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SUBSTITUENT EFFECTS IN π-(TRICARBONYLCHROMIUM)ARENES

II *. AN IR STUDY OF THE CO STRETCHING VIBRATIONS IN ALKYLSUBSTITUTED π-(TRICARBONYLCHROMIUM)BENZENES

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Summary

The IR wavenumbers and half-band width's of the carbonyl stretching vibrations of several substituted π-(tricarbonylchromium)benzenes in isooctane solution are reported. Only small perturbations of C_{3v} symmetry are observed. The shape of the out-of-phase band is influenced by electronic effects, conformer distribution and solute-solvent interaction. The asymmetry of the E-band in (1′-t-butyl-2′,2′-dimethylpropyl)-π-(tricarbonylchromium)benzene is ascribed to a direct steric effect.

The correlation between the CO force constants and electronic substituent parameters is satisfactory for the monosubstituted complexes. The substituent effects are approximately additive for the di- and tri-alkylsubstituted benzene complexes.

Introduction

Several papers [1—4] report on the carbonyl stretching vibrations of π-(tricarbonylchromium)benzene and its derivatives, obtained from IR measurements on solutions of the complexes. Two well-resolved CO stretching modes are observed, in accordance with the symmetry C_{3v}. The wavenumber of the CO modes is known to reflect the effect of a substituent on the coordinated aromatic ring [1,4—6]. The occasional splitting of the out-of-phase band has been attributed to an active lowering of the symmetry [7—9] by the substituents on the aromatic ring.

So far, no systematic IR study of the CO stretching modes of alkylsubstituted π-(tricarbonylchromium)benzenes is available. NMR work [10—13] is indicative

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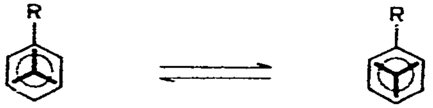
* For part I see ref. 12.

for a fast equilibrium on the NMR time-scale, between conformers I and II. The question arose whether substituent effects on this conformational equilibrium could be detected by IR spectroscopy. To investigate this, the carbonyl region of several monoalkylsubstituted π-(tricarbonylchromium)benzenes was measured accurately. Furthermore, some other monosubstituted π-(tricarbonylchromium)-benzenes and a series of di- and trialkylsubstituted π-(tricarbonylchromium)-benzenes have been included in this study.



I

II

Experimental

Preparation of most of the substituted π-(tricarbonylchromium)benzenes has been described in Part I [12]. The complexes of fluorobenzene and biphenyl were prepared by the same method (m.p.'s found are 121—122°C and 84—85°C, respectively).

The IR spectra were measured on a Perkin—Elmer 521 grating spectrometer. The spectral slit-width for the CO region was approximately 2 cm^{-1}. Spectra were recorded with a speed of 7.5 cm^{-1} min^{-1}; some ill-defined maxima were recorded with a speed of 4.0 cm^{-1} min^{-1}. Isooctane (Uvasol, Merck) was used as the solvent. Concentrations amounted to about 0.001 *M*. Sodium chloride solution cells with a path length of 0.550 mm were used. The solutions were protected by a germanium filter against the visible part of the radiation, emitted by the IR light-source, and were kept in the dark outside the apparatus to prevent light-induced destruction of the complexes. The wavenumbers of the absorption maxima were calculated from the digital output of the spectrometer, using the computer program of Jones et al. [14]. The wavenumber scale was calibrated using the wavenumbers of water and deuterium chloride absorptions in this region [15]. The wavenumbers are given in Table 1 and are the average of the results from three measurements. S.d.'s in wavenumbers are 0.2 cm^{-1}, unless stated otherwise. The half-band width's have been taken from the recorder-paper, using twentyfold wavenumber scale-expansion. These are accurate within 0.2 cm^{-1}. The experimental error in extinction coefficients is estimated to be ± 10%. The force constants given have been calculated adopting the Cotton—Kraihanzel approximation [16] for *cis*-$(CO)_3ML_3$. In case of asymmetry or splitting of the *E*-mode the averaged wavenumber value at half band-height was used in this calculation, which seems a reasonable approximation for a small perturbation of C_{3v} symmetry [9]. The data obtained are given in Table 1.

The spectra at low temperature were obtained, using a Beckman-RIIC VLT-2 variable temperature cell holder. A solution cell (0.5 mm) with silver chloride windows was used.

Some representative examples of the spectra (only the *E*-mode) are shown in Fig. 1.

TABLE 1

DATA [a] ON THE IR CARBONYL STRETCHING BANDS OF π-(TRICARBONYLCHROMIUM)BENZENE AND DERIVATIVES

Substituents	A_1			E			K(CO) (mdyn Å^{-1})	k_i (mdyn Å^{-1})
	$\Delta\nu_{max}$ (cm^{-1})	ϵ_{max} (m^2. mol^{-1})	$\Delta\nu_{1/2}$ cm^{-1}	$\Delta\nu_{max}$ (cm^{-1})	ϵ_{max} (m^2. mol^{-1})	$\Delta\nu_{1/2}$ cm^{-1}		
None		850	4.0		840	8.1	15.188	0.356
Me	− 4.7	760	3.8	− 5.4	590	9.8	15.108	0.359
Et	− 5.3	770	4.0	− 5.9	590	10.4	15.099	0.358
neoPent	− 5.4	1030	3.6	− 5.8	830	9.1	15.100	0.357
i-Pr	− 6.1	790	3.8	− 7.4 [c]	580	11.4	15.080	0.362
t-Bu	− 7.2	790	3.8	− 6.5 [b] −11.0 [b]	440 430	13.1	15.060	0.363
CEt$_3$	− 8.9	1090	3.6	−10.5	790	10.6	15.033	0.363
CH-t-Bu$_2$	− 8.6	960	3.6	−11.0 [c]	630	11.0	15.039	0.362
OMe	− 5.4	900	4.1	− 7.6	840	9.0	15.081	0.366
SiMe$_3$	− 6.3	990	3.7	− 5.2	720	10.1	15.101	0.349
Ph	− 3.7	980	3.8	− 1.2	700	10.5	15.156	0.342
F	+ 7.5	800	4.0	+ 10.9 [d]	600	11.8	15.329	0.346
COOMe	+ 8.2	830	4.1	+ 12.4 [c]	570	12.3	15.373	0.329
CF$_3$	+ 14.8	850	4.1	+ 21.3 [d]	530	12.0	15.473	0.333
1,2-Me$_2$	−10.1	830	4.1	− 9.5 [d]	460	13.6	15.016	0.361
1,2-Et$_2$	−12.0	1040	4.1	− 9.9 [d]	630	13.6	15.002	0.353
1,2-neoPent$_2$	−13.4	1170	3.6	−11.5 [b] −16.5 [b]	640 620	13.6	14.973	0.357
1,2-i-Pr$_2$	−12.6	1090	3.8	− 9.6 −18.8	570 610	15.7	14.976	0.362
1,2-t-Bu$_2$	−15.4	1160	3.9	−13.4 −20.3	610 570	14.9	14.933	0.361
1,2-(SiMe$_3$)$_2$	−11.5	1070	3.9	− 7.1 [d]	600	12.3	15.033	0.342
1,3-Me$_2$	− 9.2	1040	3.7	−10.3	900	9.0	15.033	0.360
1,3-t-Bu$_2$	−14.4	1110	3.6	−14.5 [b] −17.0 [b]	600 590	13.0	14.950	0.360
1,3-(SiMe$_3$)$_2$	− 9.6	1220	3.6	− 8.0	910	9.0	15.055	0.346
1,4-t-Bu$_2$	−14.6	1090	3.5	−16.5 [d]	690	10.6	14.941	0.363
1,4-(SiMe$_3$)$_2$	−11.3	1110	3.6	−10.9	1090	9.1	15.016	0.352
1-Me-3,5-t-Bu$_2$	−19.3	1070	3.4	−21.5	910	8.2	14.865	0.364
1,2,4-t-Bu$_3$	−22.2	1110	3.6	−25.8 [c]	680	11.1	14.823	0.362
1,3,5-Me$_3$	−13.4	990	3.7	−14.7	960	7.2	14.966	0.360
1,3,5-Et$_3$	−15.5	770	4.2	−17.3	690	8.9	14.928	0.362
1,3,5-neoPent$_3$	−16.1	930	3.6	−16.2	830	7.6	14.936	0.354
1,3,5-i-Pr$_3$	−18.1	920	3.9	−20.2	850	7.6	14.885	0.363
1,3,5-t-Bu$_3$	−20.8	1090	3.3	−23.1	970	6.8	14.841	0.364

[a] Solvent isooctane: temperature ~30°C: s.d.'s in wavenumbers are less than 0.2 cm^{-1}, see experimental part: $\Delta\nu_{max} = \nu_{max}(R) - \nu_{max}(H)$, whereas for π-(tricarbonylchromium)benzene $\nu_{max}(H)$ equals 1984.3 and 1916.5 cm^{-1} for the A_1- and E-mode respectively. [b] S.d. 0.5 cm^{-1}. [c] Asymmetric at high-frequency. [d] Asymmetric at low-frequency.

Discussion

The absorptions in the carbonyl stretching region of substituted π-(tricarbonylchromium)benzenes can be assigned, using local C_{3v} symmetry, to a non-degenerate symmetric vibration (A_1) and a doubly-degenerate asymmetric vibration (E). Strictly speaking, however, the symmetry is at best C_{1v} ($2A' + A''$) for a mono-

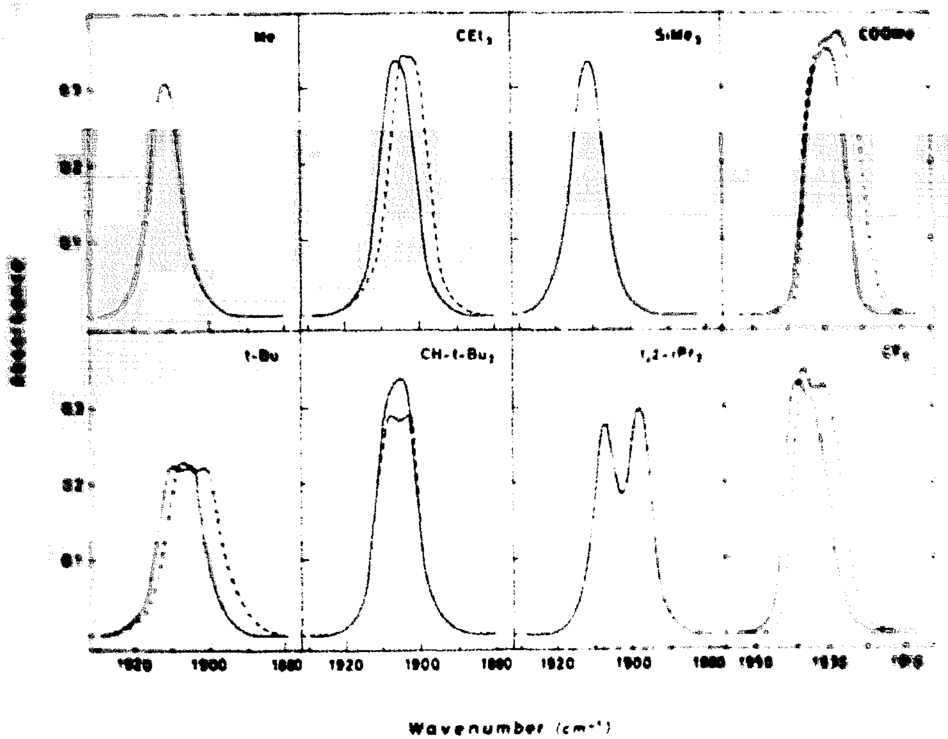


Fig. 1. Out-of-phase carbonyl stretching bands of substituted π-(tricarbonylchromium)benzenes. —— 30° C, ······ at −68° C.

substituted complex. A splitting of the asymmetric mode can be expected for a small perturbation of C_{3v} symmetry by the substituent R on the benzene ring. Indeed, such a lifting of the degeneracy of the E-mode is shown by some compounds of this type [1,7]. Both electronic effects of the substituents and solvent-solute interactions [9] are presumed to play a role.

From ^{1}H and ^{13}C NMR studies [10—13] it is likely that the equilibrium between conformers I and II for small substituents lies not extremely on one side in solution and that the barrier to rotation about the Cr—arene bond in monoalkylsubstituted π-(tricarbonylchromium)benzenes is small (probably less than 2 kcal mol^{-1} for R = t-Bu [17]). However, the time-scale of IR is much shorter than that of NMR. Consequently, the separate conformers with different orientations of the Cr(CO)$_3$ group with respect to the arene ring, may contribute to the observed IR spectrum.

Generally, we observed two bands in the CO region for substituted π-(tricarbonylchromium)benzenes, which were assigned to the adequate symmetry types, in view of intensity ratio and half-band width [18].

A_1-mode. In all cases only one high-wavenumber band (A_1) was observed (apart from the ^{13}C-satellite which gives this mode a characteristic skew appearance at the low wavenumber wing). The width's show only small differences. A rather narrow A_1-mode is observed for the compounds, in which the rotation of the Cr(CO)$_3$ moiety is considered to be severely restricted.

E-mode. The low-wavenumber absorption bands differ considerably in shape, which is illustrated in Fig. 1 and by the tabulated half-band width's. It is evident from Table 1 that this band broadens for the monoalkylsubstituted complexes in the order H < Me < Et < i-Pr < t-Bu. As shown in Fig. 1 two bands with about equal intensity are observed for R = t-Bu. However, the increase in band width is not continued for complexes carrying very bulky alkyl groups like CEt_3 and $CH\text{-t-}Bu_2$

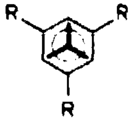
The order in experimental band width's is inconsistent with an electronic perturbation of C_{3v} symmetry, since the electronic effects of the present alkyl groups are approximately equal. Steric effects of the alkyl group, influencing solvent-solute interactions, cannot be solely responsible, because of the discontinuity in half-band width observed in the series investigated. Therefore it is tempting to assume that the conformer distribution is involved as well. This indicates a pronounced conformational preference for R = Me and Et (conformer *I*), for R = CEt_3 and $CH\text{-t-}Bu_2$ (conformer *II*) and little or no preference for R = i-Pr and t-Bu. The accordance between this result and the conformer distribution for these compounds, obtained from ^1H NMR [12] is satisfactory. Clearly, both conformer distribution and solute—solvent interactions play an important role in the experimental band width's. Furthermore, a direct steric perturbation of C_{3v} symmetry may be responsible for the asymmetry of the *E*-band of (1'-t-butyl-2',2'-dimethylpropyl)-π-(tricarbonylchromium)benzene.

The relatively narrow low-wavenumber band for R = $SiMe_3$ as compared with R = t-Bu, is consistent with the change in conformer population obtained from ^1H NMR [12]. The asymmetry of the *E*-bands of methyl π-(tricarbonylchromium)-benzoate and (trifluoromethyl)-π-(tricarbonylchromium)benzene, in which relatively strong electronic effects are operative, is not surprising.

The 1,2-dialkylsubstituted π-(tricarbonylchromium)benzenes show the largest band width's of all alkylsubstituted complexes investigated. This is in accordance with an electronic perturbation of the symmetry; the order of dipole moments of the aromatic ligands is $\mu_{1,2} > \mu_1, \mu_{1,3} > \mu_{1,4}, \mu_{1,3,5}$.

For the symmetric trialkylsubstituted complexes C_3 symmetry applies to all orientations of the $Cr(CO)_3$ group. ^1H NMR spectroscopy [10,12] indicates that conformers III and IV are preferred by the 1,3,5-trimethyl- and the 1,3,5-tri-t-butyl substituted complexes, respectively. For the other 1,3,5-trialkylsubstituted π-(tricarbonylchromium)benzenes, the conformational preference for either III or IV is less pronounced, which might explain the trend in band width's observed.

III



IV

At low temperatures (−68° C) the A_1-band is shifted slightly to lower wavenumber. This applies also to the position of the *E*-band. Furthermore, in a number of cases the asymmetry of the out-of-phase band at ambient temperature leads to a small splitting at low temperature, as is given in Fig. 1 (dotted lines). Although

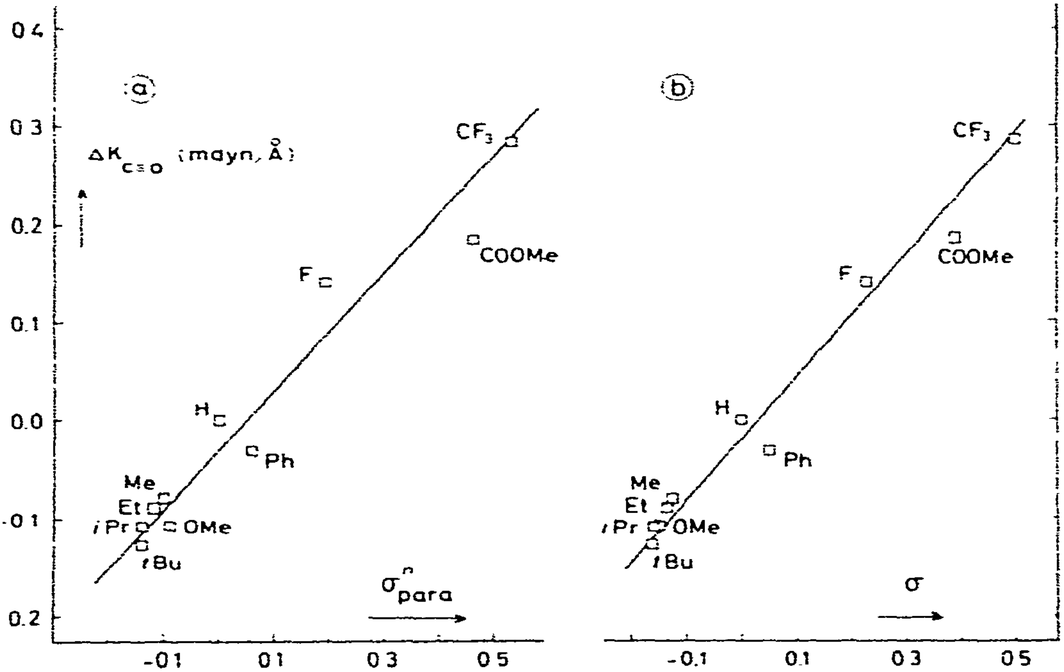


Fig. 2. Plots of ΔK(CO) vs. (a) σ^n_{para} [19], $\rho = 0.566$, correlation coefficient = 0.972, s.d. = 0.036 mdyn Å^{-1}; (b) σ, derived from σ_{meta}, σ^n_{para}, $\Delta\sigma^+_R$ [19] and f_m (see text), $\rho = 0.584$, correlation coefficient = 0.989, s.d. = 0.024 mdyn Å^{-1} and $r = 0.226$.

a small change in conformer population cannot be excluded over this temperature range, increased anisotropy of the solvent at different sites of the molecule is considered to be the main cause of the splitting.

The substituent effects on the frequency of the in- and out-of-phase mode follow a regular electronic order. Consequently, this also applies to the calculated force constants, which are given in Table 1. Two correlations with σ-parameters are given (see Fig. 2). The correlation with σ^n_{para}-values [19] is fair (Fig. 2,*a*), a better correlation is obtained with the equation $\Delta K(\mathrm{CO}) = \rho\sigma$ and σ-values:

$$\sigma = f_m\sigma_m + (1 - f_m)(\sigma^n_p + r\Delta\sigma^+_R)$$

(Fig. 2,*b*), in which f_m is the fraction of conformer II. Fractions were taken from our ^{1}H NMR work [12] for the alkyl substituents and were set to 0.5 for the other substituents. At this point it is noteworthy, that the force constant of the methoxybenzene complex and the resonance parameter (r) do not point to a strong electron-donation from this substituent. This is in contrast with the assumption made to explain the conformational preference in the solid state [20]. For the di- and tri-substituted complexes investigated the substituent effects are approximately additive.

Conclusions

Since the electronic substituent effects play a role in both electronic perturbation of C_{3v} symmetry and conformational preference in the complexes, it is difficult to distinguish between these in attributing the band shapes observed. In alkylsubstituted π-(tricarbonylchromium)benzenes, where steric substituent effects oppose electronic effects in determining the conformational preference, it is possible to observe small effects which cannot be explained on the basis of the static model [8]. These effects might be due to changes in conformer population with increasing size of R in the particular series.

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