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ELECTRIC DIPOLE MOMENTS AND ANISOTROPIC OPTICAL POLARISABILITIES OF METHYL- AND t-BUTYL-SUBSTITUTED (η^6-BENZENE)TRICARBONYLCHROMIUM(0) COMPLEXES: THEIR RELEVANCE TO THE NATURE OF THE CHROMIUM–ARENE BOND

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Summary

Determinations of the electric dipole moments, carbonyl stretching frequencies and anisotropic optical polarisabilities are reported for $[Cr(CO)_3(\eta^6\text{-}C_6H_6)]$ and for nine of its methyl- and t-butyl-substituted derivatives in cyclohexane solution. The effects of progressive substitution are approximately additive. For each complex, the molecular optical anisotropy from experiment is opposite in sign to that predicted from additivity of the anisotropies of the component arene and $Cr(CO)_3$ fragments. Coordination between the fragments leads to a very large enhancement of polarisability along the Cr–arene axis while the polarisabilities perpendicular to that axis (parallel to the benzenoid ring) are lowered. The electron system constituting the Cr–arene bond is highly polarisable along the bond and provides a channel of relatively free electron movement between the arene and $Cr(CO)_3$. The results are consistent with a postulated large magnetic anisotropy for the Cr–arene bond. The aromatic character of the complexed arene is diminished relative to that of the free ligand.

Introduction

Much interest has centred on the nature of the Cr–arene bond in the complexes $[Cr(CO)_3(\eta^6\text{-arene})]$ and on the transmission of electronic effects between the benzenoid system, substituent groups on the arene, and the coordinated $Cr(CO)_3$ moiety. It has been proposed that the metal–ring bond involves a mixing of the metal valence orbitals with both the σ-framework and the π-system of the aromatic ring resulting in ring → metal electron displacement and concomitant metal → ring

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(π^*) "back-bonding" [1,2]. The $Cr(CO)_3$ group in such complexes is thought to be strongly electron-withdrawing [3], i.e. a net electron charge drift occurs from the arene to the metal. Competing arguments have been advanced to suggest (a) a predominant depletion of electrons from the arene ring carbon σ-orbitals rather than the ring π-system or (b) that the arene π-electron density is preferentially depleted thus diminishing the aromaticity of the benzenoid nucleus. A substantive account, detailing the many relevant references, is given in the recent review of Davis and Kane-Maguire [4].

Direct evidence for arene → Cr electron charge displacement is provided by electric dipole moment measurements [5–10]. It was found that the dipole moment of the parent complex $[Cr(CO)_3(\eta^6\text{-}C_6H_6)]$ is increased by electron-releasing substituents on the benzene ring and is decreased by electron-withdrawing substituents. The dipole moment can also be affected by interaction of the complex with electron-donor solvents such as dioxane or benzene, where, it is thought, the arene group acts as an electron acceptor [7,10].

This paper reports a systematic study of the dipole moments, infrared carbonyl stretching frequencies (A_1) and electric birefringences of $[Cr(CO)_3(\eta^6\text{-}C_6H_6)]$ and of a series of methyl- and t-butyl-substituted derivatives. All of the measurements were made in dilute solution in cyclohexane which is regarded as an "innocent" solvent. From analysis of the experimental data, the polarisability anisotropy of each of the solute molecules was derived. These were compared with the anisotropies of the uncomplexed arene molecules to gauge the effects of complex formation. Changes in the directional polarisabilities, electric dipole moments and carbonyl infrared stretching frequencies with methyl and t-butyl substitution were explored.

Experimental

The complexes were prepared by refluxing under nitrogen, $Cr(CO)_6$ with an excess of the arene in either 2-picoline or 2,4,6-trimethylpyridine except in the case of the tri-t-butylbenzene complex which was prepared in n-butyl ether [3,11,12]. They were purified by repeated sublimation. The melting points agreed well with the literature values. In each case purity was confirmed by microanalysis. Cyclohexane was fractionated and stored over sodium; appropriate physical constants for the solvent are given in [13].

Solute dipole moments μ and electric birefringences, the latter expressed as molar Kerr constants ${}_{m}K$, were determined at 298 K. The apparatus, techniques of measurement, symbols and methods of calculation have been described before [13–15]. For each compound incremental changes in the relative permittivities, densities, refractive indices and Kerr constants ($\Delta\epsilon$, Δd, Δn, and ΔB, respectively) were measured for a range of solutions having solute weight fractions w_2. The Δn and ΔB measurements were made at 589 nm. Coefficients $\alpha\epsilon_1$, β, γ and δ were derived from the measured quantities using the relations: $\alpha\epsilon_1 = \Sigma\Delta\epsilon/\Sigma w_2$; $\beta = \Sigma\Delta d/d_1\Sigma w_2$; $\gamma = \Sigma\Delta n/n_1\Sigma w_2$; $\delta = \Sigma\Delta B/B_1\Sigma w_2$. The subscripts 1 and 2 refer in turn to the solvent and solute. Oxygen was removed from the solvent by saturating it with dry nitrogen; the preparation and handling of solutions were carried out under dry, inert (N_2) atmosphere. The results are summarised in Table 1. Included also in this table (column 9) are electric dipole moments, designated μ(loss), which were obtained from measurements of the microwave dielectric loss at frequencies 1.141,

TABLE 1

MOLAR POLARISATIONS AND REFRACTIONS, DIPOLE MOMENTS AND MOLAR KERR CONSTANTS OF COMPLEXES [$Cr(CO)_3(\eta^6$-arene)] FROM MEASUREMENTS IN CYCLOHEXANE AT $T = 298$ K AND λ 589 nm

Arene	$\alpha\epsilon_1$	β	γ	δ	$_\infty P_2$ (cm^3)	R_D (cm^3)	$10^{30}\ \mu$ [a] (Cm)	$10^{30}\ \mu$(loss) (Cm)	$10^{27}\ _\infty(_mK_2)$ [b] (m^5 V^{-2} mol^{-1})
benzene	8.73	0.464	0.094	391	486	57.3	15.2 ± 0.1	15.2 ± 0.1	1239 ± 58
toluene	9.09	0.436	0.090	423	540	62.3	16.2 ± 0.1	–	1430 ± 20
p-xylene	9.44	0.410	0.089	392	596	67.9	16.9 ± 0.1	–	1404 ± 20
mesitylene	9.76	0.386	0.084	350	652	72.8	17.7 ± 0.1	18.0 ± 0.3	1323 ± 28
durene	10.1	0.382	0.083	340	709	76.6	18.5 ± 0.1	–	1355 ± 22
pentamethylbenzene	10.5	0.376	0.080	287	777	80.4	19.4 ± 0.1	–	1197 ± 56
hexamethylbenzene	10.7	0.372	0.075	318	829	84.0	20.1 ± 0.1	$20.5+0.2$	1400 ± 140
t-butylbenzene	8.40	0.385	0.081	375	599	76.0	16.8 ± 0.1	16.6 ± 0.1	1497 ± 20
p-di-t-butylbenzene	8.33	0.338	0.074	309	723	94.7	18.4 ± 0.2	18.1 ± 0.2	1489 ± 70
1,3,5-tri-t-butyl-benzene	8.06	0.289	0.062	241	829	112	19.7 ± 0.1	19.8 ± 0.3	1355 ± 65

[a] Dipole moments were derived on the basis that the molar distortion polarisation equals 1.05 R_D. [b] The term $_\infty(_mK_2)$ refers to the solute molar Kerr constant at infinite dilution.

TABLE 2

CHANGES $\Delta\nu(A_1)$ IN THE IR CARBONYL A_1 BAND OF $[Cr(CO)_3(\eta^6\text{-}C_6H_6)]$ WITH PROGRESSIVE METHYL AND t-BUTYL SUBSTITUTION [a]

Arene	$\Delta\nu(A_1)$ [b] (cm^{-1})
benzene	–
toluene	−4.4
p-xylene	−9.1
mesitylene	−12.9
durene	−17.9
pentamethylbenzene	−21.8
hexamethylbenzene	−25.8
t-butylbenzene	−7.4
p-di-t-butylbenzene	−14.1
1,3,5-tri-t-butylbenzene	−19.8

[a] $\Delta\nu$ is the difference between the A_1 stretches of the complexes and of the parent complex. [b] Uncertainty ±0.2 cm^{-1}.

3.031 and 8.544 GHz. The experimental technique and the method of data analysis are described in [16,17]. Solute dipole moments and molar Kerr constants are given in SI units throughout. The conversion factors from the electrostatic (c.g.s., e.s.u.) system are, respectively: 1 Cm = 0.2998×10^{30} D, 1 m^5 V^{-2} mol^{-1} = 0.8988×10^{15} e.s.u. mol^{-1}. Infrared spectra were recorded on a Perkin–Elmer 580B spectrophotometer in dilute cyclohexane solution. The IR results are listed in Table 2. ^{1}H NMR spectra were recorded on a Bruker WM400 NMR spectrometer.

Discussion

Dipole moments

The dipole moments, μ (Table 1) were derived by the refractivity method, which requires an arbitrary assignment of atomic polarisation [15,18]. This procedure had been used for the previous dipole moment determinations [5–10]. It can reasonably be regarded as valid since atomic polarisations are known usually to be small [18] and because the orientation polarisations for these highly dipolar complexes would be expected to be overwhelmingly large and insensitive to errors in the allowance for atomic polarisations. Uncertainty persists, however, since it is known that some classes of metal complexes exhibit unusually large atomic polarisations, i.e. of the order of hundreds of cm^3 units [19,20]. To put the issue beyond doubt, an independent and definitive determination of the dipole moments of six of the complexes was made from measurements of the microwave dielectric loss [17]. The dipole moments so derived, μ(loss), agree closely with the corresponding values μ from the refractivity method, see columns 8 and 9 of Table 1.

The dipole moments μ of the methyl-substituted benzene complexes bear a linear relation to the number of methyl substituents irrespective of the positions of the methyl groups on the aromatic ring. The least squares line of best fit is given by: $10^{30}\mu_n = 15.3 + 0.81n$, where n is the number of methyl groups. This is in substantial though not exact agreement with the earlier observations in [6,7]. A linear correlation is observed also with the t-butyl-substituted benzene complexes: 10^{30}

$\mu_n = 15.3 + 1.51n$, where n now refers to the number of t-butyl groups. In each case, the molecular dipole moment lies along the Cr–arene bond axis except for the complexes with toluene, pentamethylbenzene and t-butylbenzene wherein it is located very close (within 5°) * to that axis. For both groups of complexes, an additivity scheme is apparent such that each methyl substituent causes an electron charge shift in the arene → Cr direction equivalent to a dipole moment increment of 0.8×10^{-30} Cm, and each t-butyl substituent results in an increment of 1.5×10^{-30} Cm in the same direction. The larger value for the t-butyl group reflects an electron-donor ability which is greater than that of methyl in the substituted η^6-benzenetricarbonylchromium(0) complexes.

IR spectra

Electron displacements arene → $Cr(CO)_3$ are accompanied by a lowering of the carbonyl stretching frequencies [4]. The $\Delta\nu(A_1)$ values for the methyl-substituted (η^6-benzene)tricarbonylchromium(0) complexes in Table 2, show a near linear dependence on the number of methyl groups n: $\Delta\nu(A_1) = -4.3n$. Similarly for the t-butyl complexes: $\Delta\nu(A_1) = -6.6n$. This further attests to the approximately additive substituent effects earlier described in [22]. For the t-butyl substituted complexes, the $\Delta\nu(A_1)$ values, in common with the $\Delta\mu$ increments, are greater than for the corresponding methyl-substituted compounds. The observed trends are explained in terms of increasing electron-charge displacement, with progressive methyl or t-butyl substitution, to the metal and thence from the metal to the CO groups, increasing the strength of Cr–CO bonds and decreasing the CO bond order in comparison with the unsubstituted complex [23].

Molecular polarisabilities

For $[Cr(CO)_3(\eta^6\text{-}C_6H_6)]$ and its substituted derivatives in which the arene has three or higher fold symmetry, the molecular optical anisotropies $\Gamma = (b_1 - b_2)$, can be obtained from the experimental molar Kerr constants using eq. 1 from the Langevin–Born treatment as modified by Le Fèvre [14,24].

$$_{\mathrm{m}}K = (N/405kT\epsilon_0)\left[({}_{\mathrm{D}}P/{}_{\mathrm{E}}P)\Gamma^2 + (kT)^{-1}\mu^2\Gamma\right] \tag{1}$$

The terms b_1 and $b_2 = b_3$ refer, respectively, to the principal molecular polarisabilities in the direction of the Cr–arene bond axis 1 (in Fig. 1) and to those, 2 and 3, in a plane perpendicular to that axis, i.e. parallel to the plane of the arene ring: ${}_{\mathrm{D}}P$, ${}_{\mathrm{E}}P$, N, k, T and ϵ_0 refer, in turn, to the molar distortion polarisation, the molar electron polarisation, Avogadro's number, the Boltzmann constant, the absolute temperature and the permittivity of a vacuum. The permanent electric moment is located along the 1 axis so that $\mu_1 = \mu$(observed) and $\mu_2 = \mu_3 = 0$. The ratios ${}_{\mathrm{D}}P/{}_{\mathrm{E}}P$ were taken as 1.1 [14]; possible variations are unimportant in view of the absolute predominance of the $\mu^2\Gamma$ terms for these highly dipolar substances. The experimental Γ values thus obtained for the benzene, mesitylene, hexamethylbenzene and 1,3,5-tri-t-butylbenzene complexes are given in Table 3. For the complexes of lower symmetry, $b_1 \neq b_2 \neq b_3$; the locations of the principal axes are similar to those shown in Fig. 1. For these molecules the molecular anisotropies $\Gamma = b_1 - (b_2 + b_3)/2$, were derived using the more general form of eq. 1 shown on p. 665 of [25].

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* Estimated using the dipole moments of toluene, pentamethylbenzene and t-butylbenzene [21].

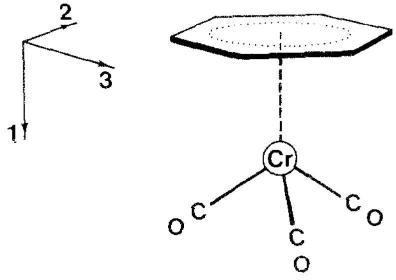

Fig. 1. The principal axes in $[Cr(CO)_3(\eta^6\text{-}C_6H_6)]$.

The experimental Γ values are now compared with those predicted from additivity [24] of the polarisability anisotropies of the non-bonded arene and $Cr(CO)_3$ fragments. The directional polarisabilities of the methyl- and t-butyl-substituted benzenes (the free arene ligands) have previously been determined [21]. The polarisability anisotropy of the $Cr(CO)_3$ fragment would be ca. 0 for C–Cr–C bond angles close to 90° [26]. Though each CrCO group is expected to be anisotropically polarisable (reasonably, an ellipsoid of revolution about the bond axis), the sum of the polarisability tensors of three such groups mutually disposed at 90°, gives an optically isotropic $Cr(CO)_3$ segment [24]. The calculated molecular Γ values are listed in column 3 of Table 3.

The important result emerges that for all of the complexes examined, coordinative interaction between the arene and $Cr(CO)_3$ fragments leads to a change in the algebraic sign of the molecular optical anisotropy. For each of the free (non-complexed) methyl- and t-butyl-substituted benzenes, the "in-plane" polarisabilities are substantially greater than the polarisability perpendicular to the aromatic ring plane [21]. Coordination with $Cr(CO)_3$ results not only in permanent electron-charge

TABLE 3

MOLECULAR POLARISABILITY ANISOTROPIES $10^{40}\ \Gamma(\mathrm{Cm^2\ V^{-1}})$ AND PRINCIPAL POLARISABILITIES $10^{40}\ b_i\ (\mathrm{Cm^2\ V^{-1}})$ FOR THE COMPLEXES $[Cr(CO)_3(\eta^6\text{-ARENE})]$ [a]

Arene	Γ(exp.) [b,c]	Γ(calc.)	b_1 [d]	(b_2+b_3) [d]	$b_2 = b_3$ [d,e]
benzene	5.34 ± 0.25	−4.6	27.7	44.8	22.4
toluene	5.55 ± 0.08	−5.2	30.0	48.9	(24.5)
p-xylene	4.97 ± 0.07	−5.8	31.9	53.9	(27.0)
mesitylene	4.24 ± 0.09	−6.1	33.5	58.6	29.3
durene	4.00 ± 0.07	−6.8	34.9	61.9	(31.0)
pentamethylbenzene	3.22 ± 0.15	−7.3	36.1	65.7	(32.9)
hexamethylbenzene	3.48 ± 0.35	−7.8	37.7	68.5	34.3
t-butylbenzene	5.34 ± 0.07	−5.2	35.6	60.6	(30.3)
p-di-t-butylbenzene	4.42 ± 0.21	−5.7	42.9	76.9	(38.5)
1,3,5-tri-t-butylbenzene	3.52 ± 0.17	−6.3	49.5	92.0	46.0

[a] Polarisabilities are expressed in SI units; conversion factor from the c.g.s., e.s.u. system is: 1 $\mathrm{Cm^2\ V^{-1}} = 0.8988 \times 10^{16}\ \mathrm{cm^3}$. [b] Solution of the quadratic equation 1 yields an alternative set of Γ values. These, however, are physically impossible and have been ignored. [c] Errors in Γ derive from the uncertainties in the experimental μ and $_mK$ values of Table 1. [d] Errors in Γ confer < 1% uncertainty to the experimental b_i values. [e] Values in parentheses were obtained on the basis that $b_2 = b_3$.

displacement perpendicular to the benzenoid ring, but also in very large enhancement of polarisability in the same direction. From studies of conjugated systems, Le Fèvre et al. [24,27,28] have shown that polarisability exaltation (corresponding to an enhanced degree of electron displacement in a perturbing field) will occur in the direction of maximum electromeric shift. The present work provides strong evidence for an unexpectedly high degree of electron mobility in the direction of the Cr–arene bond for each of the $[Cr(CO)_3(\eta^6\text{-arene})]$ complexes.

To specify the directional polarisabilities of the complexes, molar refraction data were used to provide a second equation in b_i [24].

$$_{E}P = N(b_1 + b_2 + b_3)/9\epsilon_0 \qquad (2)$$

As refractivity dispersion data do not exist for these complexes, the molar electron polarisation was taken as 0.96 times the appropriate experimental R_D. This factor derives from the methylbenzenes and the t-butylbenzenes [21]; a more precise

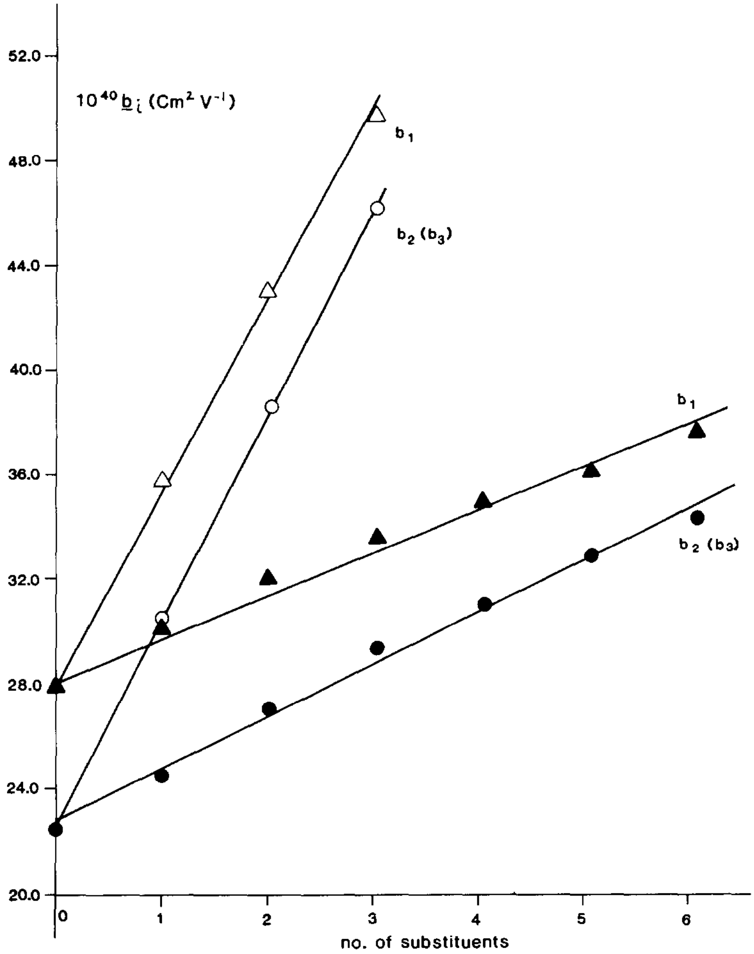

Fig. 2. Plots of directional polarisabilities b_i with number of substituent groups n. ▲ and ● refer to the methyl-substituted complexes; △ and ○ refer to the t-butyl-substituted complexes.

estimate is not critical to the argument. Using Σb_i from eq. 2 and the experimental Γ values from Table 3, the molecular polarisability parameters shown in columns 4–6 of this table are derived.

In the four cases where symmetry allows the complete specification of the (experimental) molecular polarisabilities, $b_1 > b_2 (= b_3)$. The predominance of b_1 is seen also for the complexes of lower symmetry for which the polarisabilities parallel to the arene plane would be approximately equal, i.e. $b_2 \approx b_3$. The experimental b_i values in Table 3 show regular trends with the number of methyl or t-butyl groups (Fig. 2), i.e. substituent effects are approximately additive and are not much affected by the positions of the substituents on the aromatic ring. The complexes tend to become less anisotropic as methyl or t-butyl substituent groups are inserted: each substituent results in an increase of the polarisabilities in the aryl plane more so than perpendicular to that plane, hence there is an overall convergence of b_1 and b_2 with progressive substitution.

The polarisability tensor of the (η^6-arene)Cr segment was specified in each case, by deducting from the molecular b_i values of [$Cr(CO)_3$(η^6-arene)], the polarisability contributions of $Cr(CO)_3$. The $Cr(CO)_3$ group is isotropically polarisable with b(mean) equal to 10.8 (10^{-40} Cm^2 V^{-1}), i.e. half the molecular b(mean) of $Cr(CO)_6$ which was derived from the measured R_D of 51.4 cm^3 [29]. Possible variations in b(mean) of $Cr(CO)_3$ when transferred to the [$Cr(CO)_3$(η^6-arene)] complexes, would not detract from the subsequent discussion. The polarisabilities b_i for (η^6-arene)Cr are given in Table 4 together with the polarisabilities of the free arene ligands. Differences Δb_i between the b_i values of the (η^6-arene)Cr group and the corresponding free arene are given in columns 6 and 7 of this table. The Δb_1 and Δb_2 (Δb_3) values are surprisingly constant across the range of compounds studied. Most striking is the large positive Δb_1 found for each complex which indicates that the electron system constituting the Cr–arene bond is very highly polarisable along the bond axis, providing a channel of relatively free electron movement between the

TABLE 4

ANISOTROPIC POLARISABILITIES 10^{40} b_i (Cm^2 V^{-1}) OF (η^6-ARENE)Cr IN COMPARISON TO THOSE OF THE FREE ARENE LIGANDS

Arene	(η^6-arene)Cr		Arene		b_i(η^6-arene)Cr $-$ b_i(arene)	
	b_1	$b_2 = b_3$ [a]	b_1	$b_2 = b_3$ [a,b]	Δb_1	$\Delta b_2 = \Delta b_3$ [a]
benzene	16.9	11.6	8.0	12.6	8.9	−1.0
toluene	19.2	(13.7)	9.7	(14.9)	9.5	(−1.2)
p-xylene	21.1	(16.2)	11.4	(17.2)	9.7	(−1.0)
mesitylene	22.7	18.5	13.2	19.3	9.5	−0.8
durene	24.1	(20.2)	14.7	(21.5)	9.4	(−1.3)
pentamethylbenzene	25.3	(22.1)	16.4	(23.7)	8.9	(−1.6)
hexamethylbenzene	26.9	23.5	18.0	25.8	8.9	−2.3
t-butylbenzene	24.8	(19.5)	15.7	(20.9)	9.1	(−1.4)
p-di-t-butylbenzene	32.1	(27.7)	23.5	(29.2)	8.6	(−1.5)
1,3,5-tri-t-butylbenzene	38.7	35.2	31.2	37.5	7.5	−2.3

[a] Values in parentheses were obtained on the basis that $b_2 \approx b_3$. [b] Polarisabilities b_2 and b_3 are known for the free ligands [21]; average values of the "in-plane" polarisabilities are presented here to enable comparison with the quantities in column 3 of this Table.

arene and $Cr(CO)_3$. The large polarisability anisotropy for this system suggests a concomitant large magnetic anisotropy. If the treatment of Gans and Mrowka [30] is invoked, the maximum magnetic susceptibility is predicted to be at right angles to the Cr–arene axis (the maximum polarisability axis), and a picture emerges which is consistent with a solid-state ^{13}C NMR study by Maricq et al. [31]. They found that large upfield changes in ^{13}C chemical shifts in aromatics when they form π-complexes with $Cr(CO)_3$, are predominantly due to a very large specific increase in screening when the external magnetic field lies in the plane of the aromatic ring and along the bond linking the carbon with its attached hydrogen or other substituent. The effect was viewed in terms of a greatly enhanced circulation of electrons about an axis parallel to the C–H or C–substituent bond.

The Δb_2 (Δb_3) values of Table 4 are negative, indicating small overall polarisability decreases with complex formation. If allowance is made for transverse polarisability contributions of the electron system constituting the Cr–arene bond to b_2 and b_3, it follows that the "in-plane" polarisabilities of the coordinated arene segment would in each case be substantially smaller than those of the free arene molecule. Since benzenoid π-electrons are much more polarisable in the aromatic ring plane than electrons localised in the σ-framework, the results are interpreted to indicate a diminution of the "in-plane" polarisabilities of the arene π-system on coordination with $Cr(CO)_3$, and hence a lowering of the aromatic character. Though the electric field associated with the Cr–arene dipole would most likely cause inductive withdrawal of σ-electrons, the depletion of electron density in the coordinated arene would be due mainly to displacements of ring π-electrons towards $Cr(CO)_3$. Supporting evidence for these conclusions comes from a study of the benzylic coupling between the arene proton and those of the *ortho*-methyl groups in (η^6-pentamethylbenzene)tricarbonylchromium(0). Although the coupling is not resolvable for this and for other complexes of this study, it was found that on complexation, the width of the aromatic proton resonance of pentamethylbenzene decreases by 1.2 Hz (in acetone-d_6 solvent, 298 K). A similar effect is observed in cyclohexane-d_{12}. Since benzylic coupling constants are known to correlate well with the aromatic C–C π-bond order [32], this result indicates a significant decrease in the aromaticity of the aryl ring on complexation.

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