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THE CONFORMATIONS OF SOME MONO-SUBSTITUTED DERIVATIVES OF (η^6-BENZENE)TRICARBONYLCHROMIUM(0) FROM DIPOLE MOMENT AND ELECTRIC BIREFRINGENCE STUDIES

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ABSTRACT

Experimental dipole moments and molar Kerr constants (at 589 nm) are reported for (η^6-C_6H_5Y)$Cr(CO)_3$, where Y = CHO, $COCH_3$, $COOCH_3$, OCH_3, NH_2, $N(CH_3)_2$ and $NH(CH_3)$, examined as solutes in dioxan at 298 K. Analysis of these data in conjunction with infrared evidence, shows that the preferred conformational dispositions of the substituent groups in the complexes are close to those of the free arene ligands.

INTRODUCTION

It is accepted that in (η^6-arene)tricarbonylchromium(0) complexes electronic interaction occurs between the arene group and the $Cr(CO)_3$ moiety such that there is a shift of electrons from the aromatic ring towards the metal [1]. In the complexes (η^6-C_6H_5Y)$Cr(CO)_3$ the extent of charge transfer to the metal is related to the electron donating or electron accepting properties of Y. This has been shown by infrared spectral [2—4] and dipole moment [5] evidence and is supported by molecular orbital calculations [6, 7]. The electronic transmissions could affect the stability of the preferred molecular conformational forms normally associated with the free ligands. Further, the steric influence of the $Cr(CO)_3$ on the substituents Y is unknown. It is the purpose of this work to investigate these factors examining primarily the electric birefringences of the complexes (η^6-C_6H_5Y)$Cr(CO)_3$ where Y = H, CHO, $COCH_3$, $COOCH_3$, OCH_3, NH_2, $N(CH_3)_2$ and $NH(CH_3)$. This property is known to be an acutely sensitive index of molecular polarity and structure [8].

EXPERIMENTAL

All the tricarbonyl complexes except that of benzaldehyde were prepared via the triamminetricarbonylchromium(0) intermediate which was synthesised by the procedure of Razuvaev et al. [9]. This was refluxed in dioxan with a slight excess of the arene ligand for five hours. Filtration produced orange to yellow solutions which were concentrated then chromatographed (Merck neutral alumina, grade III, 16.5 cm by 1.5 cm column). Elution with ether/hexane mixtures and subsequent concentration yielded crystals of the arene tricarbonyls. The benzaldehyde complex could not be prepared in reasonable yield by this method because of excessive decomposition and it was synthesised by the method of Rausch et al. [10] which involves the acid hydrolysis of benzaldehydediethylacetaltricarbonylchromium(0). All syntheses were carried out under nitrogen. The complexes $(\eta^6\text{-}C_6H_5Y)Cr(CO)_3$ had the following melting points: Y = H, 162—163°C (hexane/ether); CHO, 78.5—79.5°C (hexane/ether); $COCH_3$, 90.5—93°C (heptane); $COOCH_3$, 97—98°C (heptane); OCH_3, 84—85°C (heptane); NH_2, dec. 173°C (hexane/ether); $N(CH_3)_2$, 142—143°C (hexane/ether); $NH(CH_3)$, 122—123°C (hexane/ether). These compare well with the literature values [9, 11, 12].

The apparatus, techniques of measurement, symbols and methods of calculation have been described before [8, 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 solvent and solute. The measurements were made in dioxan solutions at 298 K; the low solubility in cyclohexane or carbon tetrachloride precluded measurements in these solvents. Dioxan was purified by passing through a 50 cm column of activated neutral alumina. It was then refluxed, distilled and stored over sodium wire. The solvent constants ϵ_1, d_1, n_1 and B_1 for dioxan are given in ref. 13. Oxygen was removed from the solvent by saturating with dry nitrogen; the preparation and handling of solutions was carried out under an inert (N_2) atmosphere. The results are summarised in Table 1. The solute dipole moments (μ) and electric birefringences, expressed as molar Kerr constants (${}_mK$), are given in S.I. units throughout. The conversion factors from the electrostatic (c.g.s., e.s.u.) system are, respectively: 1 Cm $= 0.2998 \times 10^{30}$ D, 1 $m^5V^{-2}mol^{-1} = 0.8988 \times 10^{15}$ e.s.u. mol^{-1}.

Infrared spectra were recorded on a Perkin-Elmer 457 Grating Infrared Spectrophotometer (0.1 mm, KBr windows). The solutions were ca. 0.005 M and spectra were calibrated against known bands of polystyrene (accuracy ±2 cm^{-1}).

DISCUSSION

The procedure adopted in this work involves comparison of the measured molar Kerr constant of the complex $(\eta^6\text{-}C_6H_5Y)Cr(CO)_3$ with values computed for the range of stereostructures generated by rotation of the substituent group Y about the C_{ar}—Y axis. Such calculations may be made for a

TABLE 1

Molar polarisations and refractions, dipole moments and molar Kerr constants (from observations on solutions in dioxan at 298 K)

C_6H_5Y in (η^6-$C_6H_5Y)Cr(CO)_3$	$\alpha\epsilon_1$	β	γ	δ	$_\infty P_2$ (cm^3)	R_D (cm^3)	$10^{30}\mu$ (Cm)^{a,b}	$10^{27}{}_\infty({}_mK_2)^c$ (m^{5}V^{-2}mol^{-1})
C_6H_6	16.1	0.312	0.628	591	607	60.6	17.2	1610 ± 83
C_6H_5CHO	14.3	0.297	0.587	185	616	67.6	17.2	561 ± 28
$C_6H_5COCH_3$	13.7	0.288	0.560	199	630	70.8	17.4	606 ± 33
$C_6H_5COOCH_3$	11.6	0.290	0.486	163	574	72.0	16.5	556 ± 28
$C_6H_5OCH_3$	16.5	0.272	0.531	440	714	67.2	18.7	1380 ± 67
$C_6H_5NH_2$	19.8	0.315	0.639	734	790	65.1	19.8	2150 ± 110
$C_6H_5N(CH_3)_2$	20.6	0.262	0.561	721	922	72.8	21.4	2360 ± 110
$C_6H_5NH(CH_3)$	20.8	0.285	0.683	697	883	72.8	20.9	2160 ± 110

[a]Calculated on the basis that $_DP = 1.05R_D$. [b]Uncertainty <2%. [c]The term $_\infty({}_mK_2)$ refers to the solute molar Kerr constant at infinite dilution.

particular geometric model of the molecule provided that the appropriate segment anisotropic polarisabilities and dipole moments are known [8, 13]. In practice a suitable set of molecule-fixed orthogonal axes X, Y, Z were chosen and the elements of the matrix (b_{xx}, b_{yy}, etc.) which defines the molecular polarisability tensor for that structure, were determined by transformation of the bond and group polarisabilities into this axis system [16]. Vector summation of all component group moments along the same axes gave μ_x, μ_y and μ_z. The quantities so derived were substituted in eqn. (1) to give the predicted molar Kerr constant for that structure [16]. Conformational forms $0° \leqslant \phi \leqslant 90°$ were considered; the reference model, having $\phi = 0°$, is that in which the plane of the benzene ring contains the symmetry plane of the substituent Y (for all Y studied except $NHCH_3$). Regular angles were assumed in Y: 120° about C(sp^2); tetrahedral angles about N and O. The results are not sensitive to variations in these angles since the molecular polarisability anisotropy is determined overwhelmingly by that of the arene-$Cr(CO)_3$ moiety.

$$\begin{aligned}{}_mK(\text{calc.}) = (N_A/810kT\epsilon_0)\ \{ ({}_DP/{}_EP)[(b_{xx} - b_{yy})^2 + (b_{yy} - b_{zz})^2 \\ + (b_{zz} - b_{xx})^2 + 6(b_{xy}{}^2 + b_{xz}{}^2 + b_{yz}{}^2)] + (kT)^{-1}[\mu_x{}^2(2b_{xx} - b_{yy} - b_{zz}) \\ + \mu_y{}^2(2b_{yy} - b_{xx} - b_{zz}) + \mu_z{}^2(2b_{zz} - b_{xx} - b_{yy}) + 6(b_{xy}\mu_x\mu_y + b_{xz}\mu_x\mu_z \\ + b_{yz}\mu_y\mu_z)]\} \qquad (1)\end{aligned}$$

Polarisability contributions for the substituent groups Y were calculated from data in the literature: b_L(C—H) = b_T(C—H) = b_V(C—H) = 0.72 [17]; b_L(C—C) = 1.08, b_T(C—C) = b_V(C—C) = 0.29 [17]; b_L(C=O) = 2.56, b_T(C=O) = 1.56, b_V(C=O) = 0.51 [18]; b_L(C—O) = 0.99, b_T(C—O) = b_V(C—O) = 0.51 [19]; b_L(N—H) = 0.56, b_T(N—H) = b_V(N—H) = 0.92 [20]; b_L(N—C) = 0.63,

b_T(N—C) = b_V(N—C) = 0.77 [20]. Polarisabilities are expressed throughout as 10^{40} b/Cm^{2}V^{-1} (1Cm^{2}V^{-1} = 0.8988 × 10^{16} cm^3); the data were obtained from electric birefringence measurements at 589 nm. Those for the (η^6-C_6H_5)Cr(CO)$_3$ group were obtained by subtracting one C—H bond contribution from the principal polarisabilities of the benzene complex. The symmetry of the latter compound is such that b_1 (coincident with the dipole axis) $\neq b_2 = b_3$ and $\mu_1 = \mu_{\text{obs.}}$, $\mu_2 = \mu_3 = 0$. The molecular polarisabilities can be directly obtained from the experimental $_\infty({}_\text{m}K_2)$, μ and R_D of Table 1 by solution of eqns. (1) and (2) [8]. The values

$$_\text{E}P = 0.95R_\text{D} = N_\text{A}\ (b_1 + b_2 + b_3)/9\epsilon_0 \tag{2}$$

are: $b_1 = 29.4$, $b_2 = b_3 = 23.9$. It is pertinent to note that the dipole moment of (η^6-C_6H_6)Cr(CO)$_3$ measured in dioxan is somewhat greater than that in benzene or in cyclohexane, suggesting a degree of solute—dioxan interaction [21, 22]. Recent studies have clearly shown, however, that despite such associations the polarisability anisotropies of the benzene, mesitylene and hexamethylbenzene complexes in dioxan are virtually identical to those from cyclohexane [23]. This is attributed to the non-dipolar and near optically isotropic characteristics of the associating dioxan molecules.

It should be possible in principle to calculate μ values for the various conformational forms of the complexes under study by vector additivity of the moments of (η^6-C_6H_6)Cr(CO)$_3$ and the appropriate free ligand C_6H_5Y (designated here as μ_0 and μ_y, respectively). The vector specification of the moments of C_6H_5Y in dioxan was obtained from refs. 24—30. A complicating factor is the existence of two mesomeric moments; one represents a change in the substituent group moment ($\Delta\mu_y$) in the aromatic ring plane and along the C_{ar}—Y bond axis, while the other ($\Delta\mu_0$) is directed along the tricarbonyl ternary axis [5, 31]. $\Delta\mu_0$ can be regarded as a measure of the charge transfer between the arene and the metal as a result of the presence of substituent Y. This moment increment would be positive for an electron donor group Y (i.e. directed from the arene to the metal) and negative for an electron-withdrawing substituent. It was accepted following the work of Lumbroso et al. [5] that $\Delta\mu_y$ is very small and it has been neglected in these calculations. The measured dipole moment of the monosubstituted complex could thus be expressed as the vector sum of the moments μ_0, μ_y and $\Delta\mu_0$. It followed that a theoretical value of $\Delta\mu_0$ could be derived for each geometric model examined since μ(complex), μ_0 and μ_y are known. Hence μ_x, μ_y and μ_z could in turn be evaluated for that structure and be used in eqn. (1) together with the polarisability tensor components to calculate $_\text{m}K$ for that conformer. The calculated $\Delta\mu_0$ would vary with conformational change accompanying rotations of the substituent Y. Functions $\Delta\mu_0(\phi)$ were derived vectorially for each of the complexes (η^6-C_6H_5Y)Cr(CO)$_3$ as well as functions $_\text{m}K(\phi)$.

The transmission of substituent effects in these complexes is also shown in their infrared spectra. Electron donating groups Y tend to lower the CO bond order while electron withdrawing groups have the reverse effect [2, 4].

The measurements, summarised in Table 2, clearly indicate (i) a solvent dependence which tends to confirm the solute—dioxan interactions referred to earlier and (ii) that ν_{CO} (A_1 and E) are related qualitatively to the electron donor/acceptor nature of the substituent Y.

Complexes $(\eta^6\text{-}C_6H_5Y)Cr(CO)_3$*;* $Y = COCH_3$*, CHO or* $COOCH_3$

Initially, complexes with electron withdrawing substituents Y were examined. Since the $Cr(CO)_3$ group is also predominantly an electron acceptor, the mutually competitive effects of Y and $Cr(CO)_3$ would tend to minimise interaction moments. The approach is illustrated with reference to the acetophenone complex, structures of which corresponding to ϕ = 0° and +90° are shown in Fig. 1. The computed theoretical ${}_mK(\phi)$ and $\Delta\mu_0(\phi)$ functions are given in graphical form in Figs. 2 and 3 respectively.

The thicker curve in Fig. 2 represents ${}_mK(\phi)$ values obtained on the basis of strict bond and group polarisability additivity in accord with the valence optical scheme. The thinner curve represents a parallel set of calculations which were made taking into account the observed polarisability "exaltation"

TABLE 2

The effect of solvent on the CO stretching frequencies (cm^{-1})

C_6H_5Y in $(\eta^6\text{-}C_6H_5Y)Cr(CO)_3$	Band	C_6H_{12}	C_6H_6	$CHCl_3$	C_6F_6	$C_4H_8O_2$	CS_2
C_6H_6	A_1	1988	1976	1978	1981	1968	1978
	E	1919	1900	1898	1905	1892	1906
C_6H_5CHO	A_1	1996	1987	1990	1993	1981	1988
	E	1932	1917	1919	1924	1911	1922
$C_6H_5COCH_3$	A_1	1996	1984	1989	1993	1982	1990
	E	1935, 1926	1915	1919	1922	1911	1920, 1929
$C_6H_5COOCH_3$	A_1	1998	1989	1995	1995	1981	1993
	E	1943, 1934	1922	1926	1932	1918	1926, 1933
$C_6H_5OCH_3$	A_1	1980	1967	1976	1975	1967	1974
	E	1909	1892	1891	1900	1887	1900
$C_6H_5NH_2$	A_1	1978	1962	1968	1971	1955	1969
	E	1906	1883	1881	1890	1873	1893
$C_6H_5N(CH_3)_2$	A_1	1969	1957	1959	1964	1955	1962
	E	1897, 1892	1876	1871	1880	1871	1882
$C_6H_5NH(CH_3)$	A_1	1975	1960	1964	1966	1955	1965
	E	1898	1880	1876	1884	1872	1886

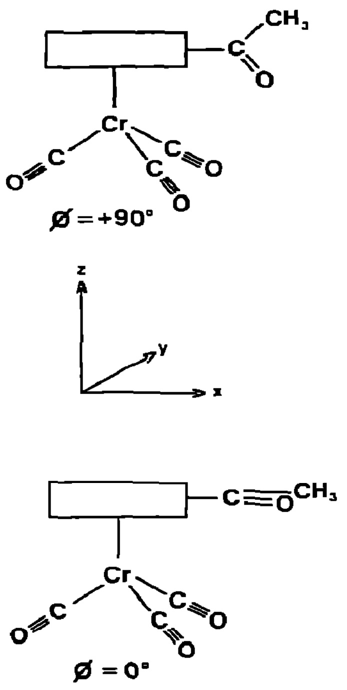
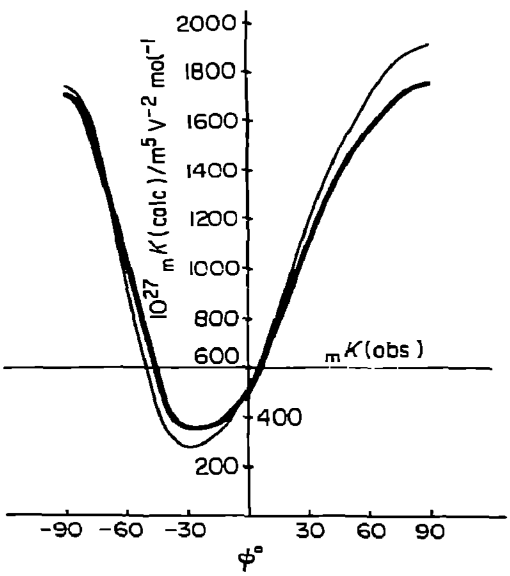


Fig. 1. Conformations of the acetophenone complex.



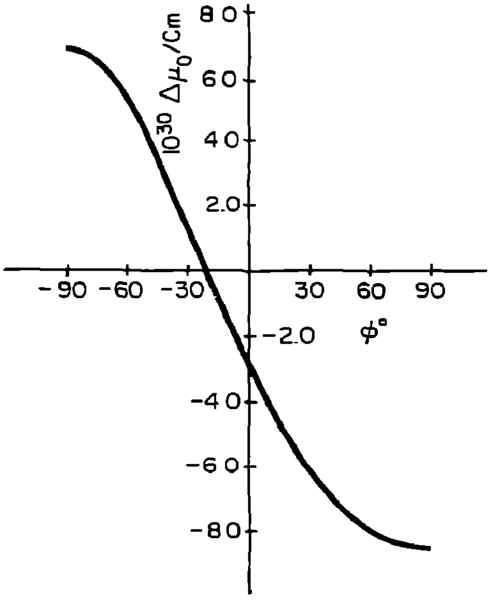


Fig. 2. Computed $_{m}K(\phi)$ functions.

Fig. 3. Computed $\Delta\mu_0(\phi)$ functions.

for acetophenone [26]. The latter is a correction term (0.56) introduced to account for perturbations arising from substituent—ring interactions in the free ligand. It is seen that this factor has little effect on the calculated $_{m}K(\phi)$

values for the complex. The experimental and computed molar Kerr constants are in agreement when ϕ equals ca. +5° or, alternatively, ca. —45°. The former value is favoured since, from Fig. 3, it corresponds to an algebraically negative $\Delta\mu_0$ (ca. —3 Cm) and hence an electron charge shift from $Cr(CO)_3$ towards the arene system. This would be expected for the electron withdrawing acetyl group Y and is compatible with the higher carbonyl stretching frequency observed relative to the benzene complex (Table 2).

A similar analysis of the experimental data was made for the benzaldehyde complex. As with the acetophenone analogue the computed ${}_mK(\phi)$ for this molecule is a very sensitive function and spans a range of approximately 1100 units. Comparison with the experimental ${}_\infty({}_mK_2)$ leads to ϕ values of ca. —5° or ca. —40°. Inclusion in the calculations of the polarisability exaltation found for the free benzaldehyde ligand (2.6) [26] results in ϕ estimates for the complex of ca. 0° or ca. —50°. A ϕ value of —5° corresponds to $\Delta\mu_0$ of ca. —3 Cm. The infrared data of Table 2 are compatible with the negative $\Delta\mu_0$. The results clearly suggest that the CHO group is virtually coplanar with the arene ring plane.

With the methylbenzoate complex the $COOCH_3$ was taken as coplanar, stabilised through dipole—dipole interactions involving antiparallel dispositions of the C=O and C—O—C moments. Directed polarisability exaltations have not been evaluated for the free ligand. The ${}_mK(\phi)$ and $\Delta\mu_0(\phi)$ functions are qualitatively similar to those of Figs. 2 and 3 except that the lower part of the curve for ${}_mK(\phi)$ is flatter so that the experimental ${}_\infty({}_mK_2)$ could be taken as equal to ${}_mK$(calc.) over the ϕ range of ca. —10° to ca. —20° (taking error estimates into account). Only the smaller angle corresponds to a negative $\Delta\mu_0$ (ca. —1 Cm). Together with the infrared data of Table 2, this indicates that the lower value ϕ of ca. —10° is the more probable. The result is close to that of the solid-state configuration determined by X-ray analysis [32, 33].

The conclusion can reasonably be drawn that in each of the complexes acetophenone, benzaldehyde- and methyl benzoate-tricarbonylchromium(0) the preferred solution-state conformations are such that the arene substituent group Y has a near planar arrangement with the aromatic ring plane. This result casts some doubt on the suggestion of Nicholls and Whiting [12] who postulated that the $Cr(CO)_3$ moiety has a steric effect comparable with that of a large *ortho* substituent such as a methyl group. The data of Table 1 cannot be interpreted to give information on the relative dispositions of the tricarbonylchromium(0) and arene groups. Such conformational possibilities have been extensively studied and it is thought that the free energy differences between rotamers is very low [34]. Our analysis of the electric birefringences of the complexes $(\eta^6\text{-}C_6H_5Y)Cr(CO)_3$ in terms of the preferred conformations of the substituents Y is not affected by rotations of the symmetric $Cr(CO)_3$ groups.

Complexes (η^6-C_6H_5Y)$Cr(CO)_3$; $Y = NH_2$, $N(CH_3)_2$, $NH(CH_3)$ or OCH_3

Electromeric interactions in these complexes lead to electron donation from Y into the arene system, an effect which would be enhanced through π-depletion into the $Cr(CO)_3$ group. For each compound ${}_mK$(calc.) and $\Delta\mu_0$ were plotted as functions of ϕ. The situation is complicated in the anilines because of nitrogen inversion. For the aniline and the *N,N*-dimethylaniline complexes, coincidence of the experimental and the calculated molar Kerr constants could not be achieved for any conformational form. The calculated ${}_mK(\phi)$ values vary sensitively with rotations of the amino group. With the aniline complex best agreement is obtained for the rotamer (described here as $\phi = -90°$) in which the symmetry plane of the C_{ar}—NH_2 group is perpendicular to the aromatic ring plane and the nitrogen lone pair is *trans* to $Cr(CO)_3$. The divergence between predicted and found ${}_mK$ values is ca. 90 for this conformer. Somewhat less favoured is the inverted form ($\phi = +90°$) in which the N lone pair is *cis* to $Cr(CO)_3$. In these structures the N lone pair is positioned for maximum orbital overlap with the aromatic π-system. Rotations of the amino group away from either of the dispositions described above rapidly lowers ${}_mK$(calc.), e.g. the intermediate form $\phi = 0°$ (where the bisector of NH_2 lies in the C_6 plane) has a disparity of 400 ${}_mK$ units with respect to the experimental value. The data are interpreted in terms of the existence in solution of the preferred conformations —90° (predominantly) and +90°. This gives an overall positive $\Delta\mu_0$ value and is compatible with the observed decrease in the carbonyl stretching frequency relative to the unsubstituted benzene complex (Table 2). Use of the small polarisability corrections (exaltations) found appropriate for the free aniline ligand [28] increases the disparity between the calculated and observed ${}_mK$ values but it does not affect the conclusions. It may be that electromeric shifts from NH_2 into the arene system are transmitted in part to $Cr(CO)_3$ and the concomitant polarisability exaltation has a component along the arene—chromium axis.

With the *N,N*-dimethylaniline complex closest agreement between ${}_mK$(calc.) and ${}_mK$(obs.) is obtained for conformations analogous to those for the aniline ligand. Again the *trans* lone pair form is marginally favoured over the *cis* (the disparity is 23 and 36 units of ${}_mK$, respectively). This result satisfies also the $\Delta\mu_0$ and the infrared spectral criteria. In the case of the less symmetric *N*-methylaniline complex the ${}_mK(\phi)$ and $\Delta\mu_0(\phi)$ functions are more complicated. Definitive conclusions cannot be drawn. Approximately equal contributions from conformers with *trans* and *cis* arrangements of the nitrogen lone pair relative to $Cr(CO)_3$ are reconcilable with the data but other interpretations cannot be precluded.

The anisole complex also does not give agreement between experimental and calculated ${}_mK$ values. The divergence varies from ca. 200 to ca. 700 as the methoxy group is rotated away from coplanarity with the arene ring. The results are not conclusive but suggest that a near planar anisole group (ϕ = ca. 0°) is favoured. The structure would be characterised by a positive $\Delta\mu_0$ value

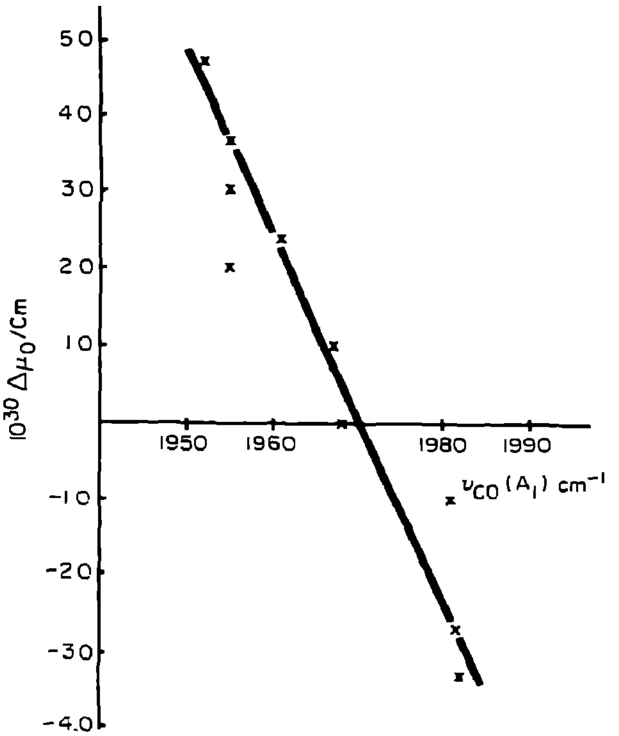


Fig. 4. ν_{CO} for $Cr(CO)_3$ group complexes as a function of the $\Delta\mu_0$ corresponding to the preferred molecular conformation. Points for 1,3,5-trimethylbenzene and hexamethylbenzene complexes are included [23]. With the aniline type complexes average $\Delta\mu_0$ values for ϕ = +90° and —90° were used.

and, from Table 2, a decreased carbonyl force constant. The preferred conformation so specified for the solute resembles the solid state configuration [35].

CONCLUSIONS

The preferred solute conformations of the complexes $(\eta^6\text{-}C_6H_5Y)Cr(CO)_3$ in dioxan are specified by values ϕ approximately (i.e. within 10°) 0° for $Y = COCH_3$, CHO, $COOCH_3$ and OCH_3 and ±90° for $Y = NH_2$, $N(CH_3)_2$ and $NH(CH_3)$. The most favoured Y orientations are those which have maximum orbital overlap between the substituent group and the arene π-system. Electronic rather than steric influences appear to be dominant in the molecules studied. The steric effect of the $Cr(CO)_3$ group is not as great as originally proposed [12]. It is found that ν_{CO} for the series in dioxan is an almost linear function of the $\Delta\mu_0$ corresponding to the preferred molecular conformation (Fig. 4).

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