

## The Crystal and Molecular Structure of *anti*-1,6:8,13-Bismethano[14]annulenicarbonylchromium, a *pentahapto*-Complex

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**Summary** The *anti*-1,6:8,13-bismethano[14]annulene ligand is non-planar and contains a mainly localised double-bond system: the chromium atom makes short contacts with only five carbon atoms of the ligand and these are in the end ring which contains only two double bonds.

THE synthesis of *anti*-1,6:8,13-bismethano[14]annulene (I) and a tricarbonylchromium derivative (II) thereof has recently been achieved.<sup>1</sup> The preparation and properties of (I) have been described<sup>2</sup> and, on the basis of the latter

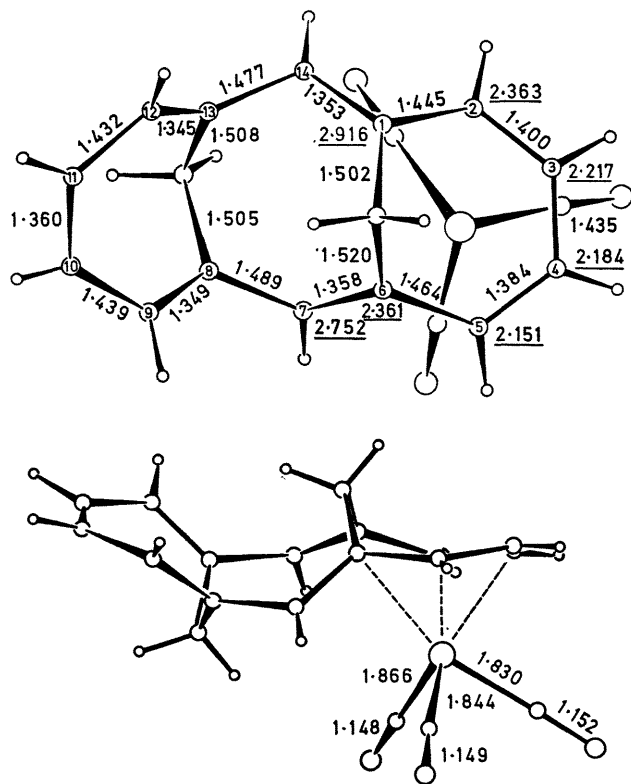


FIGURE. Plan and elevation of *anti*-1,6:8,13-bismethano[14]-annulenicarbonylchromium showing principal interatomic distances.

together with the u.v. and n.m.r. spectra, a polyene structure has been assigned. We undertook the X-ray analysis of

(II) for comparison with other bridged annulenes and their complexes.

**Crystal data:**  $C_{19}H_{14}O_3Cr$ ,  $M = 342.3$ , triclinic,  $a = 6.858$  (3),  $b = 10.390$  (7),  $c = 10.926$  (8) Å,  $\alpha = 100.45$  (7),  $\beta = 97.80$  (10),  $\gamma = 84.97$  (4)°,  $U = 756.9$  Å<sup>3</sup>,  $D_c = 1.50$ ,  $Z = 2$ , space group  $P\bar{1}$  ( $C_i^1$ , No. 2) by analysis, four-circle diffractometer data,<sup>3</sup> 2238 reflexions with  $F_0 > 5\sigma$  (counting statistics), Fourier methods, least-squares,  $R = 4.0\%$  (refinement complete).

The Figure shows the molecular shape and includes some bond-length data.

The perimetral C-C bond lengths reflect the polyene nature of the ligand. The values not only locate the seven double bonds unambiguously but also show that the chromium atom is bonded to that end ring which contains only two double bonds. This arrangement is unique, as far as we are aware, since hitherto tricarbonylchromium has always been regarded as a strong trienophile and it is therefore most unusual for the metal grouping to reject the available triene ring and prefer the diene one. It has also hitherto been the case that, in complex formation with annulenes, the resultant structure contains a mirror plane of symmetry or closely approximates to this. In the present complex the possible mirror symmetry is destroyed by two distortions: (i) a minor one whereby the tricarbonyl group rotates about its approximate three-fold axis so that the projection of the  $Cr(CO)_3$  group upon the plane defined by C(2), C(3), C(4), and C(5) shows that the corresponding C-C bonds of the ligand in projection are not bisected and (ii) there are only five Cr-C distances in the range 2.15–2.36 Å so that these appear to form a dienyl arrangement with the metal although the C-C separations are not consistent with this description. We regard the distances to C(1) of the end ring and to C(7) of the middle ring, 2.916 and 2.752 Å, as non-bonding. The mass spectrum is in agreement with the molecular formula and excludes the possibility of a hydride. It is usual to invoke interaction of the  $Cr(CO)_3$  group with six  $\pi$ -electrons in compounds of this type. In the present case this would presumably require involvement of the double bond between C(6) and C(7). It is clear that this molecule does not fit into previously known categories.

The ligand is considerably less planar than *cis*-1,6:8,13-bisoxido[14]annulene.<sup>4</sup> This arises mainly from a twist about the central ring. The non-bonded C(1)–C(6) and C(8)–C(13) separations, 2.410 and 2.364 Å, respectively, are some 0.2 Å greater than the value reported for tricarbonyl-1,6-methano[10]annulenechromium<sup>5</sup> but are only slightly less than that in tricarbonyl-*exo*-7-phenylcycloheptatrienechromium.<sup>6</sup>

(Received, January 12th, 1971; Com. 056.)

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