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SUBSTITUENT EFFECTS IN π-(TRICARBONYLCHROMIUM)ARENES

IV *. ^{1}H NMR SPECTROSCOPY OF SUBSTITUTED METHYL π-(TRICARBONYLCHROMIUM)BENZOATES

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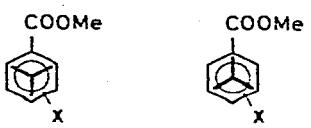
Summary

The ^{1}H NMR spectra of a series of thirty substituted methyl π-(tricarbonylchromium)benzoates (and the corresponding free ligands) have been recorded and analysed. A comparison of the chemical shifts of the aromatic protons in the complex and ligand often allows conclusions regarding the preferred orientation of the tricarbonylchromium group in the complexes studied.

Introduction

Recently, we studied the effects of ring substitution on the CO stretching vibrations in methyl π-(tricarbonylchromium)benzoates by IR spectroscopy [1]. In order to explain some anomalous substituent effects on the ester CO wavenumber, it was assumed that the orientation of the $Cr(CO)_3$ group with respect to the arene ring is involved. Assuming a conformational equilibrium between I and II, we found relatively low ester CO wavenumbers in complexes with an ex-



I II

pected preference for I, whereas enhanced ester CO wavenumbers were observed in complexes with an expected preference for II.

Since ^{1}H NMR spectroscopy has proved to be useful in studying the conformational preference of π-(tricarbonylchromium)arenes [2,3,5], we have used this

* For Part III see ref. 1.

(continued on p. 324)

TABLE 1

PROTON NMR DATA [a] OF SUBSTITUTED METHYL BENZOATES AND THEIR π-$Cr(CO)_3$ COMPLEXES

Substituent(s)	Type [b]	δ					δ(CH_3)	δ(CH_2)	δ(CH)	δ(CH_3) COOMe
		H_2	H_3	H_4	H_5	H_6				
2-Me [c]	L		7.29	7.43	7.27	7.86	2.55			3.82
2-Me [c]	C		5.44	5.94	5.49	6.34	2.50			3.85
2-Et	C		5.47	5.98	5.52	6.33	1.26	2.37 [d], 2.90 [d]		
2-i-Pr	C		5.59	5.93	5.53	6.21	1.23, 1.29		3.71	3.85
2-t-Bu [c]	L		7.30	7.39	7.23	7.53	1.37			3.83
2-t-Bu [c]	C		5.67	5.68	5.62	5.78	1.38			3.88
2-OMe	L		7.17	7.52	6.97	7.70	3.82			3.86
2-OMe	C		5.51	6.03	5.18	6.33	3.83			3.87
3-Me [c]	L	7.81		7.39	7.33	7.79	2.32			3.84
3-Me [c]	C	6.10		5.79	5.77	6.07	2.17			3.80
3-Et	C	6.26		5.85	5.70	6.26	1.27	2.56 [c, d], 2.58 [c, d]		3.90
3-i-Pr [c]	L	7.92		7.53	7.44	7.86	1.27		3.03	3.86
3-i-Pr [c]	C	6.23		5.96	5.69	6.25	1.27, 1.28		2.74	3.86
3-t-Bu [c]	L	8.13		7.81	7.61	7.93	1.33			3.88
3-t-Bu [c]	C	6.40		6.17	5.60	6.35	1.37			3.88
3-OMe [c]	L	7.53		7.19	7.41	7.59	3.84			3.80
3-OMe [c]	C	6.11		5.95	6.23	6.01	3.83			3.83
3-Cl [c]	L	7.94		7.64	7.53	7.93				3.95
3-Cl [c]	C	6.29		6.03	5.90	6.08				3.94
3-CF_3 [c]	L	8.25		7.99	7.79	8.27				3.95
3-CF_3 [c]	C	6.59		6.41	5.81	6.55				3.95
3-COOMe	L	8.62		8.27	7.66	8.27				3.95
3-COOMe	C	6.87		6.55	5.76	6.55				3.93
4-Me	L	7.86	7.24		7.24	7.86	2.37			3.83
4-Me	C	6.32	5.52		5.52	6.32	2.30			3.83
4-Et	L	7.90	7.29		7.29	7.90	1.22	2.70		3.85
4-Et	C	6.30	5.56		5.56	6.30	1.27	2.57		3.87
4-neoPent	L	7.94	7.32		7.32	7.94	0.90	2.59		3.87

4-neoPent	C	6.32	5.51		5.51	6.32	1.00	2.37		3.89
4-i-Pr	L	7.95	7.40		7.40	7.95	1.27		3.01	3.87
4-i-Pr	C	6.28	5.64		5.64	6.28	1.29		2.80	3.89
4-t-Bu	L	7.97	7.52		7.52	7.97	1.31			3.86
4-t-Bu	C	6.18	5.85		5.85	6.18	1.35			3.89
4-CEt_3	L	7.97	7.49		7.49	7.97	0.64	1.75		3.88
4-CEt_3	C	6.11	5.89		5.89	6.11	0.89	1.76		3.93
4-NMe_2	L	7.84	6.72		6.72	7.84	3.02			3.78
4-NMe_2	C	6.37	5.21		5.21	6.37	3.02			3.82
4-OMe	L	8.03	7.07		7.07	8.03	3.91			3.87
4-OMe	C	6.46	5.57		5.57	6.46	3.86			3.86
4-Ph	L	8.12	7.82		7.82	8.12				3.93
4-Ph	C	6.45	6.09		6.09	6.45				3.92
4-Cl	L	8.01	7.55		7.55	8.01				3.90
4-Cl	C	6.44	5.88		5.88	6.44				3.89
4-COOMe	L	8.13	8.13		8.13	8.13				3.95
4-COOMe	C	6.33	6.33		6.33	6.33				3.97
4-CF_3	L	8.25	7.90		7.90	8.25				3.97
4-CF_3	C	6.29	6.07		6.07	6.29				3.93
3,5-Me_2	L	7.66		7.22		7.66	2.30			3.83
3,5-Me_2	C	5.89		5.67		5.89	2.30			3.93
3,5-t-Bu_2	L	7.93		7.79		7.93	1.33			3.88
3,5-t-Bu_2	C	6.49		6.33		6.49	1.37			3.90
3,4-$(OMe)_2$	L	7.54			7.05	7.65	3.85, 3.87			3.89
3,4-$(OMe)_2$	C	6.20			5.78	6.09	3.87			3.87
3,5-$(OMe)_2$	L	7.17		6.70		7.17	3.82			3.87
3,5-$(OMe)_2$	C	5.52		5.63		5.52	3.87			3.93
3,5-Cl_2	L	7.87		7.70		7.87				3.97
3,5-Cl_2	C	6.17		6.38		6.17				3.97
2,4,6-Me_3	L		6.89		6.89		2.22			3.83
2,4,6-Me_3	C		5.27		5.27		2.25(4), 2.28(2, 6)			3.90
3,4,5-$(OMe)_3$	L	7.31				7.31	3.89(3, 5) 3.81(4)			3.87
3,4,5-$(OMe)_3$	C	5.57				5.57	3.95(3,5) 3.84(4)			3.91

[a] Solvent, acetone-d_6; δ-values are given in ppm relative to tetramethylsilane as internal standard. [b] Free ligand (L) or π-$Cr(CO)_3$ complex (C). [c] From 360 MHz spectra. [d] ABX_3-system (cf. ref. 3).

technique to obtain additional evidence for the conformational preference of the $Cr(CO)_3$ group in methyl π-(tricarbonylchromium)benzoates. The series studied includes some thirty substituted methyl π-(tricarbonylchromium)benzoates, of which eleven have been the subject of previous papers [4,5].

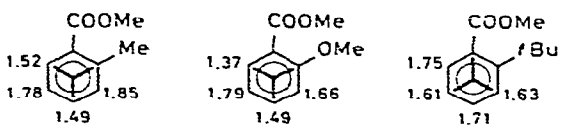
Experimental

The preparation and a number of physical properties of the complexes have been described previously [1,3—5]. ^1H NMR spectra of the compounds, dissolved (~0.5 *M*) in acetone-d_6 containing tetramethylsilane as internal reference, were recorded on Varian T-60, XL-100-15 and Bruker HX-360 spectrometers. All assignments have been checked and, if necessary, corrected by matching simulated and experimental spectra. Computations for spectrum simulation were performed on an IBM 370/158 computer, using the program LAME [6]. The δ-values obtained are considered to be better than ±0.02 ppm. The methyl signals of the methoxy-substituted esters have been assigned by analogy with the methyl signals in the corresponding benzoic acids. The results are listed in Table 1. It should be noted that some of the chemical shifts of the aromatic protons reported by Klopman and Noack [4] require revision.

Discussion

Jackson et al. [2,7] have proposed that aromatic protons eclipsed by carbonyl groups are relatively deshielded in π-(tricarbonylchromium)arenes. E.g. when conformation I prevails, H_2, H_4 and H_6 resonate at relatively low magnetic field. A direct comparison of the chemical shifts in complexes and ligands seems most appropriate for revealing conformational effects of the $Cr(CO)_3$ moiety. The shift in shielding of a proton upon introduction of the $Cr(CO)_3$ group, $\Delta(H_x)$, is defined here as $\Delta(H_x) = \delta(H_x)_{ligand} - \delta(H_x)_{complex}$.

The comparison between the chemical shifts of the aromatic protons of the free and complexed *ortho*-substituted methyl benzoates is given below by the Δ-values. The conformational preferences are estimated from the Δ-values. In

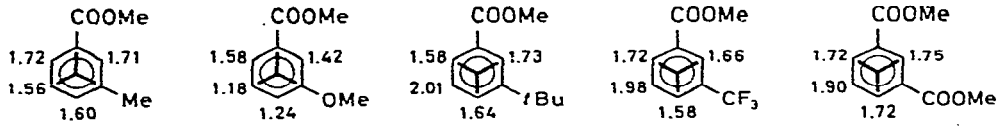


the *ortho*-substituted compounds (X = alkyl or methoxy) electronic effects of the COOMe group and the substituent cooperate in the distribution of electron density on the aromatic ring, thus favouring conformation I. With increasing bulk of the alkyl group, the contribution of II to the conformational equilibrium is expected to increase. Although from molecular models both conformation I and II seem unlikely for X = 2-t-Bu *, the ^1H NMR data obtained point to a slight dominance of conformation II in this complex.

For some of the *meta*-substituted complexes the $\Delta(H_x)$-values are given below. For X = 3-Me and 3-OMe the electronic effects of the substituents do not

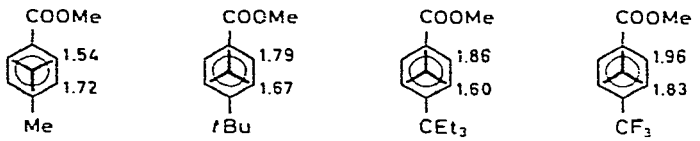
* In this complex the COOMe group and the aromatic ring are not coplanar (cf. ref. 1).

cooperate; the Δ-values obtained indicate a slight preference for conformation II. On the other hand, it is apparent that in a complex with a bulky *meta* alkyl



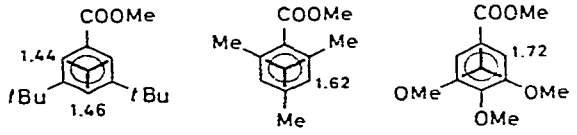
substituent (X = 3-t-Bu) the $Cr(CO)_3$ group prefers conformation I. Two electron-withdrawing substituents in 1,3-position cooperate in the charge distribution on the aromatic ring. This may explain the strong preference for conformation I, as inferred from the Δ-values, for X = 3-CF_3 and 3-COOMe.

We can deal briefly with the *para*-alkylsubstituted methyl π-(tricarbonylchromium)benzoates, since our results are in close agreement with those of Ashraf and Jackson [5]. For a number of the *para*-substituted complexes the estimated preferences are depicted below. The Δ-values obtained indicate that the conformational preference for II is more pronounced for X = 4-CEt_3 than for



X = 4-t-Bu. For X = 4-CF_3 it seems that conformation II predominates, perhaps because of the somewhat stronger electron-withdrawing effect of the CF_3 group (compared with the COOMe group) together with its bulk. For the other *para*-substituted complexes studied the differences between $\Delta(H_{2,6})$ and $\Delta(H_{3,5})$ are too small to permit conclusions about the conformational preference of the $Cr(CO)_3$ group.

Some of the di- and tri-substituted complexes involved in this study show a clear preference for a single conformation, which is given below. The chemical



shifts of the protons of the ester methyl group in the ligands as well as in the complexes follow roughly the electronic order of the substituents. For these methyl protons the shift upon complexation is negative in most cases, but the significance of the value of Δ is doubtful.

Nonequivalence in spectra of ethyl- and isopropyl-substituted methyl π-(tricarbonylchromium)benzoate *

The diastereotopic geminal methyl groups in methyl 2- and 3-isopropyl-π-(tricarbonylchromium)benzoate show chemical shift nonequivalence; the magnitude of this effect is 0.06 and 0.01 ppm, respectively. For X = 2-Et and 3-Et, it was found that the methylene protons are anisochronous by 0.53 and 0.02

* Cf. the diastereotopy in related $Cr(CO)_3$ complexes [8,3].

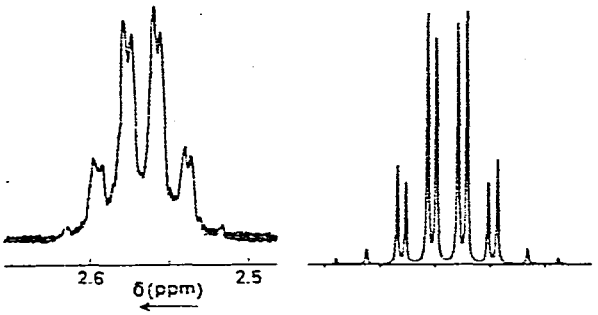


Fig. 1. ^{1}H NMR pattern of the methylene protons in methyl 3-ethyl-π-(tricarbonylchromium)benzoate at 360 MHz; experimental (left) and calculated (right) ABX_3-system, $J_{(AX)} = J_{(BX)} = 7.0$ Hz, $J_{(AB)} =$ (—)14.0 Hz and $\nu_A - \nu_B = 7.8$ Hz.

ppm, respectively. The methylene region of the spectrum for X = 3-Et is shown in Fig. 1. It seems that the nonequivalence of the protons in these compounds arises mainly from the close proximity of anisotropic groups, such as the COOMe and $Cr(CO)_3$ groups.

The ^{1}H NMR results support earlier conformational proposals [1], which were introduced to explain some anomalous substituent effects on the ester CO wavenumbers. Similar conformational conclusions from ^{1}H NMR spectroscopy [9] were reached for the corresponding benzoic acids.

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