The Molecular Structures of Phenanthrenechromium Tricarbonyl and 9,10-Dihydrophenanthrenechromium Tricarbonyl

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AN *X*-ray analysis of dibenzenechromium by Jellinek[1] suggested that there was alternation of long and short bonds in the aromatic rings but the most recent *X*-ray[2] and electron diffraction[3] work has not confirmed this result. Since such alternation would imply that the ring π-electrons are localised by the metal atom the point is of importance to an understanding of bonding in metal sandwich compounds. Structural studies on arene-chromium tricarbonyls provide information relevant to the problem and those of Bailey and Dahl on benzenechromium tricarbonyl[4] and hexamethyl-benzenechromium tricarbonyl[5] show that alternation of long and short bonds in the aromatic ring is unlikely. We now report that the structures of 9,10-dihydrophenanthrenechromium tricarbonyl and of an orthorhombic modification of phenan-threnechromium tricarbonyl show no sign of bond alternation induced by the chromium atom. The structure of a monoclinic modification of phenan-threnechromium tricarbonyl has been described by Deuschl and Hoppe[6] but no conclusions could be

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TABLE 1

Molecular dimensions in phenanthrenechromium tricarbonyl

C(1)–C(2)	1·389 ± 0·007 Å	Cr–C(1)	2·212 ± 0·005 Å
C(2)–C(3)	1·385 ± 0·007	Cr–C(2)	2·210 ± 0·005
C(3)–C(4)	1·410 ± 0·006	Cr–C(3)	2·206 ± 0·005
C(4)–C(12)	1·439 ± 0·006	Cr–C(4)	2·208 ± 0·004
C(1)–C(11)	1·440 ± 0·006	Cr–C(11)	2·289 ± 0·004
C(11)–C(12)	1·410 ± 0·006	Cr–C(12)	2·289 ± 0·004

TABLE 2

Mean dimensions of carbonyl groups in some chromium tricarbonyls

	Cr–C	C–O	Cr–O	∠ Cr–C–O	∠ O–Cr–O
$C_{14}H_{10}Cr(CO)_3$	1·84 Å	1·15 Å	2·99 Å	178°	89°
$C_{14}H_{12}Cr(CO)_3$	1·84	1·14	2·98	178	89
$C_6H_6Cr(CO)_3$	1·84	1·14	2·98	179	88
$C_6Me_6Cr(CO)_3$	1·81	1·16	2·98	178	90

drawn from the bond lengths as only projection data were used.

The orthorhombic modification of phenanthrenechromium tricarbonyl crystallises in the space group *Pbca*, with eight $C_{14}H_{10}Cr(CO)_3$ units in a cell of dimensions $a = 12·14$, $b = 18·08$, $c = 12·34$ Å. A Hilger and Watts linear diffractometer[7] was used to measure 4169 independent reflections. The discrepancy index, R, is 0·12 after Fourier and least-squares refinement.[8] A diagram of the molecule is shown in the Figure and some molecular dimensions are given in Table 1.
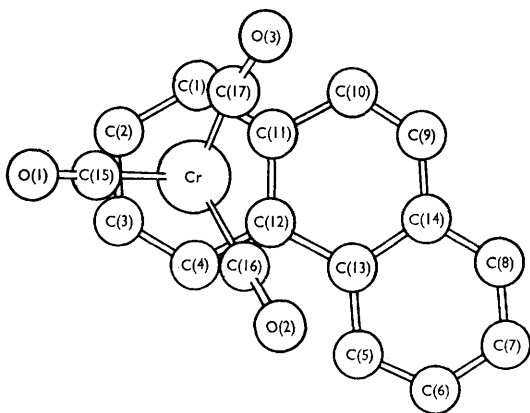
FIGURE

A molecule of phenanthrenechromium tricarbonyl viewed down the normal to the mean plane through the phenanthrene moiety

The mean C–C bond lengths in the bonded and non-bonded side rings are respectively 1·412 and 1·396 Å. V.B. calculations give 1·399 Å for the

mean C–C bond length in the side ring of free phenanthrene and the latest X-ray study yielded a value of 1·405 Å.[9]

In the side ring bonded to chromium the means of the two sets of three alternate bond lengths are 1·403 and 1·421 Å and the respective root-mean-square deviations from these means are 0·010 and 0·026 Å. The V.B. calculations give 1·388 and 1·409 Å for the same sets of alternate bond lengths in free phenanthrene.[9] This suggests that the chromium causes a general lengthening of C–C bonds in the ring rather than additional bond length alternation.

The Cr–C(11) and Cr–C(12) distances are significantly greater than the other Cr–C(bonded ring) distances. Of the C–C bonds opposite carbonyl groups the C(11)–C(12) bond is the one with least double-bond character in free phenanthrene.[9]

9,10-Dihydrophenanthrenechromium tricarbonyl crystallises in the monoclinic space group $P2_1/c$, with four $C_{14}H_{12}Cr(CO)_3$ units in a cell of dimensions $a = 10·50$, $b = 12·73$, $c = 11·98$ Å, $\beta = 118·9°$. Partial three-dimensional data, consisting of 1973 independent reflections, have been refined by Fourier and least-squares methods to a discrepancy index, R, of 0·10. Molecular geometry and intermolecular contacts are consistent with other analyses of arenechromium tricarbonyls.

As in the phenanthrene compound the chromium bonds to a side ring. The carbonyl groups have the staggered conformation with carbonyl–chromium vectors pointing towards the mid-points of ring C–C bonds. This is the expected conformation when the bonded ring does not carry directing groups.[10]

The mean C–C bond length in the bonded aromatic ring is 1·409 Å with individual values ranging from 1·437 ± 0·013 Å to 1·387 ± 0·016 Å

and the mean C–C bond length in the nonbonded ring is 1·391 Å. In the bonded side ring the means of the two sets of three alternate bond lengths are 1·407 and 1·412 Å and the respective root-mean-square deviations from these means are 0·006 and 0·021 Å. The effect of the chromium has again been to increase the mean C–C bond length in the bonded ring rather than to induce bond alternation.

The Cr–C(bonded ring) distances range from 2·196 ± 0·009 Å to 2·249 ± 0·008 Å with a mean of 2·224 Å which agrees well with the 2·23 found in $C_6H_6Cr(CO)_3$,[4] $C_6Me_6Cr(CO)_3$,[5] and $C_6H_5(OMe)Cr(CO)_3$.[11]

The mean dimensions of the carbonyl groups in $C_{14}H_{10}Cr(CO)_3$ and $C_{14}H_{12}Cr(CO)_3$ are given in the first two rows of Table 2. The agreement is excellent and all values are close to similar ones for $C_6H_6Cr(CO)_3$[4] and $C_6Me_6Cr(CO)_3$[5] which are given in rows 3 and 4 for comparison.

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