

## METAL-STABILIZED CARBANIONS

### III\*. THE EFFECT OF COORDINATION WITH $\pi$ -TRICARBONYL- CHROMIUM ON THE PARATROPIC PROPERTIES OF BIPHENYLENE. AN NMR STUDY

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#### Summary

The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of biphenylene and its mono- and bis-tricarbonylchromium complexes have been recorded and analyzed. The comparison of the data for the complexes with those for the free ligand suggests that a substantial reduction of the paratropic character of the molecule occurs upon complexation. In the bis-complexed biphenylene, the two electronic sextets behave as separate non-interacting systems.

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#### Introduction

There is both theoretical and experimental evidence for the presence of an induced paramagnetic ring-current in the four-membered ring of biphenylene (BPH) [1]. This current exercises a substantial shielding effect on the surrounding protons which appear at higher fields than those of benzene. The effect, attributed to a net paratropism, is largely present in the  $4n$   $\pi$ -electron systems [2]. It was also shown [1] that a relation exists between the localization of the  $\pi$  electrons "in" and "around" the four-membered ring of BPH and the magnitude of the ring-current. Much more difficulty, however, arises in using  $^{13}\text{C}$  NMR data to recognize ring-current effects, and different interpretations for the low field chemical shifts of the cyclobutane carbons in BPH have been advanced [3,4].

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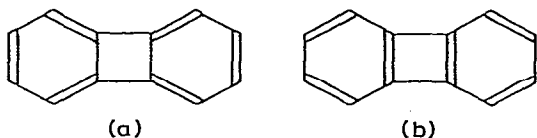
\* For Part II, See Ref. 5.

One of our recent interests is to determine what effect  $\pi$ -complexation of a tricarbonylchromium (TCC) unit has on the electron distribution of charged intermediates. In particular, we have been concerned with studies of anions from condensed polycyclic hydrocarbons possessing cyclic arrays of  $p$  orbitals containing  $4n$  or  $4n + 2$   $\pi$ -electrons [5,6]. In connection with the problem of paratropism which is present in some of the charged species investigated, we have synthesized the mono- and bis-tricarbonylchromium complexes of biphenylene and have recorded and analyzed their  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra.

## Results and discussion

Table 1 lists the  $^1\text{H}$  NMR parameters of BPH, TCC-BPH and  $(\text{TCC})_2\text{-BPH}$ . They were obtained by analyzing the spectra of the compounds in acetone- $d_6$  as AA' BB' spin systems with a modified version of the LAOCOON III program [7]. The assignment of resonances to the  $\alpha$ - and  $\beta$ -positions was unambiguously performed by selective deuteration of the  $\beta$ -positions. Both experimental and computer-simulated spectra of TCC-BPH, together with the spectrum of the synthetic mixture of mono- and bis-complexed ( $\beta,\beta,\beta',\beta'-d_4$ )-BPH are reported in Fig. 1.

The chemical shift and coupling constant values for BPH are in good agreement with those reported for other solvents [1,8,9]. For this ligand it was suggested [1] that a high exocyclic bond order lowers the "anti-aromaticity" of the four-membered ring since a tetramethylenecyclobutane-like structure (a) is preferred to a cyclobutadiene-like one (b). The difference between the coupling



constants  $^3J_{\alpha\beta}$  and  $^3J_{\beta\beta'}$  (1.38 Hz, see Table 1) is evidence for the importance of structures with the double bonds "outside" the central ring.

As shown in Table 1, upon complexation both the six-membered rings of the TCC unit show  $^1\text{H}$  resonances at considerably higher fields than those of BPH. Furthermore, in contrast with the ligand, the  $\alpha$ -protons of  $(\text{TCC})_2\text{-BPH}$  are more deshielded than the  $\beta$ -protons. The large upfield shift upon complexation of the aromatic protons in "diatropic"  $4n + 2$   $\pi$ -systems,  $\Delta(\text{C-L})$ , (usually ranging from  $-1.8$  to  $-2.5$  ppm) is a well recognized phenomenon, and its origin has been the subject of considerable speculation in recent years [10]. In the case of the  $4n$   $\pi$   $(\text{TCC})_2\text{-BPH}$  system, this upfield shift is much reduced, and values of  $\Delta(\text{C-L}) = -0.788$  and  $-1.110$  ppm have been found for the  $\alpha$  and  $\beta$  protons, respectively.

We attribute this reduced effect to a substantial reduction of the paratropic contributions to the chemical shift on going from the uncomplexed to the complexed system. The fact that the  $\alpha$ -protons in  $(\text{TCC})_2\text{-BPH}$  are more deshielded than the  $\beta$  protons is further evidence for the absence of a paratropic current in the bis-complexed molecule, the effect of which is stronger in the  $\alpha$  positions, which are nearer to the four-membered ring, than the  $\beta$  positions. The coordi-

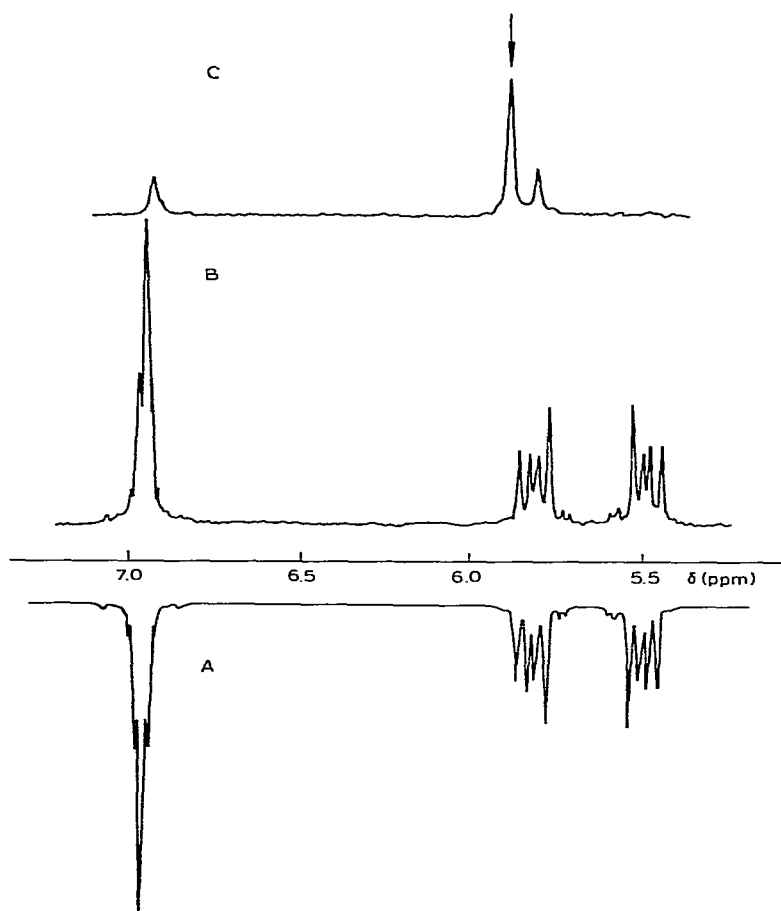


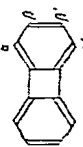
Fig. 1.  $^1\text{H}$  NMR spectra (in  $\text{CD}_3\text{COCD}_3$  at 303 K) of: TCC-BPH (computer simulated; A); TCC-BPH (experimental; B);  $(\beta,\beta,\beta',\beta'-d_4)\text{-(TCC)}_2\text{-BPH}$ ; the arrow indicates the resonance of the  $(\beta,\beta,\beta',\beta'-d_4)\text{-(TCC)}_2\text{-BPH}$ ; C).

nation of the TCC would strongly decrease the electronic interactions between the two 6  $\pi$ -electron systems which become two independent aromatic  $4n + 2$   $\pi$ -structures; as a consequence, the electronic arrangement with exocyclic double bond fixation which is suggested [1] to minimize the degree of anti-aromaticity in BPH would become less important. The finding that the difference between  $^3J_{\alpha\beta}$  and  $^3J_{\beta\beta'}$  is lowered from 1.38 to 0.54 Hz upon complexation (see Table 1) strongly supports our hypothesis.

An intermediate structure would explain the  $^1\text{H}$  NMR parameters for the monocomplex TCC-BPH. For the complexed ring, the  $\delta$  values are quite close to those shown by  $(\text{TCC})_2\text{-BPH}$ ; but the  $^3J_{\alpha\beta} - ^3J_{\beta\beta'}$  difference,  $\Delta^3J$  0.79 Hz, which is intermediate between those shown by BPH and  $(\text{TCC})_2\text{-BPH}$ , indicates that electronic structures with some double bond fixation may still contribute to the resonance hybrid; this is supported by the  $\Delta^3J = 0.84$  Hz value found for the coupling constants of the uncomplexed ring. On the other hand, the protons of the uncomplexed ring of TCC-BPH resonate at lower field ( $\Delta_{\text{C-L(av.)}}^{\text{free ring}}$

TABLE 1

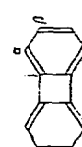
<sup>1</sup>H NMR PARAMETERS <sup>a</sup> OF BIPHENYLENE, FREE AND COMPLEXED WITH TRICARBONYLCHROMIUM

Compound	$\delta_\alpha = \delta_{\alpha'}$	$\delta_\beta = \delta_{\beta'}$	${}^3J_{\alpha\beta}$	${}^3J_{\beta\beta'}$	${}^4J_{\alpha\beta'}$	${}^5J_{\alpha\alpha'}$	$\Delta^{\alpha}(\text{C-L})^b$	$\Delta^{\beta}(\text{C-L})^b$	$\Delta^3J^c$
BPH 	6.691	6.763	6.86	8.24	0.77	1.00	—	—	1.38
TCC-BPH (Free ring)	6.936	6.985	7.14	7.98	1.03	0.51	+0.245	+0.222	0.84
(Complexed ring)	5.815	5.494	6.01	6.80	0.71	1.02	-0.876	-1.267	0.79
(TCC) <sub>2</sub> -BPH	5.903	5.653	6.09	6.63	0.65	0.99	-0.788	-1.110	0.54

<sup>a</sup> Solvent CD<sub>2</sub>COOD<sub>3</sub>;  $\delta$  (ppm) from internal TMS;  $J$  in Hz;  $T$  303 K. <sup>b</sup>  $\Delta^i(\text{C-L}) = \delta^i_{\text{complex}} - \delta^i_{\text{free ligand}}$ . <sup>c</sup>  $\Delta^3J = {}^3J_{\beta\beta'} - {}^3J_{\alpha\beta}$  (Hz).

TABLE 2

<sup>13</sup>C NMR PARAMETERS <sup>a</sup> OF BIPHENYLENE, FREE AND COMPLEXED WITH TRICARBONYLCHROMIUM

Compound	$C_j$	$C_\alpha$	$C_\beta$	$C \equiv O$	$\Delta^i(\text{C-L})^b$	$\Delta^{\alpha}(\text{C-L})^b$	$\Delta^{\beta}(\text{C-L})^b$
BPH 	152.3	118.0(165)	129.0(160)	—	—	—	—
TCC-BPH (Free ring)	148.3	119.6(167)	129.8(162)	—	-4.0	+1.6	+0.8
(Complexed ring)	116.5	88.4(176)	88.7(174)	233.4	-36.8	-29.6	-40.3
(TCC) <sub>2</sub> -BPH	113.0	88.5(176)	89.9(174)	233.4	-39.3	-29.5	-40.1

<sup>a</sup> Solvent THF- $d_6$ ;  $\delta$  (ppm) from internal TMS (in brackets: <sup>1</sup> $J(\text{C-H})$  coupling constants in Hz);  $T$  303 K. <sup>b</sup>  $\Delta^i(\text{C-L}) = \delta^i_{\text{complex}} - \delta^i_{\text{free ligand}}$ .

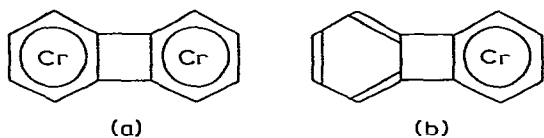
+0.233 ppm) than those of BPH. This effect can also be attributed to the lowered (but not eliminated) contribution of paratropic currents to the shifts of the uncoordinated ring protons. More convincing evidence should come from the NMR data on charged  $4n \pi$  systems [11] for which the cancellation of the paratropic currents seems much larger. However, an alternative explanation would be the strong electron-withdrawing effect of TCC, which is also the cause of the down-field effect in diatropic systems (e.g. TCC-fluorene [5]).

The  $^{13}\text{C}$  parameters are given in Table 2. The anomalously high field and low field shifts shown by  $\text{C}_\alpha$  and  $\text{C}_j$  respectively, in BPH were first attributed to the presence of a paramagnetic ring-current [3]. Lately, however, they have been justified on the basis of additivity relationships [4]. By the appropriate choice of model compounds, it was shown that the  $^{13}\text{C}$  shift values (in particular for the quaternary carbon) do not vary significantly between biphenylene and benzocyclobutane and the conclusion has been drawn that the effect of the paramagnetic ring current on  $^{13}\text{C}$  shifts is "insignificant relative to the  $^{13}\text{C}$  shift range" [4].

A number of features emerge from the comparison of the  $^{13}\text{C}$  data for the complexed and uncomplexed rings.

- The overall range of chemical shifts exhibited by BPH, 34.3 ppm, is lowered to 24.5 ppm for  $(\text{TCC})_2\text{-BPH}$ ;
- the  $\text{C}_\alpha$  and  $\text{C}_\beta$  carbon atoms resonate in the complexed ring at approximately the same frequency, whereas in the ligand the shift difference is 11 ppm;
- the  $\text{C}_j$  chemical shift values of the complexed rings are not anomalously low; they resemble that for  $\text{C}_j$ , for example, of the complexed ring of biphenyl ( $\delta(\text{C}_j)$  110.6 ppm) or indane ( $\delta(\text{C}_j)$  114.5 ppm) [12];
- the chemical shift values of the uncomplexed ring carbons in TCC-BPH are similar to those of the parent ligand.

Features a, b and c strongly suggest that the electron density in the complexed rings of  $(\text{TCC})_2\text{-BPH}$  (a) and of TCC-BPH (b) is uniformly distrib-



uted and structures with a high degree of bond fixation are of very low importance. Thus,  $^{13}\text{C}$  data confirm the explanations made on the basis of the  $^1\text{H}$  NMR data, namely that on complexation with TCC the benzene rings of BPH become separate electronic sextets of non-interacting systems. The similarity of the  $^{13}\text{C}$  chemical shifts for the free ring of TCC-BPH and free BPH suggests close resemblance of the electronic structures of the free six-membered rings. A dimethylenebenzocyclobutene-like structure (see (b)) for TCC-BPH would thus account well for the observed  $^{13}\text{C}$  chemical shifts.

Finally, examination of the  $\Delta(\text{C-L})$  values shown in Table 2 is instructive. In polycyclic aromatic  $4n + 2$  hydrocarbons, either condensed or uncondensed, the average shift of the complexed ring is about 35 ppm upfield [12] with respect to the free arenes, whereas the corresponding shifts in the uncomplexed

ring carbons are noticeably smaller (ca.  $\pm 2-3$  ppm).

For BPH systems also, the complexation effect,  $\Delta(C-L)$ , is on average ca. 35 ppm upfield; however, it depends upon the position of the carbon and it shows an alternating trend. The origin of this alternating behaviour lies in the "anomalous" shift values in the free BPH, while the resonances of the complexed ring carbons are close to those of the carbons of complexed  $4n + 2$  arenes.

In conclusion, the effect of TCC complexation on the  $^1H$  chemical shifts is drastically reduced in the BPH system compared with other aromatic structures; on the other hand, the effect on the  $^{13}C$  shifts is that usually observed in aromatic compounds. This differing effect on  $^1H$  and  $^{13}C$  chemical shifts can be accounted for in terms of the hypothesis that while the paramagnetic (and diamagnetic) ring-current contribution is readily observed by proton NMR spectroscopy,  $^{13}C$  NMR (as indicated by a study of bridged annulenes [13]) "is not suitable as a probe for the magnetic properties of cyclic  $\pi$  systems".

On the basis of these observations, it can safely be concluded that in  $4n \pi$  systems in which the paratropic currents contribute to the  $^1H$  shifts to a greater extent than in BPH, (e.g. the benzotropenyl anion), the TCC complexing effect,  $\Delta(C-L)$ , on the proton spectra is close to zero or even positive, whereas the  $\Delta(C-L)$  for  $^{13}C$  nuclei is still high and negative.

Studies of paratropic  $4n \pi$  charged systems and of the TCC-effect on chemical shifts will be the subject of a forthcoming paper.

## Experimental

HPLC analyses were performed on a Perkin-Elmer Series 3 liquid chromatograph equipped with a  $C_{18}$ -reversed phase Perkin-Elmer ODS-HC SIL-X-1 analytical column and a Perkin-Elmer LC-75 detector controlled by a Perkin-Elmer LC-75 Autocontrol unit. A Perkin-Elmer  $C_{18}$ -ODS preparative column was used for the quantitative separations with 70% aqueous methanol as eluent.

$^1H$  NMR measurements were made at 303 K on a Varian FT-80A spectrometer operating at 79.542 MHz. The  $^{13}C$  NMR spectra were recorded at the same temperature on a Bruker WH-90 FT spectrometer operating at 22.63 MHz.

TCC-BPH was prepared in 60% yield following Rausch [14].  $(TCC)_2$ -BPH was obtained in 19% yield by refluxing a suspension of 0.66 g of TCC-BPH and 1.02 g of  $(NH_3)_3Cr(CO)_3$  in 20 ml of anhydrous, oxygen-free dioxane under nitrogen for 4 h. The HPLC analysis of the resulting orange solution showed the presence of both mono- and bis-complexed BPH. Since  $(TCC)_2$ -BPH quickly decomposes during the column chromatography, the complexes were quantitatively separated by preparative HPLC. The analytical and physical properties agree well with those reported [14].

The mono- and bis-complexed  $\beta,\beta,\beta',\beta'$ -tetradeuteriobiphenylenes were obtained in a single-stage synthesis by refluxing 0.078 g of the deuterated ligand with 0.300 g of  $(NH_3)_3Cr(CO)_3$  in 2 ml of absolute dioxane under nitrogen for two hours. The reaction was monitored by TLC and stopped when the ligand spot had completely disappeared. The solution was then cooled to room temperature and carefully filtered under nitrogen through a G4-glass frit. The HPLC analysis showed the presence of both mono- and bis-complexed BPH's in ca. 1/1 ratio. The solvent was removed under high vacuum and the residue used for the NMR measurements.

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