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THE RING CURRENT IN π-ARENE TRICARBONYLCHROMIUM(0) COMPLEXES (BENCHROTRENES)

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Summary

An investigation of the ring current contribution to the ^{1}H NMR chemical shifts of benzene tricarbonylchromium complexes (benchrotrenes) is presented. Appropriate model compounds are provided by the [2.2] metacyclophanes Ia—IIIa, [2.2]metaparacyclophane (IVa) and their respective tricarbonylchromium complexes Ib—IVb, in which the monitor protons are not directly attached but are in close proximity to the aromatic nuclei under consideration. The systems chosen permit a check to be made of geometry preservation on complexation, which is a necessary condition for a significant ^{1}H NMR comparison of complexed and uncomplexed arenes. The evidence indicates that the ring current shielding in benzene tricarbonylchromium complexes is considerably reduced above the ring plane. Analogous results were obtained for the [2.2]paracyclophanes Va and Vb. The observations strongly favour the ring current disrupture hypothesis, which has been questioned recently.

Introduction

Ring current considerations have been increasingly used to locate protons in the proximity of aromatic nuclei via their ^{1}H NMR spectra [1—3]. Organic chemists have adopted this model most successfully, although the theoretical background has been a matter of controversy in recent years (cf. refs. [1,4,5] and references therein). The upfield ^{1}H NMR signals of benchrotrenes (compared to the free arenes) have been tentatively explained in terms of a ring current disrupture caused by electron withdrawal due to the ligand [6]. However, comparison of the chemical shifts of complexed and uncomplexed compounds alone cannot sustain this hypothesis. Additionally a hypothetical (experimentally unavailable) reference chemical shift is needed. Thus in the case of benzene various cyclic conjugated polyenes were used to simulate the virtual shift value of cyclohexatriene [4]. Consequently, polyene $Cr(CO)_3$ complexes might provide the reference data for the corresponding arene complexes but their suitability turns out to be poor. While the inequivalent olefinic protons of the cycloheptatriene complex [7] cover a resonance frequency range of approximately 3 ppm, the case of cyclooctatetraene [8] is additionally complicated by the π-electron excess of the polyene. If we use the average shift values, which are about 5 ppm (δ) for both $Cr(CO)_3$ complexes, a comparison with corresponding data of benchrotrene protons gives no evidence for a significant ring current contribution to the chemical shifts.

To overcome these difficulties, an improved approach has been devised using compounds in which the monitor protons are not directly bound to the arene moiety but are in close proximity to it. Since in these cases reference chemical shifts are readily available, reliable shielding or deshielding contributions can be assessed experimentally. Using this approach Keller [9] recently concluded that there is general preservation of the ring current in benchrotrenes by comparing ^1H NMR spectra of a barrelane and its $Cr(CO)_3$ complex, the relevant protons being attached to a cyclopropane moiety located above the benzene ring plane. This prompts us to report our study of the ring currents in arene tricarbonylchromium complexes.

Results and discussion

For a correlation of ^1H NMR data with the local coordinates of the protons it is convenient to choose rigid systems *. Furthermore, as complexation with metal carbonyls might entail conformational changes, an assessment of such effects should be feasible. Both requirements are met in the [2.2]metacyclophanes Ib—IIIb, and in the [2.2]metaparacyclophane IVb (cf. Fig. 1) **. They are suitable for a study of the ring current effect due to the complexed moiety (influence on H-16 in Ib—IIIb and H-15(16) in IVb) and also incorporate protons which can serve for a control of the geometry (H—8) [2,10].

In any pair I—IV, H-8 is subject to the influence of an uncomplexed benzene ring, which is reflected in a chemical shift difference compared to the other protons of the same ring ($\Delta\delta_C$) ***. The $\Delta\delta_C$ values are expected to be very similar within one pair only if the geometry is preserved on complexation. Therefore, the data contained in Table 1 demonstrate that the topologies of Ia—IVa are largely retained in their respective tricarbonylchromium complexes Ib—IVb. For I these results are consistent with the similarity of the torsional angles of the ethylene bridge (57.2° and 54.7° respectively [14]). Thus the systems chosen allow a significant study to be made of the ring current effect in benchrotrenes.

The chemical shift differences $\Delta\delta_R$ in Ib—IVb reflect the shielding influence of a benchrotrene moiety on the protons of an uncomplexed arene. The observed decrease of these values compared with those of the corresponding free

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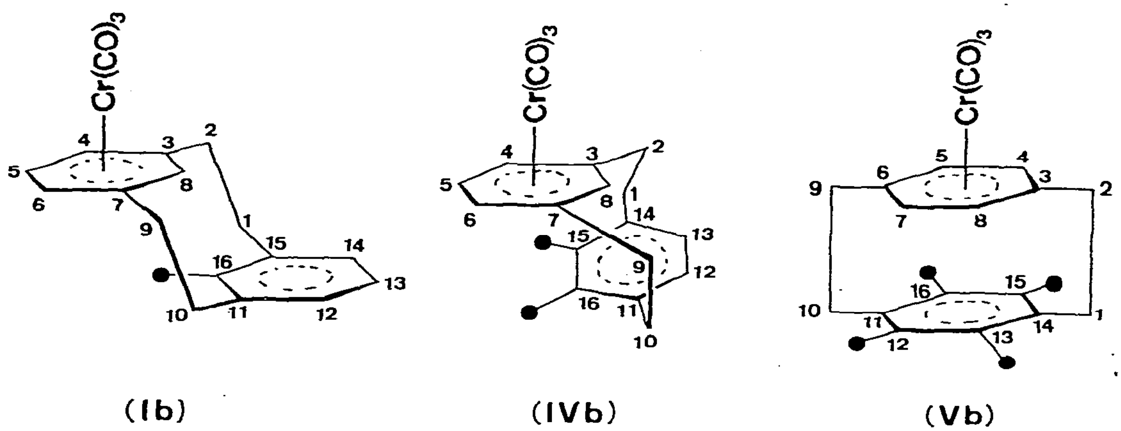
* By definition a rigid object is void of any degree of torsional freedom [10].

** The *meta* ring inversion in Ia and IVa is slow on the NMR time scale [11,12].

*** For I and IV mean values are given in Table 1 (cf. footnote *b*) to allow for the slightly different substituent effects in benzene and benchrotrene [13].



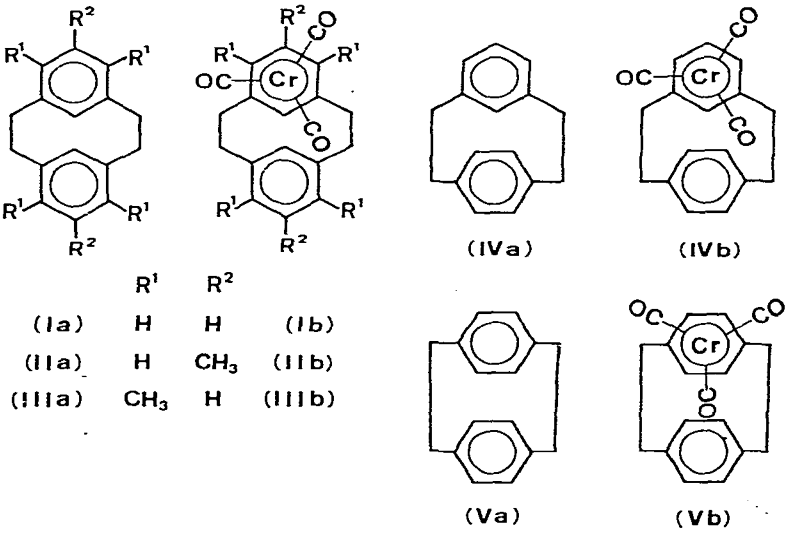
(Ib) (IVb) (Vb)

Fig. 1. Topology and monitor protons of Ib, IVb, and Vb.

cyclophanes Ia—IVa (cf. Table 1) indicates that there is attenuation of the ring current shielding for protons located above the plane of a benchrotrene as in Ib—IIIb and IVb. Corroborative evidence for a ring current disrupture in arene metal complexes is provided by the pair Va/Vb, [2.2]paracyclophane and its tricarbonylchromium complex [15], although in this case the results are less clear cut. Due to symmetry all the protons of one ring are subject to the same influence by the other, so that geometry control is not feasible without additional reference compounds. The effect of the complexed ring in Vb is assessed by comparing shifts (instead of shift differences) of H-12(13,15,16) in Va and Vb (cf. footnote ^{d} of Table 1).

The data we report show that as a rule the modification of an aromatic π-electron system by complexation with tricarbonylchromium results in an

SCHEME 1



	R^1	R^2	
(Ia)	H	H	(Ib)
(IIa)	H	CH_3	(IIb)
(IIIa)	CH_3	H	(IIIb)

TABLE 1

CHEMICAL SHIFTS (δ, ppm) AND SHIFT DIFFERENCES $\Delta\delta_C$ AND $\Delta\delta_R$ OF THE AROMATIC PROTONS OF THE CYCLOPHANES Ia—Va AND THEIR TRICARBONYLCHROMIUM COMPLEXES Ib—Vb

Proton number	I		II			III			IV		V	
	a	b	a		b	a		b	a	b	a	b
H-4	7.03	5.12	6.87		5.00	2.35	CH_3	2.20	6.76	4.83	6.46	4.64
H-5	7.27	5.47	2.33	CH_3	2.26	7.00		5.17	6.87	5.28	6.46	4.64
H-6	7.03	5.12	6.87		5.00	2.35	CH_3	2.20	6.76	4.83	—	—
H-7	—	—	—		—	—		—	—	—	6.46	4.64
H-8	4.27	2.33	4.13		2.15	4.23		2.72	5.43	3.73	6.46	4.64
H-12	7.03	7.12	6.87		6.90	2.35	CH_3	2.33	7.17	7.30	6.46	6.77
H-13	7.27	7.37	2.33	CH_3	2.37	7.00		7.10	7.17	7.30	6.46	6.77
H-14	7.03	7.12	6.87		6.90	2.35	CH_3	2.33	—	—	—	—
H-15	—	—	—		—	—		—	5.80	6.36	6.46	6.77
H-16	4.27	5.45	4.13		5.25	4.23		5.27 [c]	5.80	6.36	6.46	6.77
$\Delta\delta_C$				$\Delta\delta_{4,8}$			$\Delta\delta_{5,8}$					
	2.88 [a]	2.97 [a]	2.74		2.85	2.77		2.45	1.39 [a]	1.32 [a]	—	—
$\Delta\delta_R$				$\Delta\delta_{12,16}$			$\Delta\delta_{13,16}$		$\Delta\delta_{12,15}$			
	2.88 [b]	1.80 [b]	2.74		1.65	2.77		1.83	1.37	0.94	0.31 [d]	

[a] Mean value of $\Delta\delta_{4,8}$ and $\Delta\delta_{5,8}$. [b] Mean value of $\Delta\delta_{12,16}$ and $\Delta\delta_{13,16}$. [c] The assignment of H-5 was performed via NMDR by means of the weak coupling (~0.3 Hz) with the adjacent methyl groups (cf. also ref. [13]). [d] $\Delta\delta_R = \delta$H-12 (Vb) — δH-12 (Va).

attenuation of the ring current effect, in agreement with earlier postulates [6]. In addition, the binding of aromatic π-electrons to the *d*-orbitals of transition metals will not only influence the amount of π-electron dislocation ("ring current") but also modify the field distribution. Hence the results of Keller [9] on a barrelane $Cr(CO)_3$ complex can be rationalized in terms of an accidental coincidence of the field gradient in the vicinity of the monitor protons. But the similarity of their coordinates with those of the relevant atoms in Ib—IIIb [2] does not fit well into this picture. However, such speculation is premature, since the effects of conformational changes and other possible factors were not adequately considered in ref. [9].

Experimental

Melting points (m.p., uncorrected) were determined with a Kofler-Reichert hot stage apparatus. ^1H NMR spectra were recorded on a Varian EM 360 spectrometer at 60 MHz (room temperature, internal lock TMS) in $CDCl_3$ (5%, except for Va and Vb, where saturated solutions, <<5%, were used). For the double resonance experiments an EM 3630 Lock/Decoupler accessory was employed. Low resolution mass spectra were recorded on a Varian MAT CH 7 with Spectrosystem 166 at 80 (IIIb) and 110°C (IVb) and 70 eV. IR spectra were recorded on a Perkin—Elmer 377 in spectrograde CCl_4 (Merck). The syntheses of Ia [16], IIa [17], IIIa [17], IVa [12], Va [18], Ib [19], IIb [20], and Vb [15] were carried out as previously described.

The tricarbonylchromium complexes IIIb and IVb were prepared by heating 1 mmol of the cyclophanes IIIa and IVa and 1.5 mmol $Cr(CO)_6$ (Strem) for 5 h in diethyleneglycol dimethyl ether (Merck, LAB, distilled from CaH_2 and degassed prior to use). For further work up cf. ref. [19]. All reactions were performed under argon in the dark. Under these conditions, complexation of the *meta* ring of IVa occurred selectively. The yields were 70—80%.

On photochemical decomplexation of Ib—Vb the hydrocarbons obtained were identical with the starting materials (Ia—Va), as shown by their m.p.'s ^1H NMR and mass spectra.

Compound IIIb

M.p. 178°C (dec.) (from cyclohexane). Anal.: Found: C, 70.2; H, 6.0. Calcd. for $C_{23}H_{24}CrO_3$ (400.39): C, 68.99; H, 6.04%. MS; $m/e = 400$ (M^+). ^1H NMR, cf. Table 1. IR (cm^{-1}): 1970 (ν_{CO}-symm.), 1895 (ν_{CO}-asymm.).

Compound IVb

M.p. 153—155°C (from cyclohexane). Anal.: Found: C, 66.6; H, 4.4. Calcd. for $C_{19}H_{16}CrO_3$ (344.24): C, 66.29; H, 4.69%. MS: $m/e = 344$ (M^+). ^1H NMR, cf. Table 1. IR (cm^{-1}): 1970 (ν_{CO}-symm.), 1900 (ν_{CO}-asymm.).

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