0.18	−0.06	−0.06	+0.18	1.57		
1,2-$(SiMe_3)_2$	L		+0.30	−0.06	−0.06	+0.30	0.37		
1,2-$(SiMe_3)_2$	C		+0.03	−0.03	−0.03	+0.03	0.41		
1,3-Me_2	L	−0.40		−0.42	−0.26	−0.42	2.25		
1,3-Me_2	C	−0.31		−0.36	+0.08	−0.36	2.21		
1,3-t-Bu_2	L	+0.02		−0.26	−0.24	−0.26	1.31		
1,3-t-Bu_2	C	+0.36		+0.25	−0.26	+0.25	1.33		
1,3-$(SiMe_3)_2$	L	+0.39		+0.19	−0.02	+0.19	0.29		
1,3-$(SiMe_3)_2$	C	+0.12		+0.21	−0.30	+0.21	0.30		
1,4-Me_2 [e]	L	−0.30	−0.30		−0.30	−0.30			
1,4-Me_2 [e]	C	−0.07	−0.07		−0.07	−0.07			
1,4-t-Bu_2	L	−0.03	−0.03		−0.03	−0.03	1.29		
1,4-t-Bu_2	C	+0.05	+0.05		+0.05	+0.05	1.32		
1,4-$(SiMe_3)_2$	L	+0.18	+0.18		+0.18	+0.18	0.24		
1,4-$(SiMe_3)_2$	C	−0.07	−0.07		−0.07	−0.07	0.32		
1,3,5-Me_3	L	−0.57		−0.57		−0.57	2.22		
1,3,5-Me_3	C	−0.41		−0.41		−0.41	2.22		
1,3,5-Et_3	L	−0.45		−0.45		−0.45	1.18	2.58	
1,3,5-Et_3	C	−0.29		−0.29		−0.29	1.23	2.50	
1,3,5-neoPent$_3$	L	−0.55		−0.55		−0.55	0.92	2.47	
1,3,5-neoPent$_3$	C	−0.41		−0.41		−0.41	1.01	2.31	
1,3,5-i-Pr_3	L	−0.38		−0.38		−0.38	1.23		2.88
1,3,5-i-Pr_3	C	−0.11		−0.11		−0.11	1.25		2.67
1,3,5-t-Bu_3	L	−0.05		−0.05		−0.05	1.33		
1,3,5-t-Bu_3	C	+0.47		+0.47		+0.47	1.30		
1,3-t-Bu_2-5-Me	L	−0.08		−0.31		−0.31	1.28, 2.30		
1,3-t-Bu_2-5-Me	C	+0.16		+0.16		+0.16	1.34, 2.21		
1,2,4-t-Bu_3	L		+0.33		−0.22	+0.20	1.30, 1.53, 1.55		
1,2,4-t-Bu_3	C		+0.44		+0.24	+0.05	1.30, 1.60		

[a] Solvent, acetone-d_6: Δδ is the chemical shift increment (in ppm) on substitution relative to C_6H_6 (δ 7.35 ppm) for the free ligands and relative to $C_6H_6Cr(CO)_3$ (δ 5.63 ppm) for the complexes; δ-values are given in ppm relative to tetramethylsilane as internal standard. [b] Free ligand (L) or π-$Cr(CO)_3$ complex (C). [c] ABX_3-system, J_{AB} = 14.9 Hz, $J_{AX} = J_{BX}$ = 7.4 Hz. [d] AB-system, J_{AB} = 7.0 Hz. [e] From ref. 24.

the chemical shifts of the aromatic protons differ only slightly. Accordingly, the interpretation of the aromatic proton region of the spectra of these compounds usually requires high-field magnetic resonance techniques. The assignments of the aromatic protons in neopentylbenzene, (1′,1′-diethylpropyl)benzene and (1′-t-butyl-2′,2′-dimethylpropyl)benzene, which were not available in the literature, were obtained from 300 MHz ^{1}H NMR spectra.

A problem arises in the assignment of the aromatic protons of the 1,2-dialkylsubstituted benzenes and the corresponding π-tricarbonylchromium complexes. Since in all cases a completely symmetric signal was obtained it is not possible to assign e.g. the upfield part of it to either $H_{3,6}$ or $H_{4,5}$. For the 1,2-dimethylbenzene complex the assignment was settled by the spectrum of 4-deutero-1,2-dimethyl-π-(tricarbonylchromium)benzene. Where necessary, the signals have been tentatively assigned on the basis of additivity of the increments obtained for the monosubstituted benzenes, although this is debatable [15]. Furthermore, a conservation of this order is assumed on complex formation.

All assignments have been checked and, if necessary, corrected by matching simulated and experimental spectra. The data obtained are summarized in Tables 2 and 3.

Discussion

In substituted benzenes proton chemical shifts are known to reflect the π-electron charge densities on the carbon atoms to which the protons are attached [16]. In addition other influences, such as ring current effects and long range effects associated with the substituent, act upon the proton chemical shifts. *Ortho* protons are influenced rather strongly by inductive substituent effects. Influences on *meta* and *para* protons are generally smaller, but less perceptible to other effects [17]. For the $Cr(CO)_3$ complexes π-electron densities are not available. Since in monoalkylsubstituted π-(tricarbonylchromium)benzenes the electronic and mesomeric effects differ only slightly, it is possible to relate the shift ($\theta(H_x)$) of a certain proton on complex formation, defined as $\Delta\delta_{complex}(H_x) - \Delta\delta_{arene}(H_x)$, to conformational effects. In Fig. 1 the θ-values for *ortho*, *meta* and *para* protons are given as a function of the bulkiness of the alkyl group used. Although a theoretical basis is missing, it is generally accepted that in the preferred conformation the protons eclipsed with carbonyl groups are relatively deshielded, i.e. θ is positive [4,18]. Since threefold symmetry is clearly involved, the anisotropy of the carbon monoxide bond might be responsible for the observed deshielding. From Fig. 1 we conclude that with increasing bulkiness of R the contribution of conformer III increases at the cost of the electronically favoured conformer II. This is in accordance with the findings of Jackson et al. [4]. However, it should be emphasized here that for R = CH-t-Bu$_2$ the value of $\theta(meta) - \theta(para)$ is distinctly larger than the value * selected by Jackson et al. [4].

A high barrier to rotation (approximately 22 kcal mol^{-1} at room temperature) has been reported for the rotation about the C(sp^2)—C(sp^3) bond in (1′-t-butyl-

* These authors propose $\theta(meta) - \theta(para)$ = 0.45 ppm, to represent complete preference for conformation III.

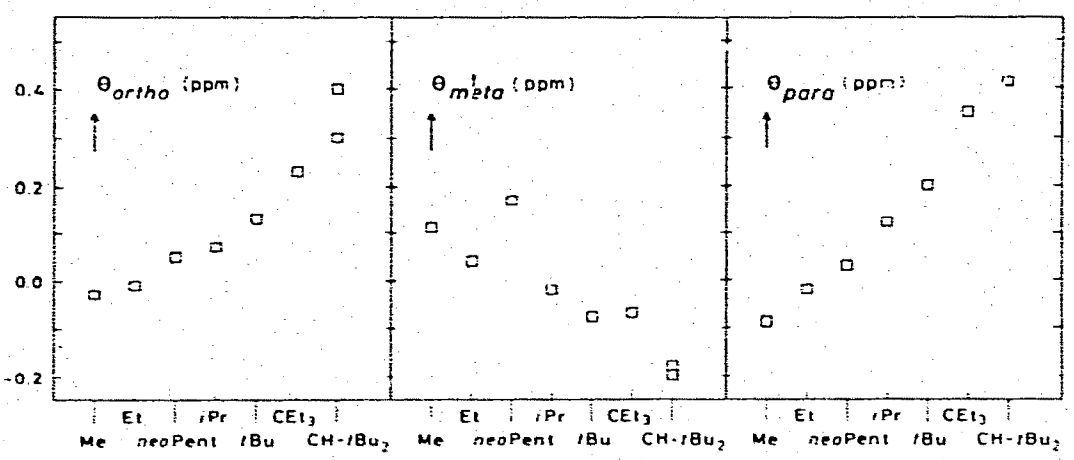


Fig. 1. θ-Values for *ortho*, *meta* and *para* protons of the monoalkylsubstituted benzenes.

2',2'-dimethylpropyl)benzene [19]. This is expressed in a significant non-equivalence of the *ortho* protons and to a lesser extent of the *meta* protons.

The preferred conformation of the CH-t-Bu_2 group with respect to the arene ring is given in Fig. 2. Moreover, it is not surprising to find the two t-Bu groups to be non-equivalent in the corresponding $Cr(CO)_3$ complex; the chemical shift of the *exo* t-Bu group corresponds to the value found in neopentyl-π-(tricarbonylchromium)benzene, whereas the *endo* t-Bu group shows an abnormal low-field resonance. The observed paramagnetic shift may be cooperatively caused by van der Waals repulsion and magnetic anisotropy of the $Cr(CO)_3$ group. For this compound it is evident from molecular models, that in conformation II one of the t-Bu groups would interact unacceptably with the $Cr(CO)_3$ moiety. The contribution of conformation II to the conformational equilibrium is therefore neglected for this compound. Unfavourable interactions are visually minimized in an approximately eclipsed conformation (III). It is supported by IR [20], that only minor distortion of valence angles are imposed by this geometry.

Starting from a complete conformational preference (III) for R = CH-t-Bu_2 (i.e. $\Theta_{max} = -1.21$ ppm), it is possible to estimate the conformer population of

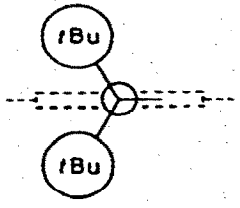


Fig. 2. Newman projection along the C(sp^2)—C(sp^3) bond in (1'-t-butyl-2',2'-dimethylpropyl)benzene.

TABLE 4

Θ-VALUES AND POPULATIONS OF CONFORMATION II (P_{II}) IN $C_6H_5RCr(CO)_3$ AT 33 ± 5°C

R	Θ [a] (ppm)	P_{II} (%) [b]
Me	+0.20	67
Et	+0.06	55
neoPent	+0.14	62
i-Pr	−0.10	42
t-Bu	−0.29	26
CEt_3	−0.43	15
$CH\text{-}t\text{-}Bu_2$	−0.60[5]	

[a] $\Theta = \theta(meta) - \theta(para)$. [b] $P_{II} = 100 \times (0.5 - \Theta/\Theta_{max})$, with $\Theta_{max} = -1.21$ ppm.

the other monoalkylsubstituted complexes, using the approach of Jackson et al. [4]. The results are given in Table 4.

The populations obtained are qualitatively in agreement with values reported previously [4]. The neopentyl group is found to act like a methyl group, probably due to its positive inductive effect. It should be noted that Roques et al. [5,6], in their treatment of ^1H and ^{13}C NMR chemical shifts of alkylbenzenes and corresponding $Cr(CO)_3$ complexes, take no account of the incomplete conformational preference reported for t-butyl-π-(tricarbonylchromium)benzene (ΔG^0 ~0.5 kcal mol^{-1} [4]). The present figures reveal a free energy difference of 0.6 and 1.0 kcal mol^{-1} in favour of conformation III for R = t-Bu and CEt_3 respectively.

Although mesomeric and electronic effects of the other substituents investigated differ considerably, the signs of $\theta(meta) - \theta(para)$ point to conformational preferences which are consistent with results from X-ray and previous ^1H NMR investigations. On the present basis further conclusions are without foundation.

A high conformational preference is obtained for trimethylsilyl-π-(tricarbonylchromium)benzene (conformation III ~80%) relatively to t-butyl-π-(tricarbonylchromium)benzene. This is explained by assuming that the steric interaction between R = $SiMe_3$ and the $Cr(CO)_3$ group (though smaller than for R = t-Bu) is hardly opposed by an electronic effect favouring conformation II.

The trifluoromethyl group is known to exert a strong electron-withdrawing effect, whereas its mesomeric effect is considered to be small. In trifluoromethyl-π-(tricarbonylchromium)benzene, this electronic effect in combination with the bulkiness of the CF_3 group, is expected to lead to a strong preference for conformation III. This is, however, not reflected in the value of $\theta(meta) - \theta(para)$. Additional work seems required to settle this.

Comparison of the Δδ-values of the 1,2- and 1,4-dialkylbenzenes with those of the corresponding $Cr(CO)_3$ complexes, does not permit firm conclusions on conformer populations. On close examination of molecular models, taking into account the small free energy differences for the monoalkylsubstituted complexes, this is not surprising.

In 1,2-diethyl- and 1,2-dineopentyl-π-(tricarbonylchromium)benzene, the methylene protons are diastereotopic, due to molecular asymmetry. The same holds for the methyl groups in 1,2-diisopropyl-π-(tricarbonylchromium)benzene. For related systems this was shown previously [21]. An excellent example of an

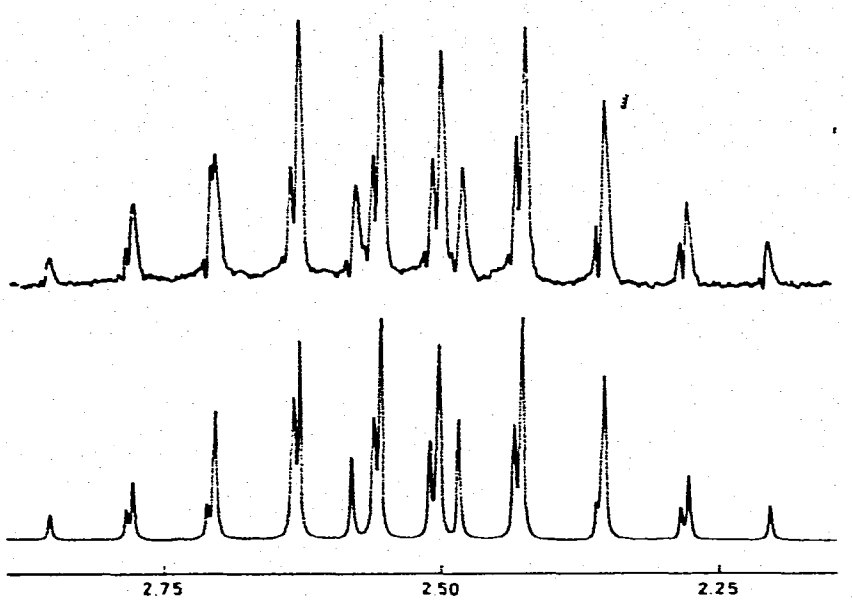


Fig. 3. Experimental (top) and calculated (bottom) ^{1}H NMR spectrum of the methylene protons in 1,2-diethyl-π-(tricarbonylchromium)benzene.

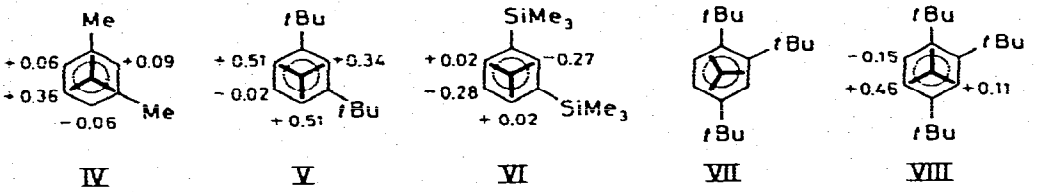


Fig. 4. Preferred conformations in some substituted π-(tricarbonylchromium)benzenes. (The figures given represent θ-values of the protons concerned.)

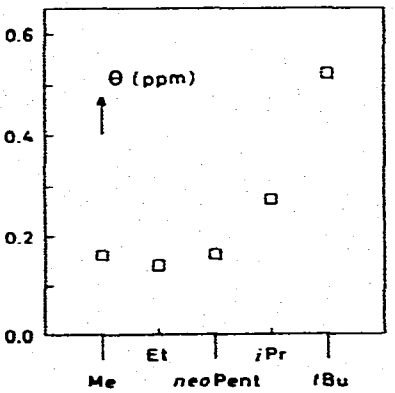


Fig. 5. θ-Values for $H_{2,4,6}$ of the symmetrically trisubstituted benzenes.

ABX_3-system is given in Fig. 3, in which observed and calculated spectra of 1,2-diethyl-π-(tricarbonylchromium)benzene are shown.

The $\Delta\delta$-values obtained for 1,3-dialkylsubstituted π-(tricarbonylchromium)-benzenes generally show preference for a single conformation. As suggested previously [4], 1,3-dimethyl- and 1,3-di-t-butyl-π-(tricarbonylchromium)benzene prefer the eclipsed conformations IV and V respectively, as clearly shown by the θ-values obtained here (Fig. 4). The preference found for 1,3-di-trimethylsilyl-π-(tricarbonylchromium)benzene (VI) is in accordance with the results obtained for the corresponding monosubstituted complex.

Further support for the dominance of steric effects on the conformer equilibrium is given by the chemical shift comparison of the symmetric trialkylsubstituted benzenes and the corresponding π-$Cr(CO)_3$ complexes. As shown in Fig. 5, β-branching of the alkyl group had almost no effect, whereas θ was found to increase progressively upon α-branching. The data obtained for the 1,3-di-t-butyl-5-methyl substituted benzene complex fit in with those of the symmetric trialkylsubstituted π-(tricarbonylchromium)benzenes. At first sight, 1,2,4-tri-t-butyl-π-(tricarbonylchromium)benzene would be expected to prefer the staggered conformation VII (Fig. 4). The observed $\theta(H_5)$ however, indicates a substantial contribution of the eclipsed conformation VIII (Fig. 4).

Furthermore, it should be noted that irrespective of conformational preference in the complexes, the protons on α-carbon atoms of the alkyl groups are relatively shielded compared to the corresponding protons in free arenes. On the other hand a deshielding of protons on β- and γ-atoms occur. Probably, this should be related to polarisation of the $C(sp^2)$—$C(sp^3)$ bond, which increases on complex formation [22,24].

Conclusions

In a π-(tricarbonylchromium)benzene complex, an alkyl group, by its electronic effect, tends to orientate the $Cr(CO)_3$ group into conformation II. Adverse steric interaction of a bulky alkyl group with a superimposed carbonyl ligand favours conformation III. The bulkiness of the alkyl group determines the conformational equilibrium constant. ^1H NMR is shown to be useful as a probe for conformation analysis.

Care should be taken not to overemphasize steric effects; the preparation of $Cr(CO)_3$ complexes from benzene derivates carrying a very bulky group or some t-Bu groups is easily achieved.

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