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Tricarbonyl(3–8-η-[2.2]paracyclophane)chromium*

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Abstract. $C_{19}H_{16}CrO_3$, FW 344·3, orthorhombic, $P2_12_12_1$; at −150°C: a = 10·651 (3), b = 13·031 (3), c = 11·071 (4) Å, U = 1536·5 (4) Å^3; at 20°C: a = 10·694 (2), b = 13·115 (2), c = 11·217 (2) Å, U = 1573·3 (5) Å^3, $Z = 4$, $D_x = 1{\cdot}453$, $D_m = 1{\cdot}445$ g cm^{-3}; R = 0·067 for 3313 non-zero reflexions. The distance between the two benzene rings in [2.2]paracyclophane is shorter than usual due to the coordination of the electron-withdrawing group, $Cr(CO)_3$, to one of the benzene rings.

Introduction. [2.2]Paracyclophane has benzene rings in the interesting boat form, resulting from a compromise between the two ethylenic bridges and the π-electron repulsion of the benzene rings. An interesting question arises as to whether or not the distance between the two benzene rings decreases when an electron-withdrawing group coordinates to one of them. In this work the molecular structure of the tricarbonylchromium complex of [2.2]paracyclophane (TCPC) (I), which was synthesized and reported by Cram & Wilkinson (1960), has been determined from an X-ray analysis. The diffraction data were measured at −150°C to obtain the molecular structure with high precision.

(I)

A Rigaku automated four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation was used for the measurement of the lattice parameters and the intensities. During the experiment the temperature of the crystal was kept constant at −150°C by Rigaku low-temperature equipment and the liquid-nitrogen gas-flow method. Intensities were measured by the θ–2θ scan method at a rate of 4° min^{-1} using a pale yellow crystal (0·25 × 0·25 × 0·25 mm). Backgrounds were counted for 5 s before and after each peak scan. The scan was repeated up to three times when the structure factor magnitude F was less than $3\sigma(F)$, where $\sigma(F)$ is the standard deviation estimated from the counting statistics. 3793 unique data (non-zero 3313) measured up to $2\theta = 70°$ were corrected for the Lp effect but not for absorption [μ(Mo $K\alpha$) = 7·7 cm^{-1}]. The structure was solved by the conventional heavy-atom method and refined by the block-diagonal least-squares procedure (*HBLS*-V, Ashida, 1973) with anisotropic

Table 1. *Fractional atomic coordinates* (×10^4, *for* H ×10^3) *with e.s.d.'s in parentheses*

Cr	4987·8 (0·6)	2365·0 (0·4)	3635·0 (0·5)
O(1)	5257 (1)	3763 (2)	5767 (3)
O(2)	7767 (1)	2586 (3)	3214 (3)
O(3)	5477 (2)	573 (2)	5264 (3)
C(1)	1951 (2)	4690 (3)	1770 (5)
C(2)	3116 (2)	4621 (3)	2665 (4)
C(3)	3620 (2)	3538 (3)	2724 (4)
C(4)	4545 (2)	3199 (3)	1926 (3)
C(5)	4657 (2)	2130 (3)	1667 (3)
C(6)	3853 (2)	1426 (3)	2197 (4)
C(7)	3127 (2)	1749 (3)	3190 (4)
C(8)	3010 (2)	2804 (3)	3460 (3)
C(9)	3591 (2)	404 (3)	1609 (5)
C(10)	2514 (2)	511 (3)	611 (5)
C(11)	1967 (2)	1584 (3)	541 (4)
C(12)	2584 (2)	2333 (4)	−119 (4)
C(13)	2452 (2)	3371 (3)	155 (4)
C(14)	1694 (2)	3683 (3)	1123 (4)
C(15)	873 (2)	2949 (3)	1605 (4)
C(16)	1020 (2)	1915 (3)	1326 (4)
C(17)	5153 (2)	3220 (3)	4951 (4)
C(18)	6698 (2)	2499 (3)	3362 (4)
C(19)	5288 (2)	1266 (3)	4622 (4)
H(1*A*)	216 (6)	524 (4)	118 (5)
H(1*B*)	129 (4)	488 (3)	230 (4)
H(2*A*)	284 (4)	489 (3)	348 (4)
H(2*B*)	376 (5)	506 (4)	235 (5)
H(9*A*)	330 (5)	−13 (4)	230 (5)
H(9*B*)	426 (6)	12 (4)	125 (6)
H(10*A*)	190 (6)	3 (5)	74 (6)
H(10*B*)	284 (6)	25 (5)	−13 (6)
H(4)	508 (5)	365 (3)	143 (4)
H(5)	530 (4)	191 (3)	106 (4)
H(7)	260 (4)	122 (3)	369 (4)
H(8)	246 (5)	300 (4)	410 (4)
H(12)	320 (4)	213 (3)	−73 (4)
H(13)	299 (5)	393 (4)	−25 (5)
H(15)	14 (5)	323 (3)	220 (4)
H(16)	54 (5)	148 (4)	176 (5)

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* Structural Chemistry of Layered Cyclophanes. IV.

temperature factors for Cr, O and C, and isotropic for H. The weighting scheme used was $w = [\sigma^2(F_o) + a|F_o| + b|F_o|^2]^{-1}$ and $w = c$ for observed and unobserved reflexions respectively. The anomalous-scattering effect of Cr ($f' = 0{\cdot}30$, $f'' = 0{\cdot}80$) was included at the final stage of refinement. The R value was 0·067 for non-zero reflexions (0·093 for all), and $R_w = 0{\cdot}071$ with $a = 0{\cdot}0435$, $b = -0{\cdot}0001$, and $c = 0{\cdot}0989$. Atomic scattering factors for heavy atoms were taken from *International Tables for X-ray Crystallography* (1974) and for H from Stewart, Davidson & Simpson (1965). The final atomic parameters are listed in Table 1.*

Discussion. An *ORTEP* (Johnson, 1976) drawing of the molecular structure is shown in Fig. 1 together with the atomic numbering. Interatomic distances and bond angles are given in Table 2, with estimated standard deviations. The structure of the [2.2]paracyclophane moiety in the TCPC molecule is compared with those of related compounds in Table 3.

Some remarkable features are: (1) angle p, which shows the out-of-plane deformation of the benzene ring, is similar in all molecules, (2) angle q, which is a measure of bond out-of-plane bending, of ring A in TCPC is slightly smaller than those in the other compounds, (3) bond angle r of ring A in TCPC shows little distortion from the standard tetrahedral angle, (4) bridge distance a in TCPC is much elongated compared with the C—C single-bond distance (1·541 Å), (5) bond d of ring A in TCPC is slightly longer than those in the other molecules, (6) the distances between the two benzene rings (e and f) of TCPC are significantly shorter than those in the other molecules, (7) the torsion angle around the bridging $-CH_2-CH_2-$ bond is correlated with the steric interaction of the methyl substituents, (8) the values of θ show that the two benzene rings are essentially parallel to each other in all molecules.

Table 2. *Interatomic bond distances* (Å) *and bond angles* (°)

Cr—C(17)	1·842 (4)	O(1)—C(17)	1·153 (5)
Cr—C(18)	1·855 (4)	O(2)—C(18)	1·156 (6)
Cr—C(19)	1·829 (4)	O(3)—C(19)	1·167 (6)
C(3)—C(4)	1·395 (5)	C(11)—C(12)	1·385 (7)
C(3)—C(8)	1·415 (5)	C(11)—C(16)	1·400 (7)
C(4)—C(5)	1·427 (5)	C(12)—C(13)	1·393 (7)
C(5)—C(6)	1·386 (6)	C(13)—C(14)	1·402 (6)
C(6)—C(7)	1·408 (6)	C(14)—C(15)	1·401 (6)
C(7)—C(8)	1·412 (6)	C(15)—C(16)	1·391 (7)
C(2)—C(3)	1·511 (6)	C(6)—C(9)	1·508 (7)
C(1)—C(14)	1·520 (7)	C(10)—C(11)	1·517 (8)
C(1)—C(2)	1·591 (7)	C(9)—C(10)	1·599 (8)
Mean* C—H = 0·99 (6) (0·89–1·08)			
C(17)—Cr—C(18)	88·8 (2)	Cr—C(17)—O(1)	179·3 (3)
C(17)—Cr—C(19)	89·1 (2)	Cr—C(18)—O(2)	178·8 (4)
C(18)—Cr—C(19)	90·0 (2)	Cr—C(19)—O(3)	179·2 (4)
C(2)—C(3)—C(4)	121·3 (4)	C(10)—C(11)—C(12)	119·8 (4)
C(2)—C(3)—C(8)	119·6 (4)	C(10)—C(11)—C(16)	122·0 (4)
C(4)—C(3)—C(8)	118·4 (4)	C(12)—C(11)—C(16)	116·9 (4)
C(3)—C(4)—C(5)	119·7 (3)	C(11)—C(12)—C(13)	121·4 (4)
C(4)—C(5)—C(6)	120·6 (4)	C(12)—C(13)—C(14)	120·4 (4)
C(5)—C(6)—C(7)	118·1 (4)	C(13)—C(14)—C(15)	116·9 (4)
C(5)—C(6)—C(9)	121·1 (4)	C(13)—C(14)—C(1)	120·4 (4)
C(7)—C(6)—C(9)	119·9 (4)	C(15)—C(14)—C(1)	121·5 (4)
C(6)—C(7)—C(8)	120·3 (4)	C(14)—C(15)—C(16)	120·4 (4)
C(7)—C(8)—C(3)	119·7 (4)	C(15)—C(16)—C(11)	121·1 (4)
C(1)—C(2)—C(3)	111·0 (4)	C(6)—C(9)—C(10)	110·7 (4)
C(2)—C(1)—C(14)	112·6 (4)	C(9)—C(10)—C(11)	113·0 (5)
Mean* C—C—H (aromatic)		120 (3) (115–125)	
C—C—H (aliphatic)		110 (4) (102–115)	
H—C—H		107 (5) (99–111)	

* Only mean values of bond distances and bond angles involving H atoms are listed. The e.s.d.'s for individual bonds are in the first set of parentheses after the value, and the ranges are in the second set.

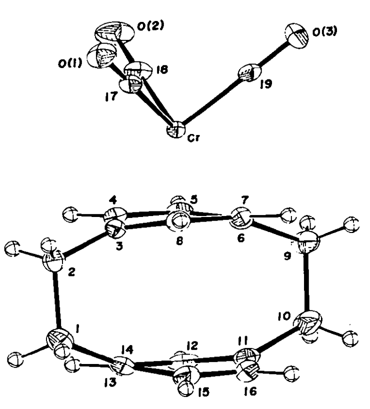

Fig. 1. Perspective view of the molecule represented by thermal ellipsoids (50%) for the heavy atoms and by spheres (0·1 Å radius) for the H atoms.

The precise molecular structure of benzenetricarbonylchromium (TCB) was determined by Rees & Coppens (1973) at 78 K. The structures of the corresponding parts of the TCPC molecule are compared with those of TCB in Table 4. The TCB molecule is located on a crystallographic mirror plane. The geometry of the benzene ring in TCB has C_{3v} symmetry to a good approximation. The bond alternation can be clearly seen in the benzene ring. The TCPC molecule has no crystallographic symmetry; however, it has approximate mirror symmetry. A tendency to bond alternation is also observed in ring A; the mean of bond distances a, c and e is 1·398 Å and that of b, d and f is 1·417 Å; these are almost exactly the same as those found in TCB (1·402 and 1·420 Å respectively). The mean structure of the $Cr(CO)_3$ group is the same in both molecules. The interatomic distances between Cr

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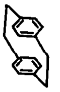
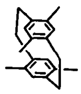
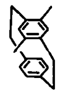
* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33591 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

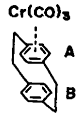
Table 3. *Mean molecular structures of TCPC and related compounds*

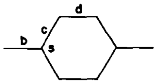
φ: torsional angle around the $-CH_2-CH_2-$ bond.
θ: dihedral angle between the benzene-ring planes (which are defined by the four C atoms not connected to the bridging methylene C atoms).
The numbers in parentheses give the e.s.d.'s of the mean structural parameters.
Mean: $x = \Sigma x_i/n$, where x_i is the individual structural parameter observed, and n is the number of chemically equivalent structural parameters. Variance: $s^2 = \Sigma(x_i - x)^2/(n-1)$. Estimated standard deviation of mean: $\sigma(\bar{x}) = (s^2/n)^{1/2}$.

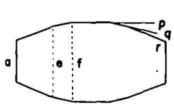












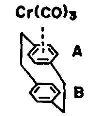
	PC$^{(1)}$	TMPC$^{(2)}$	DMPC$^{(3)}$	TCPC$^{(4)}$ Ring *A*	TCPC$^{(4)}$ Ring *B*
p	12·6°	13·1 (1)°	12·6 (2)°	12·2 (1)°	11·4 (1)°
q	11·2	10·6 (1)	10·4 (4)	8·9 (1)	11·2 (8)
r	113·7	112·2 (1)	112·6 (1)	110·9 (1)	112·8 (3)
s	117·0	117·5 (1)	118·2 (2)	118·3 (1)	116·9 (1)
a	1·562 Å	1·580 (10) Å	1·587 (12) Å	1·595 (4) Å	
b	1·509	1·514 (5)	1·530 (5)	1·510 (2)	1·519 (2)
c	1·384	1·394 (4)	1·400 (2)	1·401 (6)	1·397 (4)
d	1·386	1·382 (3)	1·407 (5)	1·420 (6)	1·392 (1)
e	2·78	2·766 (4)	2·772 (1)	2·723 (5)	
f	3·09	3·091 (1)	3·084 (2)	3·017 (2)	
φ	(3·2°)*	19·3 (1)°	9·9 (10)°	3·8 (7)°	
θ	0·0	0·1	0·2	2·2	

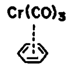
References: (1)]2.2]paracyclophane (Hope, Bernstein & Trueblood, 1972); (2) 4,7,13,16-tetramethyl[2.2]paracyclophane (Goto, Kai, Yasuoka & Kasai, 1977); (3) 4,7-dimethyl[2.2]paracyclophane (Goto *et al.*, 1977); (4) present work.

* PC has a disordered structure and this angle was determined by the analysis of anisotropic thermal parameters (Hope *et al.*, 1972).

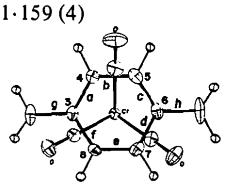
Table 4. *Molecular structures of TCPC and TCB*

The projection of the Cr(CO)$_3$ group onto ring *A* of TCPC is also shown (Johnson, 1976).





	TCPC$^{(1)}$ Ring *A*	TCPC$^{(1)}$ Ring *B*	TCB$^{(2)}$
a	1·395 Å	1·402 Å	1·402 Å*
b	1·427	1·393	1·418*
c	1·386	1·385	1·402
d	1·408	1·400	1·421*
e	1·412	1·391	1·401*
f	1·415	1·401	1·421
⟨*a,c,e*⟩†	1·398 (8)	1·393 (5)	1·402 (1)
⟨*b,d,f*⟩†	1·417 (6)	1·398 (3)	1·420 (1)
g	1·511	1·520	
h	1·508	1·517	
⟨Cr–C⟩†	1·842 (8)		1·841 (1)
⟨C–O⟩†	1·159 (4)		1·158 (1)



References: (1) Present work; (2) Rees & Coppens (1973) – bond distances are taken from the X-ray data uncorrected for thermal vibration.

* These four bonds are crystallographically unique.

† Mean bond distances with e.s.d.'s in parentheses calculated by the method shown in Table 3.

and the benzene C atoms are almost equal in TCB, ranging from 2·217 to 2·240 Å. The corresponding distances in TCPC, however, correspond to three types of bonds: short bonds: 2·191 (4) Å [Cr to C(8)] and 2·194 (4) Å [Cr to C(7)]; long bonds: 2·340 (4) Å [Cr to C(3)] and 2·344 (4) Å [Cr to C(6)]; and intermediate bonds: 2·232 (4) Å [Cr to C(4)] and 2·228 (4) Å [Cr to C(5)].

From the above observations it can be concluded that the coordination of the highly electron-withdrawing Cr(CO)$_3$ to one of the benzene rings results in remarkable structural changes in the [2.2]paracyclophane skeleton. No intermolecular atomic contact shorter than the van der Waals distance is found in the crystal.

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Bis(2,2′-bipyridyl)-*catena*-μ-tetrathionato-copper(II)

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Abstract. $C_{20}H_{16}N_4O_6S_4Cu$, $M_r = 599·54$, orthorhombic, *Pbcn*, $a = 11·260$ (10), $b = 12·839$ (10), $c = 16·170$ (11) Å, $Z = 4$, $D_x = 1·733$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $R = 0·0379$ for 1139 diffractometer data. The Cu^{II} ion lies on a twofold axis and involves a regular elongated-tetragonal octahedral stereochemistry with the two 2,2′-bipyridyl (bpy) ligands coordinating in the equatorial plane (Cu—N, 1·99 Å) but with a significant tetrahedral twist to the planes of the two ligands (56·3°). The tetrathionate ion lies on a twofold axis which bisects the central S—S bond, and bridges separate Cu^{II} atoms through semi-coordinating oxygen atoms at 2·63 Å.

Introduction. As part of a programme to examine the ability of coordinated thionate ions, $S_nO_6^{2-}$, to determine the local molecular stereochemistry of the copper(II) ion in the $(Cubpy_2)^{2+}$ cation the crystal structure of Cu(2,2′-dipyridyl)$_2S_4O_6$ has been determined.

An aqueous solution of $Na_2S_4O_6$ was prepared by adding an aqueous iodine solution to aqueous $Na_2S_2O_3$; the stoichiometric amount of a solution of $Cubpy_2Cl_2$ was added and royal-blue crystals were deposited overnight [found: C, 39·97; H, 2·74; N, 9·37; Cu, 10·43%; calculated for $Cu(C_{20}H_{16}N_4)S_4O_6$: C, 40·02; H, 2·68; N, 9·37; Cu, 10·58%]. Intensity data were collected on a Philips PW 1100 four-circle diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. A θ–2θ scan mode was used and reflections with $3·0 < \theta < 32°$ in one quadrant were examined. A constant scan speed of 0·05° s^{-1} and a variable scan width of (0·7 + 0·1 tan θ)° were used. With the acceptance criterion $I > 2·5\sigma(I)$, 1139 unique reflections were retained; Lorentz and polarization corrections were applied, but no correction was made for absorption [μ(Mo $K\alpha$) = 12·71 cm^{-1}]. The structure was solved using Patterson and Fourier techniques and refined by full-matrix least-squares analysis with isotropic temperature factors to $R = 0·10$. Anisotropic temperature factors were then refined for all non-hydrogen atoms. The positions of the H atoms were calculated geometrically and 'floated' on the adjacent carbon atoms assuming C—H 1·08 Å and a fixed temperature factor of 0·07 Å^2. The data converged when the maximum shift/e.s.d. was <0·003 with a

Table 1. *Atomic coordinates* (×10^4) *with e.s.d.'s in parentheses*

Values for H are calculated (see text).

	x	*y*	*z*
Cu	0	1533 (1)	2500
N(1)	−125 (4)	2500 (3)	3454 (2)
N(2)	625 (4)	575 (3)	3368 (2)
C(1)	−647 (5)	3430 (4)	3452 (3)
C(2)	−811 (5)	4013 (4)	4156 (3)
C(3)	−402 (6)	3604 (5)	4887 (4)
C(4)	147 (6)	2642 (4)	4910 (3)
C(5)	252 (4)	2092 (4)	4180 (3)
C(6)	766 (5)	1039 (4)	4112 (3)
C(7)	1372 (5)	539 (5)	4741 (4)
C(8)	1830 (6)	−437 (5)	4609 (4)
C(9)	1710 (5)	−898 (5)	3854 (4)
C(10)	1097 (5)	−373 (4)	3234 (4)
S(1)	4214 (1)	887 (1)	2791 (1)
S(2)	3149 (1)	1900 (1)	2059 (1)
O(1)	2227 (3)	2108 (3)	2657 (2)
O(2)	2763 (4)	1286 (3)	1366 (3)
O(3)	3851 (4)	2793 (3)	1832 (2)
H(1)	−960 (5)	3735 (4)	2869 (3)
H(2)	−1238 (5)	4766 (4)	4135 (3)
H(3)	−513 (6)	4039 (5)	5453 (4)
H(4)	490 (6)	2325 (4)	5480 (3)
H(5)	1483 (5)	924 (5)	5329 (4)
H(6)	2278 (6)	−845 (5)	5103 (4)
H(7)	2089 (5)	−1656 (5)	3735 (4)
H(8)	992 (5)	−730 (4)	2634 (4)