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THE ELECTRIC DIPOLE MOMENTS OF VARIOUS BENZENE- AND THIOPHENE-CHROMIUM TRICARBONYL COMPOUNDS

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SUMMARY

An examination of the electric dipole moments of substituted benzene- and thiophene-chromium tricarbonyl compounds reveals that the arene–$Cr(CO)_3$ group moment depends upon the nature of the arene substituent in a precise manner. That the dipole moment of tricarbonylthiophenechromium is 0.95 D higher than that of tricarbonylbenzenechromium, in spite of the lower π-basicity of thiophene, is explained by the relatively high S–Cr bond moment. Preferred conformations for tricarbonyl(aniline)- and tricarbonyl(*p*-phenylenediamine)chromium complexes are proposed, and it has been demonstrated that the tricarbonylchromium group is complexed with the benzene moiety in (benzo[*b*]thiophene)chromium tricarbonyl.

INTRODUCTION

Electric dipole moments are a most useful probe for the elucidation of the electronic distribution in a wide variety of molecules[1,2], including molecular π-complexes[3].

Although dipole moments of a number of arenechromiumtricarbonyl complexes have been studied hitherto[3], some points concerning the polarity of these molecules are worth reexamination in the light of more recent results.

EXPERIMENTAL

Benzene-, *N*,*N*-dimethylaniline-, aniline- and *p*-phenylenediamine-, as well as thiophene-chromium tricarbonyl and its 2-methyl, 3-methyl, 2-t-butyl, 3-t-butyl, 2,3-dimethyl and 2,5-dimethyl derivatives and benzo[*b*]thiophenechromium tricarbonyl were prepared by known methods[4,5]. Guilard, Tirouflet and Fournari[6] kindly provided pure samples of 2,3-dimethyl-, 2,5-dimethyl-, 2, 3,5-trimethyl- and tetramethylthiophenechromium tricarbonyl complexes and of 2-methoxycarbonyl-3-methylthiophene and 2-methoxycarbonyl-3-methylthiophenechromium tricarbonyl.

The dipole moments were measured in benzene solution at 25°. The value of the solute polarization, extrapolated to $w = 0$, was calculated from the experimental ratios:

$$\alpha = \frac{\Sigma(\varepsilon-\varepsilon_1)}{\Sigma w} \quad \text{and} \quad \beta = \frac{\Sigma(v-v_1)}{\Sigma w}$$

where w is the weight fraction of the solute and ε and v are the dielectric constant and specific volume of the solutions, respectively (subscript 1 refers to pure solvent)[7].

All weighings were carried out using a Sartorius microbalance and precautions were taken in the preparation of solutions and reference solvent to avoid contamination by air humidity.

In every case the (P_E+P_A) term was assumed to be equal to the molar refraction of the solute, as deduced from the value measured for benzenechromium tricarbonyl (65.0 cm^3). For this refraction Fischer and Schreiner[8] reported 54.08 cm^3, but more recently Strohmeier and Hellman[9] proposed a higher value (65.0 cm^3) and, from their data on p-dichlorobenzene- and p-di-fluorobenzene- p-xylenebenzene-, mesitylene- and hexamethylbenzene-chromium tricarbonyl complexes an average value of 62.8 cm^3 is derived which leads us to be confident in our value of 61.5 cm^3. A somewhat lower value (58.3 cm^3) is obtained from the sum of the refractions of benzene (26.2), chromium atom (7.2 (ref. 10)) and the CO group, 8.3 cm^3 as deduced from molar refractions (55.2 and 46.9 cm^3, both measured in liquid phase[11]) of (1,3-butadiene)iron tri- and tetra-carbonyl complexes.

The technique for determining the dielectric constants and specific volumes has been described elsewhere[12]. For the solutions examined, $w_{\max}$ (to three decimal places), α, $-\beta$, $P_{2\infty}$, R_D and μ values are given in Table 1.

TABLE 1

PHYSICAL DATA FROM BENZENE DIPOLE MOMENT DETERMINATIONS

Z in ZCr(CO)$_3$	w_{max}[a]	α	$-\beta$	$P_{2\infty}$	R_D	μ
PhH	0.006	13.3	0.369	577.8	61.5	5.03
PhNH$_2$	0.006	14.7	0.411	683.4	65.9	5.50
PhNH$_2$[b]	0.007	20.35	0.239	808.4	65.9	6.05
PhNMe$_2$	0.014	16.9	0.461	856.5	76.2	6.18
p-C$_6$H$_4$(NH$_2$)$_2$[b]	0.007	16.4	0.369	761.9	70.2	5.82
PhCOMe	0.016	11.0	0.415	577.9	71.6	4.97
C$_4$H$_4$S	0.007	18.35	0.497	790.8	59.7	5.98
2-MeC$_4$H$_3$S	0.007	18.55	0.403	856.7	64.4	6.23
3-MeC$_4$H$_3$S	0.006	18.85	0.527	861.4	64.4	6.24
2-t-BuC$_4$H$_3$S	0.005	16.2	(0.330)	897.8	78.6	6.33
3-t-BuC$_4$H$_3$S	0.006	16.3	0.330	902.9	78.6	6.35
2,3-Me$_2$C$_4$H$_2$S	0.008	18.6	0.415	910.0	69.4	6.42
2,3-Me$_2$C$_4$H$_2$S	0.016	18.8	0.416	918.4	69.4	6.44
2,4-Me$_2$C$_4$H$_2$S	0.018	17.8	0.512	868.1	69.4	6.25
2,5-Me$_2$C$_4$H$_2$S	0.005	18.5	0.415	905.4	69.4	6.40
2,5-Me$_2$C$_4$H$_2$S	0.027	18.45	0.415	902.3	69.4	6.38
2,3,5-Me$_3$C$_4$HS	0.016	18.1	0.293	949.4	75.3	6.54
MeC$_4$S	0.010	18.65	0.265	1031.3	79.2	6.82
2-MeO$_2$C-3-MeC$_4$H$_2$S[c]	0.048	2.28	0.314	105.6	41.3	1.77
2-MeO$_2$C-3-MeC$_4$H$_2$S	0.014	10.95	0.458	653.6	75.6	5.32
Benzo[*b*]thiophene	0.006	10.80	0.550	591.4	76.8	5.02

[a] Smoothed value. [b] In dioxane at 25°. [c] Uncomplexed.

RESULTS AND DISCUSSION

In this study we have measured the electric dipole moments of the complexes listed in Table 2 in benzene solution at 25°. Bibliographical results are also included in the table.

TABLE 2

DIPOLE MOMENTS OF VARIOUS ARENECHROMIUM TRICARBONYL COMPLEXES

Z in $ZCr(CO)_3$	*μ(benzene)/D*	*Literature value*
PhH	5.03	5.08[13]
C_4H_4S	5.98	5.54[14]
PhMe		5.26
2-MeC_4H_3S	6.23	
3-MeC_4H_3S	6.24	
2-t-BuC_4H_3S	6.33	
3-t-BuC_4H_3S	6.35	
o-$Me_2C_6H_4$		5.48[8]
2,3-$Me_2C_4H_2S$	6.43	
m-$Me_2C_6H_4$		5.41[8]
2,4-$Me_2C_4H_2S$	6.25	
p-$Me_2C_6H_4$		5.52[13]
2,5-$Me_2C_4H_2S$	6.39	
1,3,5-$Me_3C_6H_3$		5.52[13]
2,3,5-Me_3C_4HS	6.54	
1,2,4,5-$Me_4C_6H_2$		6.04[13]
2,3,4,5-Me_4C_4S	6.82	
Me_6C_6(hexamethylbenzene)		6.48[13]
Naphthalene		(6.40[8]),5.02[15],5.13[16]
Benzo[*b*]thiophene	5.02	
PhOH		5.18[8]
PhOMe		5.43[13]
$PhNH_2$	5.50[b]	5.52[8]
$PhNMe_2$	6.18	6.30[13]
p-$(H_2N)_2C_6H_4$	5.52[8]	
PhCOMe	4.97	
$PhCO_2Me$		4.55[8]
2-MeO_2C-3-MeC_4H_2S	5.32	
Dimethyl terephthalate		3.52[9]

[a] Recalculated from authors experimental data assuming $P_E+P_A=R_D$, to make their results comparable to ours. [b] $\mu=6.05$ D in dioxane solution (this study). [c] In dioxane, as the complex is not sufficiently soluble in benzene.

Benzenechromium tricarbonyl derivatives

Owing to their molecular structure, as revealed by X-ray diffraction studies[17,18], benzene and hexamethylbenzenechromium tricarbonyl complexes have dipole moments directed along the tricarbonyl ternary axis and oriented from the arene group to the metal atom. The same situation arises for *p*-xylene, mesitylene- and durenechromium tricarbonyl complexes since the arene moiety in these molecules is nonpolar. For naphthalenechromium tricarbonyl a small ring component may occur due to some migration of electrons from the unperturbed ring towards the complexed ring.

As noted by previous authors[3], the dipole moment of a monosubstituted benzenechromium tricarbonyl (PhX)–Cr(CO)$_3$ is not an additive vector in that it differs from the vectorial sum μ(benzenechromium tricarbonyl) $+\mu(\mathrm{PhX})=\mu_0+\mu_X$. Both components μ_0 and μ_X adopt modified values in the complex which we further define by the symbols μ_0^* and μ_X^*, respectively.

An electron-donating group, such as the Me$_2$N and (to a lesser extent) methyl, increases through its mesomeric effect the ring π-basicity and, therefore, brings about an increase in the μ_0 component. By contrast, an electron-withdrawing substituent such as acetyl or methoxycarbonyl, exerts an opposite effect upon the μ_o value[13].

It is not generally possible to derive both a ring-perpendicular moment μ_0^* and ring dipole μ_X^* from the observed dipole moment of a substituted tricarbonylbenzenechromium complex, except in two distinct cases:

For *p*-xylene-, mesitylene-, durene- and hexamethylbenzene-chromium tricarbonyl molecules we may safely infer that the ring moment is unaltered under complexation and, therefore, remains equal to zero.

For those molecular complexes having two identical angular substituents (*e.g.* COMe or CO$_2$Me), ring complexation must alter the mesomeric effects of both substituents equally and thus has no effect upon the ring moment.

The situation is much more delicate for a monosubstituted benzenechromium tricarbonyl complex and to obtain a significant μ_0^* value, we must derive μ_X^* from μ_X. Since experimental results[19,4] suggest that "the π-bound tricarbonyl group withdraws electrons at least as strongly as a *p*-nitro group (though by a quite different mechanism)[4], resolution of the vectorial equation

$$\begin{aligned}\mu(p\text{-}\mathrm{XC_6H_4NO_2}) &= \mu(\mathrm{Ph{-}X})+\mu(\mathrm{Ph{-}NO_2})+\mu_{\mathrm{int}}\\ &= \mu^*(\mathrm{Ph{-}X})+\mu^*(\mathrm{Ph{-}NO_2})\\ &= \mu'(\mathrm{Ph{-}X})+\mu'(\mathrm{Ph{-}NO_2})\end{aligned}$$

may yield information concerning the μ_X^* values.

If substituent X exhibits a negative ($-M$) mesomeric effect, the interaction moment of p-XC$_6$H$_4$NO$_2$ is low in magnitude and is probably due to mutual reduction of both X- and NO$_2$-mesomeric moments (compared to those present in PhX and PhNO$_2$, respectively). Hence we readily see that μ^*(Ph–X) must be smaller than μ'(Ph–X), being quite unlikely to attain μ[H–(X)] which implies inhibition of the X-mesomeric effect. Taking μ(Ph–COMe)$=2.92$ D[20], μ(Ph–CO$_2$Me)$=1.94$ D[21], μ(Ph–NO$_2$)$=3.95$ D, μ(p-XC$_6$H$_4$NO$_2$)$=3.29$ and 4.06 D for X$=$COMe or CO$_2$Et[1,2], we derive $\mu_{\mathrm{int.}}=0.43$ and 0.53 D, respectively*, whence μ'(Ph–COMe)$=2.65$ D, μ'(Ph–CO$_2$Me)$=1.78$ D. Since μ[H–C(=O)Me]$=2.6$ D and μ[H–C(=O)OMe]$=1.80$ D[2], *i.e.* are close to μ(Ph–X) corresponding figures, μ^*(Ph–COMe) and μ^*(Ph–CO$_2$-Me) are well defined and can be taken as 2.8 or 1.85 D.

Interaction moments are very much higher for the p-XC$_6$H$_4$NO$_2$ derivatives

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* PhCOMe and PhCO$_2$Et moments [this latter (1.93 D) being very close to μ(PhCO$_2$Me)] make angles (θ_0) of, respectively, 49 and 65° with Ph–CO bond, if calculated from dipole moments (3.10 (ref. 22) and 2.42 D (ref. 2)) of p-diacetylbenzene and diethyl terephthalate.

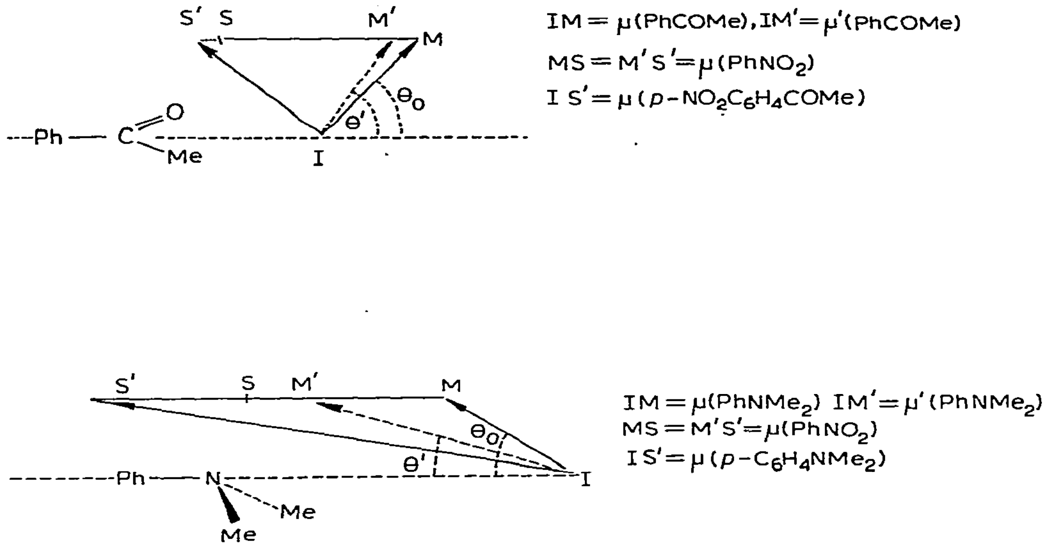

Fig. 1. Determination of μ'(PhCOMe) and μ'(PhNMe$_2$).

whose substituents X exhibit a positive ($+M$) mesomeric effect, as do NH$_2$ and NMe$_2$, being 1.03 and 1.48 D for *p*-nitroaniline and its *N*,*N*-dimethyl derivative[23]. Such high values are essentially due to some contribution of the $R_2N^+=(C_6H_4)=(NO_2)^-$ dipolar structure and also to a slight enhancement of $C_6H_4NH_2$ and $C_6H_4NO_2$ mesomeric moments. Since in aniline or *N*,*N*-dimethyl-aniline chromium tricarbonyl complexes there is only enhancement of the PhNR$_2$ mesomeric effect (and of the μ_0 component), we think that more reliable figures for μ^* (Ph–X) are, in these cases, nearer to μ(Ph–X) than to vector sums $\mu(\text{Ph–X})+\mu_{\text{int.}}=\mu'$ (Ph–X) whose values are 2.35 or 2.92 D for *p*-nitroaniline and its *N*,*N*-dimethyl derivative (see Fig. 1).

Since acetyl and methoxycarbonyl groups lie in the ring plane the partition into *O',O''-cis* and *O',O''-trans*(O', O'' = carbonyl oxygen atoms) must be the same for *p*-diacetylbenzenechromium tricarbonyl and for dimethyl terephthalatechromium tricarbonyl as for the corresponding uncomplexed molecules.

Aniline[24] and *N*,*N*-dimethylaniline[25] not being planar, chromium tricarbonyl complexes may exist in two conformations having, respectively, their (R...R) segments near to, and remote from, the chromium atom (Fig. 2), and a possibility

(I) (II)

Fig. 2. Conformers I and II for *N*,*N*-dialkylanilinechromium tricarbonyl complexes.

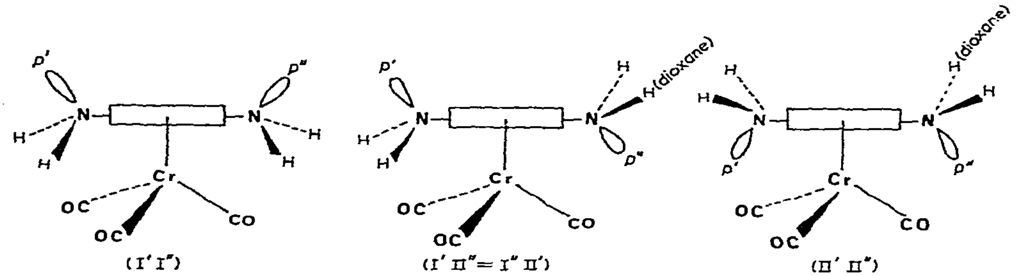

Fig. 3. Conformers I'I", II'II" and I'II"=I"II' for the *p*-phenylenediaminechromium tricarbonyl complex.

exists therefore of unequal conformational ratios for *p*-$R_2NC_6H_4NR_2$ and for its related complexes, as regards their *p',p"-cis* and *p',p"-trans* (*p',p"* = nitrogen lone pairs) conformers. Moreover, in the latter case *p',p"-cis* I'I" and II'II" conformers are to be distinguished in having their nitrogen lone pairs remote from, or near to, the chromium tricarbonyl group (Fig. 3).

No such difficulties are encountered for complexes listed in Table 3.

TABLE 3

INCREMENTS AND CARBONYL FREQUENCIES FOR ARENECHROMIUM TRICARBONYL COMPLEXES

Z in $ZCr(CO)_3$	$\Delta\mu_0(D)^a$	$\nu(CO)(cm^{-1})^b$
p-$MeO_2CC_6H_4CO_2Me$	−2.47	2000
$PhCO_2Me$	−0.91, −0.85	1997, 1930
PhCOMe	−1.01, −0.79	1985, 1915, 1901
PhH	0.0	1987, 1917
PhMe	0.22, 0.22	1983, 1914
p-Xylene	0.38	1979, 1908
Mesitylene	0.49	1975, 1905
Durene	1.01	1970, 1898
Hexamethylbenzene	1.42	1962, 1888

[a] The first value assuming $\mu^*(Ph\text{–}X) = \mu(Ph\text{–}X)$, the second value for $\mu^*(Ph\text{–}X) = \mu[H\text{–}(X)]$. The dipole moment of dimethyl terephthalate is 2.30 D[2].

[b] In cyclohexane. Except for the first[9] and the third compounds, *cf.* ref. 26.

The μ_0^* dipole moment component is a measure of the electron transfer from the ring to the metal. The greater this transfer, the higher the metal-$d_\pi \rightarrow$CO-π^* electron-donation must be. Hence we may expect a monotonic relation $\Delta\mu_0 = \mu_0^* - \mu_0$ with the chromium tricarbonyl frequencies, as in Table 3.

An examination of the results in Table 3 reveals some interesting features.

(a) The $\Delta\mu_0$ values differ little for methyl benzoatechromium tricarbonyl and acetophenonechromium tricarbonyl complexes. σ_R^0 Taft substitution constants, which are a measure of the magnitude of the substituent mesomeric effect acting on the ring π-basicity, are equal to 0.15 and 0.19 for uncomplexed methyl benzoate and acetophenone, respectively[27].

(b) Interplay of the two methoxycarbonyl mesomeric effects in dimethyl terephthalate must be mutually reduced. The $\Delta\mu_0$ value for dimethyl terephthalatechromium tricarbonyl is, however, more than twice that for methyl benzoatechromium tricarbonyl being -2.5 D instead of $2 \times (-0.9) = -1.8$ D. This shows a marked lowering in transmission of electronic (mesomeric) effects across the benzene ring in this complex, as a result of complexation (*cf.* ref. 28). Note that X-ray molecular structures for methyl benzoatechromium tricarbonyl[29] and benzenechromium tricarbonyl[17] reveal identical ring–chromium distances, indicating that the substituent effect upon the μ_0-value if purely electronic (and not geometric) in origin.

$\Delta\mu_0$ values for anilinechromium tricarbonyl and *N,N*-dimethylanilinechromium tricarbonyl were calculated assuming them to exist either as I or II, and taking respectively:

$$\mu^*(\text{Ph–NH}_2) = \mu(\text{Ph–NH}_2) = 1.53\ \text{D or}\ \mu'(\text{Ph–NH}_2) = 2.35\ \text{D}^{23},$$
$$\mu^*(\text{Ph–NMe}_2) = \mu(\text{Ph–NMe}_2) = 1.58\ \text{D or}\ \mu'(\text{Ph–NMe}_2) = 2.92\ \text{D}^{23}.$$

The resulting values can be compared to those computed for phenol- or anisolechromium tricarbonyl dipole moments (5.18 and 5.43D), adopting

$$\mu^*(\text{Ph–OH}) = \mu(\text{Ph–OH}) = 1.47\ \text{D or}\ \mu'(\text{Ph–OH}) = 1.52\ \text{D}^{23},$$
$$\mu^*(\text{Ph–OMe}) = \mu(\text{Ph–OMe}) = 1.28\ \text{D or}\ \mu'(\text{Ph–OMe}) = 1.41\ \text{D}^{23}.$$

Results are listed in Table 4.

TABLE 4

INCREMENTS AND CARBONYL FREQUENCIES[26] FOR VARIOUS ARENECHROMIUM TRICARBONYL COMPLEXES

Z in $ZCr(CO)_3$	$\Delta\mu_0(D)^a$	$\nu(\text{CO})(cm^{-1})^c$
PhMe	0.22, 0.22	1983, 1914
PhOH	(−0.06, −0.08)	
PhOMe	0.23, 0.21	1982, 1910
$PhNH_2$ as I	1.53, 1.25	1977, 1906, 1901
$PhNH_2$, as II	−0.74, (−1.07)	
$PhNMe_2$, as I	1.89, (−1.41)	1969, 1897, 1892
$PhNMe_2$, as II	0.13, (−0.40)	
p-$C_6H_4(NH_2)_2$, as I′I″	3.22^b	
p-$C_6H_4(NH_2)_2$, as II′II″	-1.64^b	
p-$C_6H_4(NH_2)_2$, as I′II″	0.79^b	

[a] The first value was computed taking $\mu^*(\text{Ph–X}) = \mu(\text{Ph–X})$, the second one assuming $\mu^*(\text{Ph–X}) = \mu'(\text{Ph–X})$.
[b] As calculated using the dipole moment (1.72 D, in dioxane[30]) of *p*-phenylenediamine supposed to be equally divided into *cis* and *trans* conformers.
[c] In cyclohexane.

The greater the Ph–X mesomeric effect, the greater the ring π-basicity and the higher $\Delta\mu_0$ must be. Since, as indicated by their mesomeric moments and σ_R^0 Taft substitution constants (see Table 5), the mesomeric effect is much greater for anilines $PhNR_2$ than for anisole, we must have at least $\Delta\mu_0(PhNR_2) = 2 \times \Delta\mu_0(PhOMe) = 0.5$ D Better values for $\Delta\mu_0(PhNR_2)$ may probably be deduced by comparing their carbonyl frequencies with those of tricarbonyl mesitylene- or durene-chromium tricarbonyl

TABLE 5

MESOMERIC MOMENTS[31,32] AND σ_R^0 TAFT SUBSTITUTION CONSTANTS[27] FOR PhOR AND PhNR$_2$ DERIVATIVES

Compound	*m(D)*	σ_R^0
PhMe	0.4	−0.10
PhOH	0.6	−0.44
PhOMe	0.9	−0.41
PhNH$_2$	1.7	−0.48
PhNMe$_2$	2.0	−0.52

whose $\Delta\mu_0$ increments are well-defined. Therefore we have deduced $\Delta\mu_0(\text{PhNH}_2) = 0.5$ D, $\Delta\mu_0(\text{PhNMe}_2) = 1.0$ D.

Now the dipole moment of a tricarbonyl–(PhNR$_2$)chromium complex is given by

$$\mu^2 = x \cdot M(\text{I}) + y \cdot M(\text{II})$$

where $x + y = 1$, and

$$M(\text{I}) = [\mu^*(\text{PhNR}_2) \cdot \cos\theta^*]^2 + [\mu_0 + \Delta\mu_0 - \mu^*(\text{PhNR}_2) \cdot \sin\theta^*]^2$$

$$M(\text{II}) = [\mu^*(\text{PhNR}_2) \cdot \cos\theta^*]^2 + [\mu_0 + \Delta\mu_0 + \mu^*(\text{PhNR}_2) \cdot \sin\theta^*]^2$$

(see Fig. 1). Taking $\Delta\mu_0 = 0.5$ D for the aniline complex and 1.0 D for its *N,N*-dimethyl derivative we derive $x = 0.66$ and 0.53 respectively, from their dipole moments (5.50 and 6.18 D).

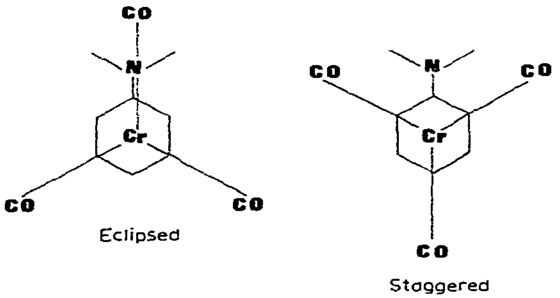

Fig. 4. Eclipsed and staggered sub-conformations for I and II conformers of anilinechromium tricarbonyl.

These results suggest that conformer I of anilinechromium tricarbonyl, as a benzene solute, is preferred. For this derivative Emanuel and Randall[33] showed that one of the Cr–C–O (nearly linear) groups eclipse the C–NH$_2$ bond (Fig. 4), the barrier to the chromium tricarbonyl group rotation being rather low [ca. 0.7 kcal/mole for n-propyl-, n-butyl-, isobutyl- and t-butylbenzenechromium tricarbonyl complexes[34]]. In conformer I, for such an orientation of the tricarbonylchromium group, the nearly sp^3 hybridized nitrogen lone pair, whose dipole moment is 3.3 D[35], points away from the Cr(CO)$_3$ radical whereas for conformerII it is nearly parallel to one of the strongly polar Cr–C–O groups, leading to a repulsive electrostatic potential[36]. This may explain why conformer I is more abundant than conformer II. In case of *N,N*-dimethylanilinechromium tricarbonyl the (I/II) conformational ratio is lower, probably due to more steric hindrance in conformer I and to a weaker repulsive potential between the nitrogen pair moment and the Cr–C–O group dipole in conformer II (the nitrogen lone pair moment steeply decreases with RNR angle increase[35], and NHN $=113°$ $54'$[24] and MeNMe $=116°$[25]).

In going from benzene to dioxane as solvent the dipole moment of anilinechromium tricarbonyl is increased by 0.55 D: (a) the μ_0^* value is somewhat increased, (b) benzene and dioxane moments of aniline are 1.53 and 1.77 D[23], respectively, (c) the conformational x ratio is changed. The first effect is likely to be small since benzene and dioxane moments for aprotic mesitylenechromium tricarbonyl are 5.59 and 5.77 D[15], respectively; it would raise the dipole moment to 5.68 D, assuming $\Delta\mu_0 = (0.5+0.2) = 0.7$ D. The second one, which derives from the fact that aniline (and by analogy its complex) combines with dioxane to give a hydrogen-bonded species[37], brings about an increase of only 0.02 D in the dipole moment. If so, the high dioxane moment of anilinechromium tricarbonyl (6.05 D) suggests that a marked lowering in the conformational x ratio occurs as a result of the solvent (dioxane) effect; in dioxane an x ratio of 0.48 is to be accepted for the complex. Unstable conformer II is much more susceptible to combination with dioxane than is conformer I (see Fig. 2).

From these facts we may infer that tricarbonyl *p*-phenylenediaminechromium tricarbonyl is a mixture of (I′ I″), (II′ II″) and mixed (I′ II″) = I″ II′) conformers (shown in Fig. 3), having a dipole moment expressed as:

$$\mu^2 = \alpha^2 \cdot M(\mathrm{I'\,II''}) + (1-\alpha)^2 \cdot M(\mathrm{II'II''}) + 2\alpha \cdot (1-\alpha) \cdot M(\mathrm{I'\,II''}).$$

It is interesting to compare the α-value with anilinechromium tricarbonyl (I/II)-ratio, equal to $x=0.66$ for the benzene solute, since on purely statistical grounds α must be equal to x. Now the $\Delta\mu_0$ value for *p*-phenylenediaminechromium tricarbonyl is to be low in magnitude since its tricarbonylchromium carbonyl frequencies are 1948, 1854 and 1816 cm^{-1}, whereas those of aniline- and benzene-chromium tricarbonyl are 1946, 1864, 1845, and 1971, 1874, 1860 cm^{-1}, respectively (all these frequencies measured on KBr films). To obtain a plausible $\Delta\mu_0$ value, say 0.5 D, for the *p*-phenylenediamine complex, an α-value as low as 0.50 must be accepted (assuming $\alpha=0.66$ or 0.59, one finds $\Delta\mu_0=1.33$ and 1.0). Hence, as a dioxane solute, *p*-phenylenediaminechromium tricarbonyl is a mixture of I′ II″ (25%), II′ II″ (25%) and mixed (50%) conformers. Note that in all four conformers propitious (C–N, Cr–CO) eclipsing is solely realizable for one of the *p*-phenylenediamine amino-groups.

This low value found for α can be explained as follows: realization probabilities of intermolecular complexes with dioxane are greater for II′II″ and mixed conformers than for I′I″ conformer, having two, one and no free amino group(s), respectively. Thus the dipole moment of *p*-phenylenediaminechromium tricarbonyl in dioxane substantiates our interpretation of the dioxane effect upon the electric moment of anilinechromium tricarbonyl.

Substituted thiophenechromium tricarbonyl complexes

On the basis of the assumption $\mu^*(\text{Me–arene}) = \mu(\text{Me–arene})$, shown to be valid for toluenechromium tricarbonyl, we compute significant μ_0^* values for the thiophenechromium tricarbonyl derivatives listed in Table 6.

TABLE 6

μ_0^* VALUES FOR A NUMBER OF ALKYL-SUBSTITUTED THIOPHENECHROMIUM TRICARBONYL COMPLEXES

Z in $ZCr(CO)_3$	*Ring moment (D)*	$\mu_0^*(D)$
$C_4H_4S^a$	0.54^2	5.95
$2\text{-}MeC_4H_3S$	0.67^2	6.19
$2\text{-}t\text{-}BuC_4H_3S$	0.7^b	6.29
$3\text{-}MeC_4H_3S$	0.82^2	6.18
$3\text{-}t\text{-}BuC_4H_3S$	0.9^b	6.28
$2,3\text{-}Me_2C_4H_2S$	1.0^c	6.34
$2,4\text{-}Me_2C_4H_2S$	0.8^c	6.20
$2,5\text{-}Me_2C_4H_2S$	0.51^2	6.38
$2,3,5\text{-}Me_3C_4HS$	0.8^c	6.49
$2,3,4,5\text{-}Me_4C_4S$	1.0^c	6.75
$2\text{-}MeO_2C\text{-}3\text{-}MeC_4H_2S^a$	1.77^d	5.02

[a] In cyclohexane $\nu(CO) = 1977, 1907, 1889$ and $1990, 1934, 1923$ cm^{-1}, respectively.
[b] Assumed, as μ(t-butylbenzene) $\cong$ μ(toluene)^2.
[c] Additive values calculated using dipole moments of 2-methyl- or 3-methyl-thiophene.
[d] This work.

As for polymethylbenzenechromium tricarbonyl complexes the methyl effect upon the μ_0^* component of the dipole moment in nearly corresponding thiophene compounds may be ascribed to a progressive increase in the π-basicity of the ring receiving more and more electrons from the methyl groups through a hyperconjugative mechanism. We observe $\Delta\mu_0 = 0.20\,n$, where n is the number of methyls, a relation which compares well with the one ($\Delta\mu_0 = 0.23\,n$) given by Randall and Sutton[13] for polymethylbenzenechromium tricarbonyl complexes.

The dipole moment found for 2-methoxycarbonyl-3-methylthiophene (1.77 D) strongly supports a planar model having its carbonyl oxygen atom far from the sulphur atom. The corresponding complex exhibits a dipole moment (5.02 D) lower than that of 3-methylthiophenechromium tricarbonyl complex by 1.27 D, whereas the $\Delta\mu_0$ value for methyl benzoatechromium tricarbonyl is only -0.9 D. This shows greater mesomeric effect of a given substituent in a 2-substituted thiophene than in the substituted benzene derivative.

Although the π-basicity (as related to the aromatic character[32]) of thiophene is weaker than that of benzene, the μ_0^* value [5.95 D, assuming μ^*(thiophene) = μ(thiophene) = 0.54 D] for thiophenechromium tricarbonyl is 0.92 D greater than the observed dipole moment of benzenechromium tricarbonyl (5.03 D).

Since the sulphur delocalized lone pair participates in bonding with the chromium atom some reduction in the ring mesomeric moment may occur. In contrast with this view, the ring geometry is not significantly altered when passing from thiophene to thiophenechromium tricarbonyl[38], showing that a great resonance decrease in the ring, as a result of complexation, is quite improbable. Note that complete resonance inhibition in the ring would lead to adopting μ(thiophene) = μ(tetrahydrothiophene) = 1.89 D and, therefore to retaining a μ_0 value (5.70 D) still much higher than 5.03 D.

Ring–chromium distances, and S–Cr and C_{ar}–Cr lengths too, are nearly equal for thiophene- and benzene-chromium tricarbonyl[38,18]. Hence the origin of the relatively high moment found for thiophenechromium tricarbonyl is purely electronic.

As a whole the negative charge of the chromium atom is greater in the thiophene than in the benzene complex, as indicated by its lower carbonyl frequencies: $\nu(CO) =$ 1977, 1907 and 1889 cm^{-1} to be compared with 1987, 1917 and (absent) cm^{-1}.

To reconcile this fact with the weaker π-basicity of thiophene we suggest what follows.

The dipole moment of the dative S–Cr bond is much greater than that of the (olefin–metal) group. From the dipole moments of cycloheptatrienemolybdenum tricarbonyl and benzenechromium tricarbonyl complexes Strohmeier and Hellmann[38] deduced μ(olefin–M) = 2.2 D [assuming μ(OC–Mo) = μ(OC–Cr) = 0.5 D], a figure close to the dipole moment of 1,3-butadieneiron tricarbonyl (2.15 or 2.26 D[40]). Dative atom–Cr bonds exhibit high moments. The S–Cr bond moment, as deduced from the dimethyl sulfoxidechromium pentacarbonyl dipole moment, is as high as 4.0 D[41], and N–Cr bond moments attain ca. 5 D in n-propylamine-, pyrrolidine- and acetonitrile-chromium pentacarbonyl complexes[42,41]. Thus we can explain why, despite the relatively weak π-basicity of thiophene leading to normal (but rather smaller than those in benzenechromium tricarbonyl) olefin–Cr component dipoles, thiophenechromium tricarbonyl has so high a moment and its metal atom more negatively charged than that in benzenechromium tricarbonyl*.

Benzo[b]thiophenechromium tricarbonyl

Benzo[b]thiophenechromium tricarbonyl exhibits a dipole moment (5.02 D) nearly equal to those (5.03 or 5.02–5.13 D) of benzene- and naphthalene-chromium tricarbonyl, and 0.96 D lower than that of thiophenechromium tricarbonyl. Aromatic character (and π-basicities) are similar for benzo[*b*]thiophene and naphthalene[43] which both are, consequently, more π-basic than benzene and thiophene. These facts may be understood by postulating:

(a) The π-basicity of the arene to be considered here is that of the ring directly united to the tricarbonylchromium group, and not the π-basicity of the arene as a whole.

(b) In benzo[*b*]thiophenechromium tricarbonyl, the tricarbonylchromium group is attached to the benzene moiety. This confirms a greater π-basicity to benzene than to thiophene, and shows that the benzene–$Cr(CO)_3$ bond, though on the whole less polar, is stronger than the thiophene–$Cr(CO)_3$ bond. Note that the NMR spectrum of benzo[*b*]thiophenechromium tricarbonyl shows that the tricarbonylchromium group only alters the benzene protons[44].

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* The same explanation holds for N-methylpyrrolechromium tricarbonyl whose dipole moment (6.2 D[45]) is 0.8 D higher than that calculated from electric moments of benzenechromium tricarbonyl (5.03 D) and *N*-methylpyrrole (1.98 D[3]).

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