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# AN EXPERIMENTAL STUDY OF VARIOUS ARENETRICARBONYLCHROMIUM COMPLEXES

H. LUMBROSO *, Ch. LIÉGEOIS,
*Laboratoire de Chimie Générale, Université Pierre et Marie Curie, 4, Place Jussieu, 75230 Paris Cedex 05 (France)*

D.A. BROWN and N.J. FITZPATRICK
*Department of Chemistry, University College Dublin, Belfield, Dublin 4 (Ireland)*
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## Summary

For a series of arenetricarbonylchromium complexes $ZCr(CO)_3$, analysis of the electric dipole moments in benzene and carbonyl stretching frequencies in cyclohexane suggest the following: for unsubstituted $ZCr(CO)_3$, with Z = diphenyl, fluorene and *cis*-stilbene, the π-basicity to be considered is that of the ring directly united to the tricarbonylchromium group, and not that of the arene as a whole. In general, the substituent effect in *p*-substituted diphenyltricarbonylchromium complexes (Z = 4-methyl-, 4-amino- and 4,4′-dimethyldiphenyl), in which the tricarbonylchromium group is bonded to the substituted phenyl ring, is markedly weaker than that in the corresponding benzenetricarbonylchromium complexes. In 4-fluorodiphenyltricarbonylchromium, the tricarbonylchromium group is attached to the unsubstituted phenyl ring. 4-Aminodiphenyltricarbonylchromium exists in two distinct forms: one with the nitrogen lone pair away from, and the other close to, the metal atom. Diphenylmethanetricarbonylchromium (and its 4,4′-diamino derivative), indanetricarbonyl- and 4,4′-difluorodiphenyltricarbonylchromium have also been examined.

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## Introduction

While substituted benzenetricarbonylchromium complexes have been extensively studied using dipole moment measurements [1,2], infrared spectroscopy [3], $^{13}C$ NMR spectroscopy [4] and other techniques [5], diphenyltricarbonylchromium complexes have been little examined. Allegra [6] has determined the X-ray structure of diphenylbis(tricarbonylchromium) $[C_6H_5\text{-}\{Cr(CO)_3\}]_2$ while the dipole moment of diphenyltricarbonylchromium has

TABLE 1

PHYSICAL DATA FROM DIPOLE MOMENT DETERMINATIONS OF $ZCr(CO)_3$ COMPLEXES IN BENZENE AT 30.0°C

| Ligand Z | $w_{max.}$ | $\alpha$ (ml $g^{-1}$) | $-\beta$ (ml $g^{-1}$) | $P_{2\infty}$ (ml $mol^{-1}$) | $R_D$ [a] (ml $mol^{-1}$) | $\mu$ (D) |
|---|---|---|---|---|---|---|
| Diphenylmethane | 0.011 | 9.69 | 0.446 | 623.5 | 90.6 | 5.15 ± 0.03 |
| Bis(*p*-aminophenyl)methane | 0.004 | 9.70 | 0.432 | 687.1 | 99.4 | 5.41 ± 0.05 |
| Fluorene | 0.011 | 9.96 | 0.457 | 633.9 | 91.0 | 5.20 ± 0.03 |
| Indane | 0.017 | 13.36 | 0.456 | 697.4 | 97.5 | 5.46 ± 0.05 |
| *cis*-Stilbene | 0.005 | 8.90 | 0.433 | 601.9 | 97.1 | 5.01 ± 0.03 |
| Diphenyl | 0.006 | 9.71 | 0.390 | 600.8 | 87.7 | 5.05 ± 0.03 [b] |
| 4-Methyldiphenyl | 0.007 | 9.55 | 0.410 | 618.8 | 92.6 | 5.12 ± 0.03 |
| 4-Fluorodiphenyl | 0.013 | 9.05 | 0.473 | 591.8 | 87.5 | 5.01 ± 0.03 |
| 4-Aminodiphenyl | 0.013 | 10.26 | 0.512 | 649.1 | 92.1 | 5.26 ± 0.04 |
| 4,4′-Dimethyldiphenyl | 0.009 | 9.77 | 0.390 | 662.5 | 97.5 | 5.30 ± 0.03 |
| 4,4′-Difluorodiphenyl | 0.013 | 7.03 | 0.494 | 499.2 | 87.3 | 4.53 ± 0.04 |

[a] Additive values, from $R_D$(benzenetricarbonylchromium) 61.5 ml (measured in benzene [2]), $R_D$(benzene) 26.2 ml, and the refraction of the ligand Z: respectively, 55.36 [14], 64.1 (from the preceding one and aniline 30.56 ml [15]), 55.7 [16], 38.6 (from *o*-xylene 36.0 ml), 61.77 [17], 52.4 [14], 57.3, 52.2 (from fluorobenzene 25.98 ml [15]), 56.8 (from aniline 30.56 ml [15]), 56.8, 61.7 and 52.0 ml.
[b] Lit. [7]: $\mu$ 5.35 D in benzene (temperature and $_EP + {}_AP$ not specified).

been measured in benzene [7], and its infrared spectrum recorded [8]. More recently, Brown et al. [9] have examined the $^{13}C$ NMR spectra of diphenyltricarbonylchromium and its 4-fluoro-, 4-chloro-, 4,4′-dimethyl- and 4,4′-difluoro-substituted derivatives, as well as those of diphenylmethane-, 4-chlorodiphenylmethane-, dibenzyl-, *cis*-stilbene- and benzophenone-tricarbonylchromium complexes.

In the present work, electric dipole moments and carbonyl stretching frequencies have been determined for several arenetricarbonylchromium complexes (see Tables 1 and 2), and an attempt is made to interpret the results in

TABLE 2

CARBONYL STRETCHING FREQUENCIES ($cm^{-1}$) IN CYCLOHEXANE OF ARENETRICARBONYLCHROMIUM COMPLEXES

| Z in $ZCr(CO)_3$ | $\nu(C{=}O)$ [a] |
|---|---|
| Diphenylmethane | 1978s, 1968vw, 1912s, 1908(sh), 1904(sh) |
| Fluorene | 1988vw, 1974s, 1911, 1907 [b] |
| Indane | 1989vw, 1973s, 1906—1901 (doublet) |
| *cis*-Stilbene | 1978s, 1968vw, 1913s |
| Diphenyl | 1979vs, 1969(sh), 1913s [c] |
| 4-Methyldiphenyl | 1975—1977(doublet), 1911s, 1907(sh) |
| 4-Fluorodiphenyl | 1979s, 1970vw, 1915vs, 1881vw |
| 4-Aminodiphenyl | 1969w, 1965s, 1911(sh), 1908s, 1896(sh) |
| 4,4′-Dimethyldiphenyl | 1974vs, 1965vw, 1909—1905 (doublet) |
| 4,4′-Difluorodiphenyl | 1988s, 1977vw, 1929—1920 (doublet) |

[a] s, vw, (sh) and vs stand for strong, very weak, shoulder and very strong, respectively. [b] Lit. [8]: 1972, 1903 $cm^{-1}$ (NaCl prism). [c] Lit. [8]: 1983, 1916 $cm^{-1}$ (LiF prism).

terms of the molecular structure and the magnitude of the $\sigma/\pi$-bonding between the arene and the tricarbonylchromium group.

## Experimental

### *Materials*

Cryoscopic R.P. benzene (from "Prolabo", Paris) was recrystallized and dried over metallic sodium: at 30.0°C, $d_4$ 0.8682, $n_D$ 1.4957. Its dielectric constant was assumed to be 2.2642.

The arenetricarbonylchromium complexes were prepared by published methods [10].

### *Physical measurements and results*

The dipole moments were measured in benzene at 30.0°C. The total polarization of the solute, extrapolated to infinite dilution, was calculated from the ratios [11]:

$$\alpha_0 = \lim_{(w=0)} \frac{(\epsilon - \epsilon_1)}{w} \text{ and } \beta = \frac{\Sigma(v - v_1)}{\Sigma w},$$

where $w$ is the weight fraction of the solute, $\epsilon$ and $v$ are, respectively, the dielectric constant and specific volume of the solutions; subscript one refers to the pure solvent as used, i.e. prepared in the same way as the solutions. The $\alpha_0$ value has been determined by least-square analysis of the $\epsilon(w)$ polynomial function, which appeared to be linear for the compounds studied. A Sartorius microbalance was used to make up the solutions. Specific volumes have been measured with a Digital Microdensimeter DMA 02C (from "Anton Paar KG", Graz. Austria).

The distortion polarization ${}_EP + {}_AP$ was assumed to be equal to the molecular refraction of the solute ($R_D$), as calculated from $\gamma = \Delta(n^2)/w$ and $\beta$ by using an equation similar to that of Halverstadt and Kumler [11]. Differences between the refraction indices of solutions and the solvent were measured using a thermostatted "VEB Carl Zeiss" interferometer (from Jena, D.D.R.). As the measured molecular refractions differ by only 0.5—1.0 ml from additive figures, deduced from that of benzenetricarbonylchromium (61.5 ml) (see ref. [2]), we have used the latter values when calculating the dipole moments.

The technique for the measurement of dielectric constants has been described elsewhere [12,13]. For each solute examined, $w_{max.}$ (reported to only three decimal points, though it is known to at least five), $\alpha_0 = \alpha$, $\beta$ (in ml g$^{-1}$), $P_{2\infty}$ and $R_D$ (both in ml mol$^{-1}$), and $\mu$ (in Debye units) are given in Table 1.

The infrared spectra were recorded in cyclohexane, using a Perkin—Elmer 225 spectrograph calibrated with steam. The results are listed in Table 2.

## Discussion

### *Substituent effects on the dipole moments of benzenetricarbonylchromium complexes*

1. X-ray structure determinations of benzene- [18], toluene- [19], (methylbenzoate)- [20], (1-formyl-2-methoxybenzene)- [21], hexamethylbenzene-

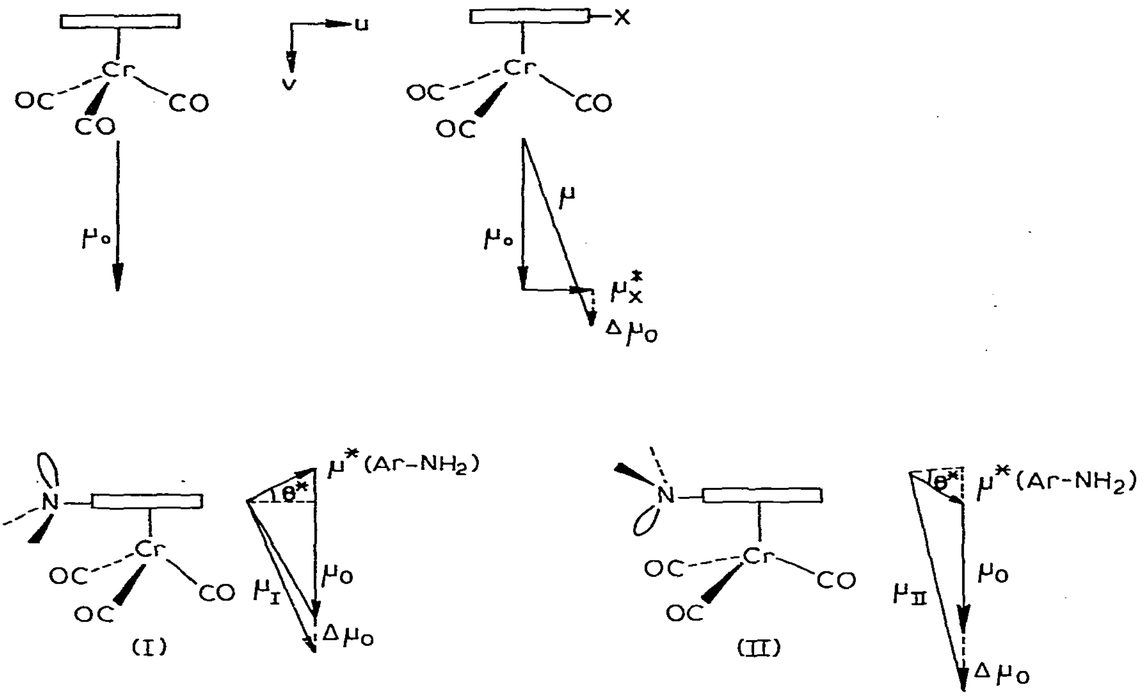

Fig. 1. The dipole moments of arenetricarbonylchromium and 4-X-substituted arenetricarbonylchromium complexes (with X axial), and of conformers I and II of 4-aminoarenetricarbonylchromium complexes, with arene = benzene or diphenyl (diagrammatic).

[22] and thiophene-tricarbonylchromium [23] complexes show the tricarbonylchromium ternary axis to be perpendicular to the planar arene ring at its geometrical centre. The same situation exists for both tricarbonylchromium groups in diphenylbis(tricarbonylchromium) [6], which are orthogonal to their respective phenyl rings. Consequently the dipole moments of a substituted arenetricarbonylchromium complex may be expressed as the vectorial sum

$$\underline{\mu} = \underline{\mu_0^*} + \underline{\mu^*}\,(\text{Ar—X})$$

$$= (\mu_0 + \Delta\mu_0)\cdot \underline{v} + \mu_x^* \cdot \underline{u}$$

where $\mu_0 = \mu[\text{arene—Cr(CO)}_3]$, and $\underline{\mu_0^*}$ and $\underline{\mu_x^*}$ denote the effective dipole moments along the two perpendicular directions ($\underline{v}$ and $\underline{u}$, respectively) * (see Fig. 1). From the experimental dipole moment values for *p*-substituted benzenetricarbonylchromium complexes, the derived $\mu_0^*$ value is found to depend on the nature of the substituent, being greater than $\mu_0$ if X is electron-donating (X = Me, OH, OMe, NH$_2$, NMe$_2$) and smaller than $\mu_0$ if X is electron-withdrawing (X = COMe [2], CO$_2$Me [24,2]) (see [1] for references). However, the halobenzenetricarbonylchromium complexes, whose dipole moments are 4.51, 4.53,

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* In the case of anilinetricarbonylchromium and 4-aminodiphenyltricarbonylchromium the vectorial equations giving the dipole moments of conformers I and II (Fig.1) are $\mu$ (I or II) = $(\mu_x^* \cdot \cos\theta^*)\underline{u}$ + $(\mu_0 + \Delta\mu_0 \mp \mu_x^* \cdot \sin\theta^*) \cdot \underline{v}$ where $\mu_x^* = \mu^*(\text{arene—NH}_2)$ and $\theta^*$ the angle of $\underline{\mu_x^*}$ with the $u$ direction.

4.65 and 4.59 D for X = F, Cl, Br or I [25], respectively, appear anomalous, since the halogens are known to be weakly $\pi$-electron-donating substituents [26]. The carbonyl stretching frequencies of substituted benzenetricarbonylchromiums confirm these views since they are smaller or higher than those of benzenetricarbonylchromium according to whether the substituent is methyl or amino [8] on the one hand, or acetyl [2], methoxycarbonyl [8,2] and fluorine [8] on the other. For halobenzenetricarbonylchromiums, the observation that $\mu_0^*$ is smaller than $\mu_0$ (5.03 D) [2] is supported by the low values found for *p*-difluorobenzene- and *p*-dichlorobenzene-tricarbonylchromium (4.40 and 4.00 D [27]) whose ligands are non-polar, and remain so when complexed.

There is controversy over the net charge on the arene ring in the unsubstituted compound. For example, SCCCMO calculations lead to $\pi$-electron withdrawal by the $Cr(CO)_3$ group compensated by $\sigma$-electron back-donation, giving a slight net negative charge on the ring and a small net positive charge on the metal atom [28], whereas a number of CNDO calculations give either net-negative [29] or net-positive charges [30,31] on the ring depending on the parameters employed. Finally, an ab initio calculation using a fairly limited basis set indicated a net-negative charge on the arene, involving both $\sigma$- and $\pi$-donation to the ring and a large positive charge on the metal [32]. In view of the success of the SCCCMO method in comparing related molecules we favour the conclusions of this method for the unsubstituted compound, namely $\pi$-electron withdrawal from and $\sigma$-back donation to the $Cr(CO)_3$ group.

For substituents where the mesomeric effect is dominant, the effect on dipole moments may be related directly to the $\pi$-basicity of the ring, thereby influencing the arene—Cr group moment and the multiplicity of the carbonyl bonds through the $\bar{\mathrm{M}}\text{—C}\equiv\mathrm{O}$ resonance form. However, for substituents with a weak mesomeric effect (e.g. the weakly $\pi$-donating halogens), account must also be taken of $\sigma$-back donation to the arene ring.

The above electronic interaction between the substituent X and $Cr(CO)_3$ group may also influence $\mu_X^*$. The fact that $\mu_X^*$ may differ markedly from $\mu$(Ph—X) (the dipole moment of the uncomplexed substituted benzene) is shown clearly by the following:

(i) Though the *p*-xylene, mesitylene, hexamethylbenzene, *p*-dichlorobenzene ligands (L) are non-polar, and must remain so when complexed, the dipole moments of (L)—$Cr(CO)_3$ complexes markedly differ from that of benzenetricarbonylchromium (5.03 D), being 5.52, 5.52, 6.04, 6.48 [7], 4.40 and 4.00 D [27], respectively. For *p*-disubstituted benzene complexes such as (*p*-phenylenediamine)- and (dimethylterephthalate)-tricarbonylchromium, ring complexation alters the mesomeric effects of both substituents equally and, thus, $\mu^*(p\text{-}XC_6H_4X)$ can still be taken as equal to $\mu(p\text{-}XC_6H_4X)$ (see ref. 2).

(ii) Chemical data suggest that the tricarbonylchromium group withdraws electrons from the phenyl ring at least as strongly as a *p*-nitro group, though by a different mechanism [33,34]. If so, $\underline{\mu}^*$(Ph—X) can be equated to a vector $\underline{\mu}'$(Ph—X) calculated by solving the vectorial equation [2]

$$\underline{\mu}(p\text{-}XC_6H_4NO_2) = \underline{\mu}'(\text{Ph—X}) + \underline{\mu}(\text{Ph—NO}_2)\,.$$

2. Analysis of the dipole moment of *p*-fluorobenzenetricarbonylchromium is

useful in interpreting that of 4-fluorodiphenyltricarbonylchromium, measured in the present work.

Taking $\mu^*$(Ph—F) = $\mu$(Ph—F) = 1.45 D [35] or equal to $\mu'$(Ph—F) = 1.60 D (from $p$-$FC_6H_4NO_2$ 2.64 D, Ph—F 1.45 D and Ph—$NO_2$ 3.95 D [35]), one derives $\mu_0^* = 4.27$ or 4.22 D, values which are 0.76 and 0.81 D less than the dipole moment of unsubstituted benzenetricarbonylchromium. This is in accord with the well-known $\pi$-inductive effect of fluorine [36] ($\sigma_I(F) = +0.51$, whereas $\sigma_I(NH_2) = 0.10$) and with the positive sign of its total Hammett $\sigma$-constant, $\sigma_p^0(F) = +0.17$ whereas $\sigma_p^0(NH_2)$ is —0.38, and finally with the inference that the $\pi$-basicity of fluorobenzene is close to that of benzene as indicated by their first ionization potentials: benzene 9.23 [37] or 9.24 eV [38], fluorobenzene 9.33 [37] or 9.19 eV [39], aniline 7.71 eV [40].

For the case of diphenylmethane which, if written as ($PhCH_2$)—Ph, resembles toluene and indane which can be related similarly to orthoxylene, it is found that all have rather similar dipole moments, viz. 0.3—0.4 D and 0.35 D, 0.55 and 0.54 D, respectively [35]. Similarly, as expected the dipole moments of (diphenylmethane)tricarbonyl- and toluenetricarbonylchromium (5.15 (Table 1) and 5.26 D [7]), indanetricarbonyl- and $o$-xylenetricarbonylchromium (5.46 (Table 1) and 5.48 D [24] *) are close to one another. The carbonyl stretching frequencies recorded in cyclohexane are also rather similar to one another:

(Diphenylmethane)—$Cr(CO)_3$: 1978, 1912 $cm^{-1}$ (this study),
(Toluene)—$Cr(CO)_3$: 1977, 1911 $cm^{-1}$ [41];
(Indane)—$Cr(CO)_3$: 1973, 1906—1901 $cm^{-1}$ (this work),
($o$-Xylene)—$Cr(CO)_3$: 1973, 1906, 1901 $cm^{-1}$ [41];
(Benzene)—$Cr(CO)_3$: 1983, 1913 $cm^{-1}$ (present work),
(Benzene)—$Cr(CO)_3$: 1983, 1915 $cm^{-1}$ [41].

### *The dipole moments of unsubstituted arenetricarbonylchromium complexes*

As a rule, the dipole moments of the arenetricarbonylchromium complexes studied are close to that of benzenetricarbonylchromium, and their carbonyl stretching frequencies (in cyclohexane) are rather close to one another (Table 3).

For diphenyl-, naphthalene-, anthracene- and phenanthrene-tricarbonylchromium complexes the results in Table 3 suggest that the $\pi$-basicity to be considered here is that of the ring directly united to the tricarbonylchromium group and not the $\pi$-basicity of the arene as a whole, since the $\pi$-basicities of diphenyl, naphthalene, anthracene and phenanthrene are much higher than that of benzene (first ionization potential $I = 9.23$ eV [38]), being in eV 8.39 [38], 8.13, 7.41 and 7.69 (or 8.12 [38]) [39], respectively. This is also supported by the fact that the dipole moments of fluorene- and diphenylmethane-tricarbonylchromium are close to one another (5.20 and 5.15 D). A similar view has been expressed for benzo[$b$]thiophenetricarbonylchromium [2], whose dipole moment (5.02 D) suggests that the tricarbonylchromium group is attached to the "benzo" moiety of the heterocyclic ring. In this respect it is noteworthy that changes in the $^{13}C$ NMR chemical shifts on passing from benzene to benzene-

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* Recalculated using $_EP + {}_AP = 71.3$ ml [from $R_D[C_6H_6Cr(CO)_3] = 61.5$ ml [2]]: 5.46 D.

TABLE 3

ELECTRIC DIPOLE MOMENTS (DEBYE UNITS) AND CARBONYL STRETCHING FREQUENCIES ($cm^{-1}$) OF ARENETRICARBONYLCHROMIUM COMPLEXES

| Z in $ZCr(CO)_3$ | $\mu$(benzene) | $\nu$(C=O) (in cyclohexane) |
|---|---|---|
| Benzene | 5.03 [2] [a] | 1983, 1913 |
| Diphenyl | 5.05 | 1979, 1913 [c] |
| *cis*-Stilbene | 5.01 | 1978, 1913 [c] |
| Naphthalene | 5.02 [27] [b] | 1977, 1918, 1905 [8] |
| Anthracene | 5.12 [42] | 1978, 1917, 1895 [8] [d] |
| Phenanthrene | 5.03 [42] | 1980, 1920, 1910 [8] |

[a] Lit. [7]: 5.08; [24] 4.92: equal value is obtained by assuming ${}_EP + {}_AP$ = 61.5 ml. [b] Recalculated: 5.08, for ${}_EP + {}_AP$ = 79.7 ml ($R_D$(naphthalene) = 44.37 ml [14]). [c] See Table 2 (underlined figures). [d] Other values [42]: 1982, 1924, 1897 $cm^{-1}$.

tricarbonylchromium (Δδ 34.47 ppm [4]) and from diphenyl to diphenylcarbonylchromium (Δδ (carbons 1—4) 30.6, 34.8, 36.0 or 35.6 ppm, for the complexed ring [9]) are of the same order of magnitude.

It follows then that the predicted dipole moment of *cis*-stilbenetricarbonylchromium should be close to that of benzenetricarbonylchromium, the more so as the non-planarity of *cis*-stilbene, with phenyl rotational angles equal to 43° [43], reduces conjugation and so further diminishes the $\pi$-basicity of the ligand. This is fully confirmed by experiment (Table 3).

### *The dipole moments of substituted diphenyltricarbonylchromium complexes*

The dipole moments of substituted diphenyltricarbonylchromium complexes can be compared with those of the corresponding benzenetricarbonylchromium complexes (listed in Table 4) since the dipole moments of identically substituted diphenyls and benzenes are close to each other [35].

1. For weakly $\pi$-electron-donating substituents, such as fluorine and chlorine, having Taft $\sigma_R^0$ constants of —0.34 and —0.22 [26], the mesomeric effect of the substituent only affects the substituted ring in the 4-substituted diphenyls. The dipole moments of fluorobenzene and 4-fluorodiphenyl, chlorobenzene and 4-chlorodiphenyl are close to each other, being 1.48 and 1.51 [44], 1.59 [35] and 1.57 D [44]. Similarly, the $^{13}C$ NMR chemical shifts of the *ortho*- and *para*-carbon atoms of the substituted ring only change on passing from diphenyl to 4-fluoro- and 4-chloro-diphenyl, being (in ppm) Δδ(3,5) = 13.0 or 0.8, Δδ(1) = 3.8 or 1.5; Δδ(2′,6′) = 0.0 or 0.1, Δδ(4′) = —0.2 or —0.6 [9] (corresponding figures for fluorobenzene and chlorobenzene are Δδ(2,6) = 12.93 or —0.43, Δδ(4) = 4.39 or 1.95 [4]).

In case of the more electron-donating amino group, with $\sigma_R^0$ = —0.47 [26], it appears that now the unsubstituted ring in 4-aminodiphenyl is weakly perturbed, since the dipole moments of aniline and 4-aminodiphenyl differ markedly, being 1.53 [44] and 1.83 D [45,46], leading to an increase of 0.31 D in the mesomeric moment ($m$ = 1.0 D for aniline). Interestingly, the interaction moment in 4-amino-4′-nitrodiphenyl (0.55 D) is smaller than that of *p*-nitroaniline (1.03 D [44]) despite the greater length of the former; details of calculations are given in the footnotes to Table 4.

TABLE 4

ELECTRIC DIPOLE MOMENTS (DEBYE UNITS) AND CARBONYL STRETCHING FREQUENCIES ($cm^{-1}$) OF SUBSTITUTED BENZENETRICARBONYLCHROMIUM AND DIPHENYLTRICARBONYLCHROMIUM COMPLEXES

| No | Z in $ZCr(CO)_3$ | $\mu$(benzene) | $\nu$(C=O) in cyclohexane |
|---|---|---|---|
| 1 | Benzene | 5.03 [2] | 1983, 1915 [41] |
| 2 | Toluene | 5.26 [7] [a] | 1977, 1911, 1909 [41] |
| 3 | Fluorobenzene | 4.51 [25] [b] | 1990, 1926, 1923 [41] |
| 4 | Aniline | 5.50 [2] [c] | 1977, 1906, 1901 [8] |
| 5 | *p*-Xylene | 5.52 [7] [d] | 1979, 1908 [8] |
| 6 | *p*-Difluorobenzene | 4.40 [27] [e] | |
| 1′ | Diphenyl | 5.05 | 1979, 1913 [f] |
| 2′ | 4-Methyldiphenyl | 5.12 | 1975—1977, 1911, 1907 [f] |
| 3′ | 4-Fluorodiphenyl | 5.01 | 1979, 1970, 1915 [f] |
| 4′ | 4-Aminodiphenyl | 5.26 | 1965, 1908 [f] |
| 5′ | 4,4′-Dimethyldiphenyl | 5.30 | 1974, 1909—1905 [f] |
| 6′ | 4,4′-Difluorodiphenyl | 4.53 | 1988, 1929—1920 [f] |

[a] Other values: 5.20 [24], 5.12 D [27]; recalculated using ${}_EP + {}_AP = R_D = 66.4$ ml (from $R_D(1) = 61.5$ ml [2]): 5.24 and 5.20 D, respectively. [b] 4.75 [24], 4.93 D [7]. [c] 5.40 [24], recalculated: 5.50 D. [d] 5.39 [24], 5.41 [27]; recalculated: 5.42 and 5.50 D. [e] Recalculated: 4.47 D. [f] See Table 2 (underlined figures).

2. For 4-methyldiphenyltricarbonyl- and 4-aminodiphenyltricarbonylchromium, 2′ and 4′, the $\Delta\mu_0$ values (listed in Table 5) and the carbonyl stretching frequencies (in Table 4) support the formulation having the tricarbonylchromium group attached to the substituted ring (Fig. 2). As a negative $\Delta\mu_0$ value for 4′ is very unlikely and since its carbonyl stretching frequencies are markedly lower than those of diphenyltricarbonylchromium, conformer II can not exist alone (see Fig. 1). Assuming $\Delta\mu_0(4') = 3 \times \Delta\mu_0(5')$ (as a trial), the dipole moment of 4′ (5.26 D) is then consistent with a mixture of I (90%) and II (10%); in the case of anilinetricarbonylchromium 4, a mixture of I (66%) and II (34%) had

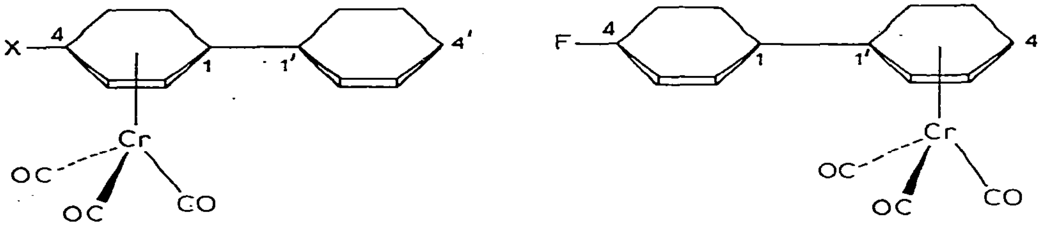
TABLE 5

$\Delta\mu_0$ INCREMENTS DERIVED FROM THE BENZENE DIPOLE MOMENTS OF ARENETRICARBONYLCHROMIUM COMPLEXES (DEBYE UNITS)

| Z in $ZCr(CO)_3$ | $\Delta\mu_0$ [a] [2] | Z in $ZCr(CO)_3$ | $\Delta\mu_0$ [a] |
|---|---|---|---|
| Benzene | 0.0 | Diphenyl | 0.0 |
| Toluene | 0.22 | *p*-Methyldiphenyl | 0.06 |
| *p*-Fluorobenzene | —0.77 | *p*-Fluorodiphenyl | —0.17 |
| Aniline, as I [b] | 1.53 or 1.25 | 4-Aminodiphenyl, as I [b] | 1.15 or 1.02 |
| Aniline, as II | —0.74 or —1.07 | 4-Aminodiphenyl, as II | —1.13 or —1.25 |
| *p*-Xylene | 0.38 | 4,4′-Dimethyldiphenyl | 0.25 |
| *p*-Difluorobenzene | —0.63 | 4,4′-Difluorodiphenyl | —0.52 |

[a] The first value was calculated taking $\underline{\mu}_x^\star(\text{Ar—X}) = \underline{\mu}(\text{Ar—X})$, second using $\underline{\mu}_x^\star = \underline{\mu}'(\text{Ar—X})$.

[b] $\mu$(4-aminodiphenyl) = 1.83 D [45,46] acting at 38.4° to the $N—C_{ar}$ bond axis ($1.83 \times \sin\theta = \mu(\text{aniline}) \times \sin\theta_0$, whence $\theta = 38.4°$ taking $\mu$(aniline) = 1.53 D and $\theta_0 = 48°$ [44]); $\underline{\mu}'$(4-aminodiphenyl) = $(1.83 \times \cos 38.4° + \Delta\mu) \times \underline{u} + (1.83 \times \sin 38.4°) \times \underline{v}$, where $\Delta\mu = 0.55$ D is the interaction moment of 4-amino-4′-nitrodiphenyl derived from its dipole moment 6.49 D [45,46], $\mu$(4-aminodiphenyl) = 1.83 D and $\mu$(4-nitrodiphenyl) = 4.41 D [46].



(X = Me or $NH_2$)

Fig. 2. The formulae of 4-methyl- and 4-aminodiphenyltricarbonylchromium complexes and of 4-fluorodiphenyltricarbonylchromium.

been postulated previously [2] *. Taking $\Delta\mu_0 = 0.5$ D, as for 4, leads to % (I) = 77 ± 7.

The dipole moments of 4-methyl-, 4-amino- and 4,4'-dimethyldiphenyltricarbonylchromium complexes, 2', 4' and 5', are smaller than those of the analogous benzenetricarbonylchromium complexes, 2, 4 and 5, showing clearly that the substituent effect upon the $\mu_0^*$ (and $\Delta\mu_0$) value is weaker in the diphenyl series (Table 5).

The results in Tables 4 and 5 suggest that the $\pi$-basicity of the substituted ring in 4-methyl- and 4-aminodiphenyl is weaker than that of toluene or aniline. The magnitude of conjugation of a substituent for both benzene and diphenyl (in position 4) is very similar, as measured by the self-polarizability of the carbon atom ($\pi_r = 0.398$ and 0.411 [47]). Moreover, transmission of the substituent (mesomeric) effect across the central bond of diphenyl, though small in itself and reduced by non-coplanarity of the system (the interangle is ~40° in diphenyl [48]), tends to withdraw electrons from the substituted ring, especially for 4-aminodiphenyl.

4-Fluorodiphenyltricarbonylchromium is interesting in that its dipole moment is 0.5 D greater than that of *p*-fluorobenzenetricarbonylchromium (4.51 D), but is slightly smaller than that calculated using diphenyltricarbonylchromium and *p*-fluorodiphenyl, viz. 5.27 D, whence $\Delta\mu_0 = -0.17$ D instead of $-0.77$ D for *p*-fluorobenzenetricarbonylchromium. This suggests that the tricarbonylchromium group is attached to the unsubstituted ring of diphenyl (Fig. 2), the more so as the carbonyl stretching frequencies are nearly equal for 4-fluorodidiphenyl- and diphenyl-tricarbonylchromium, 3' and 1', whereas they differ by 7—10 $cm^{-1}$ for *p*-fluoro- and benzenetricarbonylchromium (3 and 1). This is strongly supported by $^{13}C$ NMR chemical shifts observed for 4-fluoro- and 4-chlorodiphenyl-tricarbonylchromium, since $\Delta\delta(3,5) = -0.3$ or $-0.5$ ppm, $\Delta\delta(1) = 5.3$ or 4.6 ppm, but $\Delta\delta(2',6') = 35.2$ or 35.1 ppm, $\Delta\delta(4') = 36.0$ or 36.2 ppm, on passing from 4-fluoro- or 4-chlorodiphenyl to 4-fluoro- and 4-chlorodiphenyl-tricarbonylchromium; in going from diphenyl to diphenyl-tricarbonylchromium, $\Delta\delta(4) = 35.6$ ppm, $\Delta\delta(3,5) = 36.0$ ppm, $\Delta\delta(2',6') = -2.2$ ppm,

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* In ref. 2, p. 255, Table 4, line 7 should read as follows:

| Z in $ZCr(CO)_3$ | $\Delta\mu_0$(D) |
|---|---|
| $PhNMe_2$, as I | 1.89 (1.41) |

$\Delta\delta(4') = -0.1$ ppm [9]. Note too that the $\Delta\delta(2',6')$ and $\Delta\delta(4')$ figures for 4-fluoro- and 4-chloro-diphenyltricarbonylchromium (quoted just above) are close to that observed when passing from benzene to benzenetricarbonylchromium, $\Delta\delta = 34.47$ ppm [4].

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