

**DIELECTRIC, ELECTRO-OPTIC AND INFRARED AND  $^1\text{H}$  NMR SPECTRAL PROPERTIES OF METHYL- AND *t*-BUTYL-SUBSTITUTED ( $\eta^6$ -BENZENE)TRICARBONYLCHROMIUM(0) COMPLEXES: A STUDY OF SOLVENT EFFECTS**

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### Summary

Dipole moment, microwave dielectric absorption, electric birefringence and infrared and  $^1\text{H}$  NMR spectral data are presented for  $[\text{Cr}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_6)]$  and for some of its methyl- and *t*-butyl-substituted derivatives in the non-dipolar solvents, cyclohexane, benzene and dioxane. Atomic polarisations for these complexes are shown to be negligibly small. Specific interactions are shown to occur between dioxane or benzene solvent molecules and the coordinated arene which acts as an electrophile. The effects on such interactions of progressive methyl or *t*-butyl group insertion on the arene nucleus are studied. In 1,3,5-tri-*t*-butylbenzenetricarbonylchromium(0), “face-to-face” associations between the arene ligand and solvating benzene are sterically inhibited. Direct complexation with chromium is shown to be improbable with these solvents. The solute polarisability tensor of  $[\text{Cr}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_6)]$ , unlike the dipole moment vector, is not changed by interaction with dioxane. With methyl or *t*-butyl substitution, the solute polarisability anisotropy in dioxane tends to decrease, relative to that in cyclohexane. Electric birefringences and  $^1\text{H}$  NMR chemical shifts are interpreted in terms of transient stereospecific solute-benzene associations additional to “face-to-face” charge-transfer interactions. Benzene-induced upfield shifts of aryl protons (ASIS) decrease in magnitude with progressive methyl or *t*-butyl substitution.

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### Introduction

Much evidence exists to show that ( $\eta^6$ -arene)tricarbonylchromium(0) complexes are capable of displaying both electron donor and electron acceptor properties in

charge-transfer type interactions [1–7]. Contrary to earlier reports [4–6], it is now thought that electron acceptors such as 1,3,5-trinitrobenzene interact directly with chromium *d*-orbitals by sitting beneath the base of the pyramid defined by the three carbonyl groups [7]. With electron donor molecules such as benzene or dioxane, charge-transfer type interactions are predicted to occur preferentially through the coordinated arene which in the complex, acts as an electrophile [3]. The latter is a consequence of the high electron-withdrawing power of  $\text{Cr}(\text{CO})_3$ . Evidence for this comes primarily from electric dipole moments [1,2] though the conclusions cannot be regarded as definitive. It has been shown that the dipole moment of the complex  $[\text{Cr}(\text{CO})_3(\eta^6\text{-arene})]$  increases along the solvent series: heptane < benzene < dioxane [2].

In this paper, a comparative study is presented of the electric dipole moments, molecular relaxation times, electric birefringences and infrared and  $^1\text{H}$  NMR spectral characteristics of  $[\text{Cr}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_6)]$  and of some of its methyl- and *t*-butyl-substituted derivatives in dilute cyclohexane, benzene and dioxane solution. The data are analysed to provide information on the nature of the solute–solvent interactions and on the effect of such interactions on the solute properties of the complexes.

## Experimental

The complexes were prepared by procedures previously reported [8–10] and were purified by repeated sublimation. Solvents were fractionated then stored over sodium; the appropriate physical constants for the solvents are given in [11]. Solute dipole moments  $\mu$  and electric birefringences, the latter expressed as molar Kerr constants  ${}_mK$ , were determined by procedures described in [11–14]; optical measurements were made with light of  $\lambda$  589 nm. Microwave dielectric loss measurements made at frequencies 1.141, 3.031 and 8.544 GHz, were analysed to obtain solute dipole moments, designated  $\mu'$ , and molecular relaxation times  $\tau$  [15,16]. For each compound examined, simple Debye behaviour was observed [16]. All measurements were made at 298 K. Oxygen was removed from each solvent by saturating it with dry nitrogen; the preparation and handling of solutions were carried out under dry, inert ( $\text{N}_2$ ) atmosphere. The results are summarised in Table 1. 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:  $1 \text{ Cm} = 0.2998 \times 10^{30} \text{ D}$ ,  $1 \text{ m}^5 \text{ V}^{-2} \text{ mol}^{-1} = 0.8998 \times 10^{15} \text{ e.s.u. mol}^{-1}$ . Infrared spectra were recorded on a Perkin–Elmer 580B or 457G spectrophotometer (uncertainty  $\pm 1 \text{ cm}^{-1}$ ).  $^1\text{H}$  NMR spectra were recorded in dilute solutions using a JEOL FX60Q or Bruker WM400 NMR spectrometer.

## Discussion

### *Dipole moments*

Dipole moments  $\mu$  were determined in this and in earlier work [1,2,17] by the refractivity method on the assumption that molar atomic polarisations for these complexes are negligibly small in relation to the molar orientation polarisations. Verification of this comes from the close agreement now found between the experimental  $\mu$  values and the moments  $\mu'$  independently derived from microwave

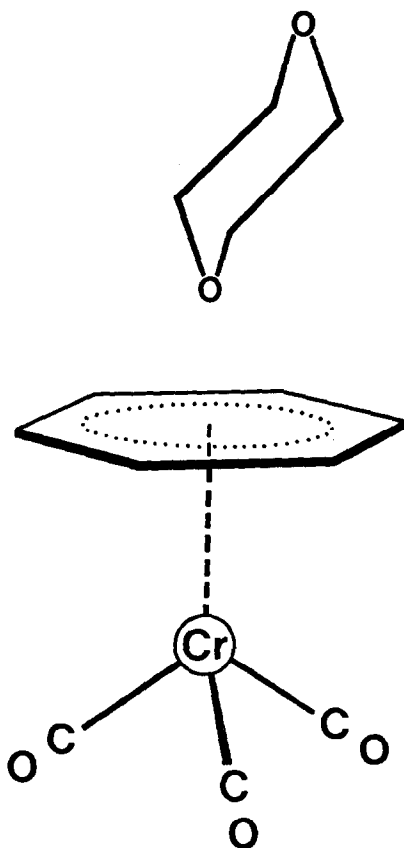


Fig. 1. Interaction between dioxane and the coordinated arene in  $[\text{Cr}(\text{CO})_3(\eta^6\text{-arene})]$ .

dielectric absorption measurements [18]. For complexes in which the molecular dipole moment lies along the Cr–arene axis, dipole reorientation can occur only through rotation of the whole molecule so that  $\mu'$  and  $\tau$  refer to the total molecular moment and the overall molecular relaxation time. This may also be regarded as applying to the *t*-butylbenzene complex since the component dipole in the arene plane would be very small compared to that along the Cr–arene axis. The comparisons between  $\mu$  and  $\mu'$  values were necessary to make certain that large atomic polarisations which have been observed in some other classes of metal complexes [19,20], do not occur with the  $(\eta^6\text{-arene})\text{tricarbonylchromium}(0)$  compounds. Thus it is established that the refractivity method is valid for determining the dipole moments for these complexes [1,2,17].

For all the solutes, the dipole moments are found to increase in the solvent sequence  $\text{C}_6\text{H}_{12} < \text{C}_6\text{H}_6 < \text{C}_4\text{H}_8\text{O}_2$ , confirming earlier observations [1,2]. The increased moments in benzene and dioxane have been attributed to charge-transfer interactions between dioxane or benzene acting as an electron donor, and the arene segment of the  $[\text{Cr}(\text{CO})_3(\eta^6\text{-arene})]$  complex which functions as an electron acceptor, see Fig. 1 and Fig. 2 (A) [3].

Near regular increases in the dipole moments are observed with progressive methyl or *t*-butyl substitution, indicating approximately additive substituent effects,

(Continued on p. 196)

TABLE 1  
ELECTRIC DIPOLE MOMENTS, MOLECULAR RELAXATION TIMES AND MOLAR KERR CONSTANTS OF COMPLEXES [Cr(CO)<sub>3</sub>(η<sup>6</sup>-arene)] IN SOLUTION IN CYCLOHEXANE, BENZENE AND DIOXANE <sup>a</sup>

arene	$10^{30} \mu(C_6H_{12})$ (Cm) <sup>b,c</sup>	$10^{30} \mu(C_6H_6)$ (Cm) <sup>c</sup>	$10^{30} \mu(C_4H_8O_2)$ (Cm) <sup>c</sup>	$10^{30} \mu(C_6H_{12})$ (Cm) <sup>b</sup>	$10^{30} \mu(C_6H_6)$ (Cm)	$10^{30} \mu(C_4H_8O_2)$ (Cm)
benzene	15.2 ±0.1	16.8 ±0.1	17.4 ±0.3	15.2 ±0.1	16.3 ±0.2	17.4 ±0.1
mesitylene	17.7 ±0.1	19.0 ±0.1	20.0 ±0.2	18.0 ±0.3	18.5 ±0.1	19.6 ±0.3
hexamethylbenzene	20.14 ±0.1	21.1 ±0.1	22.0 ±0.2	20.5 ±0.2	20.7 ±0.2	22.0 ±1.0
t-butylbenzene	16.8 ±0.1	18.3 ±0.1	18.4 ±0.2	16.6 ±0.1	17.8 ±0.1	18.6 ±0.1
p-di-t-butylbenzene	18.4 ±0.2	19.7 ±0.1	19.8 ±0.3	18.1 ±0.2	19.2 ±0.2	20.2 ±0.1
1,3,5-tri-t-butylbenzene	19.7 ±0.1	20.2 ±0.1	20.9 ±0.1	19.8 ±0.3	20.2 ±0.1	21.0 ±0.2

arene	$\tau(\text{C}_6\text{H}_{12})$ ps	$\tau(\text{C}_6\text{H}_6)$ ps	$\tau(\text{C}_4\text{H}_8\text{O}_2)$ ps	$10^{27} \frac{K(\text{C}_6\text{H}_{12})}{(\text{m}^5 \text{V}^{-2} \text{mol}^{-1})^b}$	$10^{27} \frac{K(\text{C}_6\text{H}_6)}{(\text{m}^5 \text{V}^{-2} \text{mol}^{-1})}$	$10^{27} \frac{K(\text{C}_4\text{H}_8\text{O}_2)}{(\text{m}^5 \text{V}^{-2} \text{mol}^{-1})}$
benzene	19 ±1	24 ±2	44 ±3	1239 ±58	1124 ±11	1617 ±13
mesitylene	36 ±2	35 ±2	57 ±2	1323 ±28	520 ±9	1384 ±78
hexamethylbenzene	56 ±2	51 ±2	77 ±6	1400 ±140	-1029 ±11	616 ±7
t-butylbenzene	33 ±1	37 ±1	63 ±2	-	-	-
p-di-t-butylbenzene	46 ±3	48 ±1	77 ±4	-	-	-
1,3,5-tri-t-butylbenzene	74 ±7	58 ±2	100 ±12	1355 ±65	901 ±50	1100 ±33

<sup>a</sup> Errors shown were calculated from standard deviations in the measured quantities from which  $\mu$ ,  $\mu'$ ,  $\tau$  and  $\tau_m$  were derived. <sup>b</sup> Dipole moments and molar Kerr constants in cyclohexane solution are quoted from [17]. <sup>c</sup> Derived by the refractivity method taking the molar distortion polarisation as 1.05 times the molar refraction  $R_D$ .

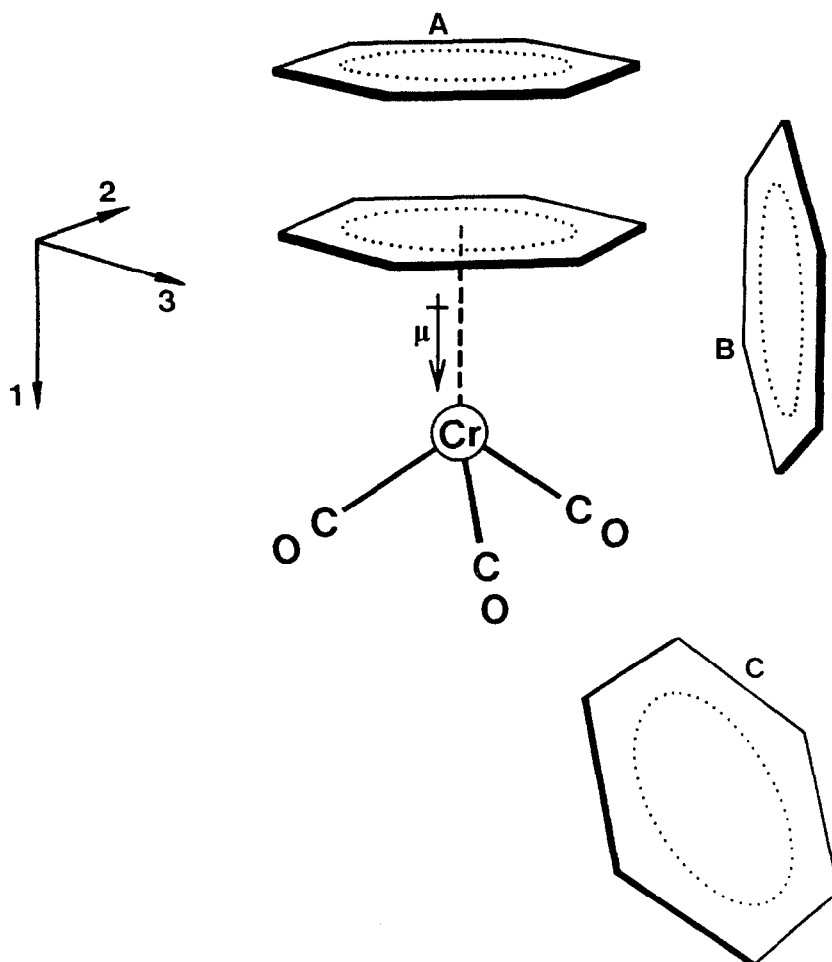


Fig. 2. Some stereospecific interactions between benzene solvent molecules and  $[\text{Cr}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_6)]$ .

irrespective of solvent. Plots of the experimental  $\mu$  values against the number of substituents are shown in Fig. 3 (similar plots are obtained if  $\mu'$  values are used). Differences  $\Delta\mu$  between  $\mu$  (donor solvent) and  $\mu(\text{C}_6\text{H}_{12})$  tend to decrease with increasing substitution, an effect which is more pronounced with the *t*-butyl-substituted complexes. From such trends in  $\Delta\mu$ , it had earlier been suggested [2] that the acceptor strength of the complexed arene would decrease with the insertion of electron-releasing substituents. Such interpretation is uncertain since it is not strictly possible to separate the effects on  $\Delta\mu$  of the electronic and steric factors governing the solute-solvent interactions. In the dipole moment plots of Fig. 3, an obvious irregularity is observed with  $\mu$  for 1,3,5-tri-*t*-butylbenzenetricarbonylchromium(0) in benzene. This results from greatly diminished "face-to-face" contact between the benzene donor and the coordinated arene, as represented by configuration A of Fig. 2, because of steric deflection by the *t*-butyl groups. Interactions with dioxane appear not to be markedly inhibited by such steric factors because of the smaller size of this solvent molecule. Computer drawn space filling models [21] of the

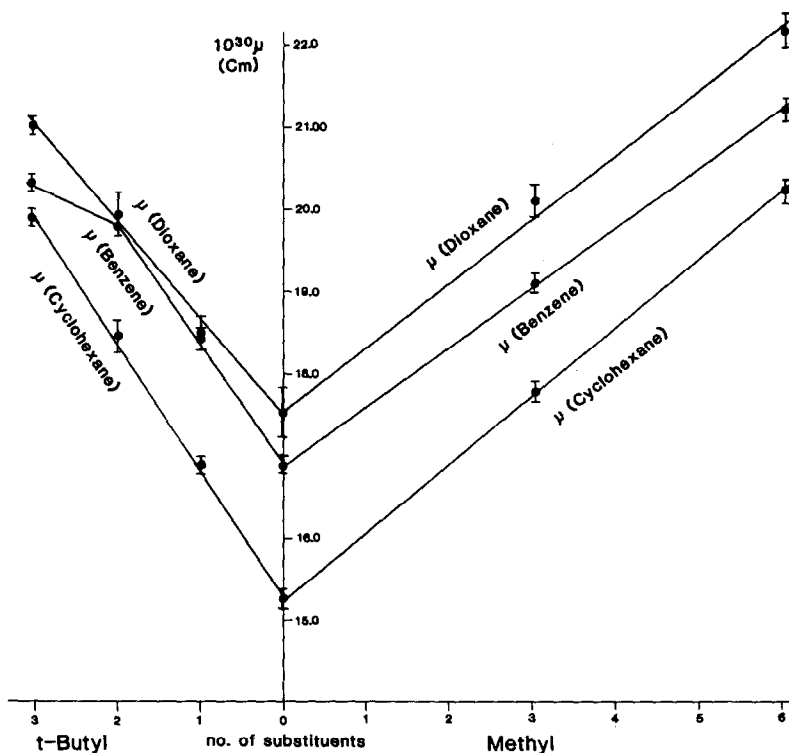


Fig. 3. Plots of the experimental  $\mu$  with number of aryl substituents in  $[\text{Cr}(\text{CO})_3(\eta^6\text{-arene})]$  for different solvent environments.

1,3,5-tri-*t*-butylbenzene complex show that the Cr atom is virtually “buried” by the *t*-butyl and carbonyl groups so that the observed dipole moment change does not arise from direct dioxane–chromium interaction.

#### *Molecular relaxation times*

For a particular solvent environment,  $\tau$  increases as the size of the solute molecule becomes larger with progressive methyl or *t*-butyl substitution. Solvent effects are clearly apparent in that  $\tau$  values in dioxane are much greater than in the other two solvents. Though this correlates with the greater macroscopic viscosity of dioxane [22], dipole rotation within the dioxane solvation shell is hindered relative to that in cyclohexane or benzene because of dipole–dipole interactions between the dipolar solute and the C–O bond dipoles of dioxane [18]. Values  $\tau$  in benzene might be expected to be smaller than in cyclohexane since benzene has a lower macroscopic viscosity [22]. Generally, however, the measured  $\tau$  values in the two solvents are similar. It may be that  $\tau$  in benzene is greater than predicted because of solute–benzene associations, in which case, the low  $\tau(\text{C}_6\text{H}_6)$  value for 1,3,5-tri-*t*-butylbenzenetricarbonylchromium(0) can be understood since such associations would be weakest with this solute.

#### *Infrared spectra*

It had earlier been reported [23] that for complexes  $[\text{Cr}(\text{CO})_3(\eta^6\text{-arene})]$ , the  $A_1$

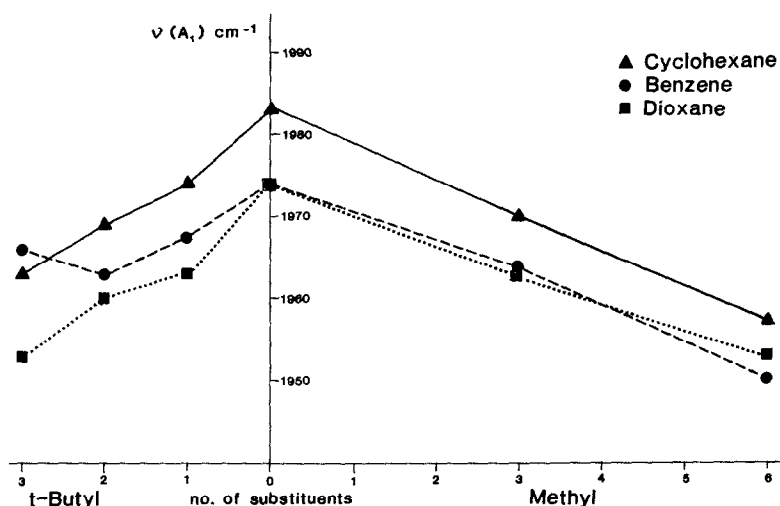


Fig. 4. Plots of the  $A_1$  infrared carbonyl stretching frequency with number of aryl substituents in  $[\text{Cr}(\text{CO})_3(\eta^6\text{-arene})]$  for different solvent environments.

carbonyl stretch is lowered on dissolution in an electron donor solvent. This is attributed to electron charge displacement from the coordinated arene into the  $\pi^*$  orbitals of the carbonyl ligands. The effect of solvent on the carbonyl  $\nu(A_1)$  is shown in Fig. 4. The results are in general accord with the occurrence of specific dioxane or benzene solvation as represented in Fig. 1 and as A in Fig. 2. It is seen from Fig. 4, that for each solvent,  $\nu(A_1)$  has a near linear dependence on the number of methyl or t-butyl substituent groups [17]. This reflects the progressive transmission of electron density from the substituent groups to the  $\text{Cr}(\text{CO})_3$  moiety. Approximate additivity of substituent effects is observed within a particular solvent environment. Deviation from regular behaviour occurs with  $(\eta^6\text{-1,3,5-tri-t-butyl-benzene})\text{tricarboxylchromium}(0)$  in benzene for which  $\nu(A_1)$  appears anomalously large. This is consistent with the conclusion already drawn from dipole moments, that "face-to-face" benzene interactions A (Fig. 2) are substantially diminished following insertion of the third t-butyl substituent on the arene. The results suggest also that such associations A are far less impeded for the case of the hexamethylbenzene complex.

#### *Electric birefringences*

For the complexes in which the arene has three or higher fold symmetry, the principal optical polarisabilities  $b_1$  and  $b_2 = b_3$ , can be obtained from the experimental molar Kerr constants and molar refractivities. The procedure is explained in [14,17]. The 1 axis is the molecular symmetry axis which is also the direction of the molecular dipole moment. The solute polarisabilities for the complexes in cyclohexane and in dioxane are given in Table 2.

Cyclohexane and dioxane molecules, unlike those of benzene, are known to be near optically isotropic [24,25] so the apparent solute polarisability anisotropy should not be much affected if the time-averaged distributions of these molecules are not random within the solvation shell encompassing the solute. Since dioxane



TABLE 2

MOLAR REFRACTIONS  $R_D$  ( $\text{cm}^3$ ) AND PRINCIPAL MOLECULAR POLARISABILITIES  $10^{40} b_i$  ( $\text{Cm}^2 \text{V}^{-1}$ ) FOR THE COMPLEXES  $[\text{Cr}(\text{CO})_3(\eta^6\text{-ARENE})]^a$

arene	$R_D(\text{C}_4\text{H}_8\text{O}_2)$	$b_1(\text{C}_4\text{H}_8\text{O}_2)$	$b_2(\text{C}_4\text{H}_8\text{O}_2)$ $= b_3(\text{C}_4\text{H}_8\text{O}_2)$	$b_1(\text{C}_6\text{H}_{12})^b$	$b_2(\text{C}_6\text{H}_{12})$ $= b_3(\text{C}_6\text{H}_{12})^b$
benzene	57.7	27.9	22.6	27.7	22.4
mesitylene	71.7	32.5	29.1	33.5	29.3
hexamethylbenzene	85.6	36.9	35.7	37.7	34.3
1,3,5-tri-t-butylbenzene	112	48.9	46.3	49.5	46.0

<sup>a</sup> Polarisabilities are expressed in SI units; conversion factor from the c.g.s., e.s.u. system is:  $1 \text{ Cm}^2 \text{V}^{-1} = 0.8988 \times 10^{16} \text{ cm}^3$ . <sup>b</sup> Quoted from ref. 17.

solvation changes the solute dipole moment, it is possible that the solute polarisability tensor may also be affected. It is seen, however, from the  $b_i$  values of Table 2 that the polarisability semi-axes of  $(\eta^6\text{-benzene})\text{tricarboxylchromium}(0)$  in dioxane are virtually identical with those in the "innocent" cyclohexane environment. Thus the polarisability tensor of this complex, unlike the electric moment, is very little changed by dioxane associations. With progressive methyl or t-butyl substitution, the apparent solute anisotropy ( $b_1 - b_2$ ) tends to become lower in dioxane relative to cyclohexane. It is seen, however, that this leads to only small changes in the apparent solute polarisabilities  $b_i$ .

The effects of benzene solvation on the solute molar Kerr constant are far more pronounced (see Table 1). Benzene molecules are highly anisotropic [26] so that if particular stereospecific solute-benzene contacts are statistically favoured, the solute anisotropy can appear to be quite different to that of the "isolated" solute. The packing of benzene molecules about the solute is influenced by steric and electrostatic factors. It is generally accepted that stereospecific solvent approaches occur preferentially at polar sites on the solute molecule [27,28]. Solute-benzene associations may broadly be categorized as those in which the plane of the solvating benzene is perpendicular or nearly so to the solute dipole, those in which the benzene plane is parallel or nearly so with the solute dipole, and angular approaches of intermediate geometry. Three examples of benzene interactions with  $[\text{Cr}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_6)]$  are represented as **A**, **B** and **C** in Fig. 2, but it is recognised that other geometric approaches would also occur within the time-averaged solvent cluster. Configuration **A** would result in a more negative apparent solute  ${}_mK$  relative to that in cyclohexane [14]. Configurations of type **B** about the perimeter of the complexed  $\text{C}_6\text{H}_6$  ligand (stabilised through solute dipole-induced dipole interactions) would contribute to a greater positive value for the apparent solute  ${}_mK$  [14]. Angular associations such as **C** in which the periphery of a solvating benzene molecule preferentially approaches the highly electronegative oxygens, would not greatly change the solute  ${}_mK$ . For the benzene, mesitylene and hexamethylbenzene complexes,  $\Delta_mK$ , defined as  ${}_mK(\text{C}_6\text{H}_6) - {}_mK(\text{C}_6\text{H}_{12})$ , equals  $-115$ ,  $-803$  and  $-2429$  ( $10^{-27} \text{ m}^5 \text{V}^{-2} \text{ mol}^{-1}$ ), respectively. Bland et al. [3] have recently presented <sup>1</sup>H NMR spectral evidence for relatively strong 1/1 interactions between benzene and  $[\text{Cr}(\text{CO})_3(\eta^6\text{-arene})]$  complexes; the geometry of interaction is that designated **A** in this work. For the solutes listed above, 1/1 solute-benzene complexes with this

geometry (assumed stable for the purposes of calculation) would have molar Kerr constants of 208,  $-124$  and  $-482$  ( $10^{-27} \text{ m}^5 \text{ V}^{-2} \text{ mol}^{-1}$ ), respectively. It is clear that solute–benzene associations of configuration **A**, though they are important, cannot alone account for the observed  $\Delta_m K$  values. Where benzene is in vast preponderance, as in this work with  $[\text{Cr}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_6)]$  dissolved in neat benzene, a balance must exist between benzene associations which increase the solute  $_m K$  and other associations which decrease it. The result is a relatively small  $\Delta_m K$  of  $-115$  ( $10^{-27} \text{ m}^5 \text{ V}^{-2} \text{ mol}^{-1}$ ). The balance would be changed with methyl substitution. Thus it would be reasonable to expect that with the hexamethylbenzene complex, the ring of methyl substituents sterically deflects solvating benzenes away from configurations **B**. This factor together with a continued high incidence of associations of type **A**, would account for the large negative  $\Delta_m K$ . More remote interactions such as those between solvating benzene molecules and the carbonyl oxygens would not be so greatly affected by the methyl substituents. In the case of ( $\eta^6$ -1,3,5-tri-*t*-butylbenzene)tricarbonylchromium(0), solute–benzene configuration **A** becomes improbable as well as those of **B** and the measured  $\Delta_m K$ ,  $-454$  ( $10^{-27} \text{ m}^5 \text{ V}^{-2} \text{ mol}^{-1}$ ), is substantially smaller than for the hexamethylbenzene complex. Only qualitative inferences can be drawn from the experimental  $\Delta_m K$  values in regard to the most probable solute–benzene interactions. Further analysis is complicated by the fact that  $\Delta_m K$  reflects the time-averaged result for all possible solute–solvent interactions [28]. Nonetheless, some insight, not otherwise available, is gained into the geometry of benzene solvation of the arene  $\pi$ -complexes.

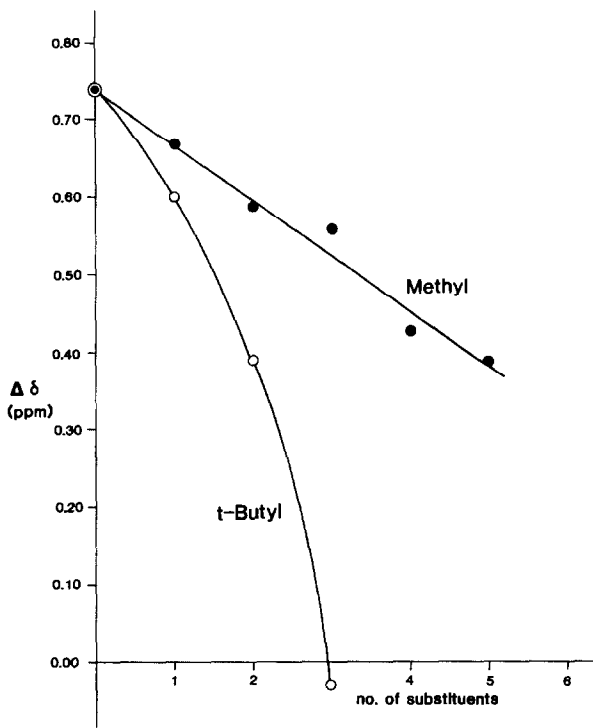


Fig. 5. Plots of  $\Delta\delta$ (ASIS) with number of aryl substituents in  $[\text{Cr}(\text{CO})_3(\eta^6\text{-arene})]$ .

*<sup>1</sup>H NMR spectra*

<sup>1</sup>H NMR chemical shifts for [Cr(CO)<sub>3</sub>(η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)] and for nine of its methyl- and t-butyl-substituted derivatives in dilute C<sub>6</sub>D<sub>12</sub> and C<sub>6</sub>D<sub>6</sub> solution are given in Table 3. Changes in chemical shift with benzene solvation (ASIS), relative to cyclohexane solution, are shown as Δδ in column 5 of this Table. A benzene induced upfield shift Δδ of 0.74 is found for the aryl protons of (η<sup>6</sup>-benzene)tricarbonylchromium(0). From this we infer that within the time-averaged cluster of benzene molecules encompassing the solute, shielding interactions such as **A** and **B** would be preponderant. It is seen also that Δδ for the aryl protons is greatest with the benzene complex and decreases with progressive methyl substitution to 0.39 for the pentamethylbenzene complex. The results are consistent with the model earlier advanced in which the occurrence of **B** type solute-benzene associations decreases with increase in the number of methyl substituents, while the incidence of the stronger **A** type interactions is not so much affected. With the t-butyl substituted complexes, Δδ (aryl protons) is found to decrease to ca. 0 for (η<sup>6</sup>-1,3,5-tri-t-butylbenzene)tricarbonylchromium(0), i.e. for this complex, solute-benzene configurations **A** and **B** are both improbable. Plots of Δδ (aryl protons) against the number of methyl or

TABLE 3

<sup>1</sup>H NMR SHIFTS δ(ppm) FOR [Cr(CO)<sub>3</sub>(η<sup>6</sup>-ARENE)] COMPLEXES IN C<sub>6</sub>D<sub>12</sub> AND C<sub>6</sub>D<sub>6</sub> SOLUTIONS AT 298 K

arene	proton	δ(C <sub>6</sub> D <sub>12</sub> ) <sup>a</sup>	δ(C <sub>6</sub> D <sub>6</sub> ) <sup>a</sup>	Δδ
benzene	Ar	5.02	4.28	0.74
toluene <sup>b</sup>	Ar	5.13	4.47	0.66
	Ar	4.87	4.19	0.68
	Me	2.10	1.50	0.60
<i>p</i> -xylene	Ar	4.98	4.39	0.59
	Me	2.04	1.50	0.54
mesitylene	Ar	4.62	4.06	0.56
	Me	2.11	1.66	0.45
durene	Ar	5.00	4.57	0.43
	Me	2.05	1.59	0.46
pentamethylbenzene	Ar	4.88	4.49	0.39
	Me	2.19	1.73	0.46
	Me	2.11	1.69	0.42
	Me	2.08	1.60	0.48
hexamethylbenzene	Me	2.16	1.72	0.44
	Me	2.16	1.72	0.44
t-butylbenzene	Ar	5.30	4.75	0.55
	Ar	5.11	4.48	0.63
	Ar	4.97	4.34	0.63
	t-Bu	1.28	0.92	0.36
<i>p</i> -di-t-butylbenzene	Ar	5.20	4.81	0.39
	t-Bu	1.28	1.02	0.26
1,3,5-tri-t-butylbenzene	Ar	5.69	5.72	-0.03
	t-Bu	1.29	1.10	0.19

<sup>a</sup> TMS was used as internal reference. <sup>b</sup> The third expected aryl-hydrogen δ value is obscured.

t-butyl substituents are given in Fig. 5. t-Butyl substitution in the arene complexes results in a much greater rate of decay of ASIS than does methyl substitution, despite the close similarity in the dipole moments of the two groups of complexes. The difference is attributed largely to steric factors affecting the geometry of interaction between solute and solvating benzene molecules.

## Conclusions

Electric polarisation and microwave dielectric absorption measurements have established that atomic polarisations in the  $[\text{Cr}(\text{CO})_3(\eta^6\text{-arene})]$  complexes are small and that dipole moments obtained using the refractivity method are accurate. It is found that the molecular dipole moment of the complex increases and the infrared carbonyl  $A_1$  stretching frequency decreases (a) with progressive methyl or t-butyl substitution (near regular trends in each non-dipolar solvent environment) and (b) with change of solvent from cyclohexane to benzene or dioxane. The latter solvents act as electron donors which participate in charge-transfer type interactions with the coordinated arene acting as an electrophile. Evidence is presented for "face-to-face" benzene solvation of the complexed arene except in the case of ( $\eta^6$ -1,3,5-tri-t-butylbenzene)tricarbonylchromium(0) where such interactions are largely precluded because of the steric effects of the t-butyl groups. Direct dioxane-chromium interactions appear not to be important. The solute polarisability tensor of  $[\text{Cr}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_6)]$ , unlike the dipole moment vector, is not much affected by interaction with dioxane. With methyl or t-butyl substitution, the solute polarisability anisotropy tends to decrease, relative to that in cyclohexane. Electric birefringences and  $^1\text{H}$  NMR chemical shifts are interpreted to indicate stereospecific benzene interactions with the complexed arene additional to "face-to-face" associations. Benzene-induced upfield shifts of aryl protons (ASIS) decrease in magnitude with progressive methyl or t-butyl substitution.

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