

π -(*exo*-2-Acetoxybenzonorbornenyl)-*exo*-tricarboxylchromium

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Abstract. Monoclinic, $P2_1/a$, $a=21.898$ (7), $b=10.428$ (7), $c=6.911$ (4) Å, $\beta=102.2$ (1)°, $\text{CrC}_{16}\text{O}_5\text{H}_{14}$, $M=338.3$, $Z=4$, $D_o=D_c=1.46$ g cm⁻³, $\lambda=0.71068$ Å, $T=23$ (2)°C, $\mu(\text{Mo K}\alpha)=7.14$ cm⁻¹. The structure consists of isolated molecules of the geometric configuration indicated by the title with no unusual intermolecular interactions.

Introduction. In the controversy over the detailed mechanism of solvolysis of benzonorbornenyl sulfonates (Bly & Strickland, 1970; Wells & Trahanovsky, 1970) a necessary prelude to the discussion of the mechanism is the knowledge of which of the four possible geometrical isomers is actually under investigation. If the geometry of a particular isomer is established by X-ray crystallography the geometry of all the others can be related by chemical means (Bly, Strickland, Swindell & Veazey, 1970). The sulfonates themselves are not amenable to single-crystal structure analysis, but an acetoxy derivative readily crystallized and proved to be a tractable problem. We wish to report the details here of the π -(*exo*-2-acetoxybenzonorbornenyl)-*exo*-tricarboxylchromium structure determination and show that the stereochemistry indicated as the 2-OMS is correct (Bly & Strickland, 1970; Wells & Trahanovsky, 1970). A preliminary communication appeared elsewhere (Lüth, Taylor & Amma, 1970).

Crystals were generously supplied by Professor R. S. Bly. The needle (symmetry axis) crystals were coated with hydrocarbon grease and sealed in Lindemann capillaries for diffraction studies. The space group and preliminary cell dimensions were determined from Weissenberg and precession photographs. Accurate cell parameters were obtained from a least-squares fit of the χ , φ , and 2θ diffractometer angles for 11 accurately centered general reflections. Systematic absences: $h0l$, $h=2n+1$; $0k0$, $k=2n+1$.

Intensity data for 2255 independent reflections were collected from a crystal $0.12 \times 0.06 \times 0.54$ mm on a Picker card-controlled automatic diffractometer to a maximum 2θ value of 65° (θ - 2θ scan, scan width = 0.70° , scan speed = 0.00833° s⁻¹). Background counts were made for 20 s each (B_1 and B_2) at $\pm 0.35^\circ$ 2θ of peak maximum. Reflections were considered absent if the integrated intensity was less than twice the estimated σ of background, $[(2.075)^2(B_1+B_2)]^{1/2}$; 1057 reflections were retained by this criterion. A standard peak was measured after every ten reflections to monitor instrument stability and crystal decomposition. In general, the variation in intensity between consecutive standard peaks was less than a standard deviation of $I_{(\text{net})}$ where $\sigma[I_{(\text{net})}] = [I_{(\text{scan})} - (2.075)^2(B_1+B_2)]^{1/2}$ and the total variation during data collection was 2σ . The take-off angle, source-to-crystal distance, and crystal-

Table 1. Final positional and thermal parameters

Anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl) \times 10^4]$.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	0.1776 (1)	0.2631 (3)	0.0817 (4)	12.9 (7)	82 (3)	166 (7)	-4 (2)	9 (2)	7 (5)
O(1)	-0.0390 (5)	0.262 (1)	0.446 (2)	17 (3)	107 (17)	264 (37)	-3 (7)	34 (9)	-8 (23)
O(2)	-0.0945 (7)	0.080 (2)	0.435 (3)	30 (5)	94 (20)	440 (59)	-10 (8)	65 (13)	-40 (28)
O(3)	0.2288 (8)	0.470 (2)	0.371 (2)	35 (5)	120 (22)	328 (55)	-14 (9)	8 (13)	-94 (28)
O(4)	0.3039 (7)	0.239 (2)	-0.028 (3)	24 (4)	212 (27)	487 (58)	-17 (11)	71 (13)	-35 (38)
O(5)	0.1412 (9)	0.472 (2)	-0.221 (3)	45 (6)	162 (27)	336 (59)	-22 (10)	-23 (15)	104 (32)
C(1)	0.0607 (8)	0.289 (2)	0.351 (3)	14 (5)	114 (27)	225 (57)	2 (8)	22 (13)	47 (29)
C(2)	0.0021 (8)	0.195 (2)	0.333 (3)	14 (5)	116 (26)	239 (63)	-2 (8)	34 (14)	-19 (29)
C(3)	-0.0285 (8)	0.192 (2)	0.105 (3)	14 (5)	132 (28)	224 (60)	-9 (9)	25 (14)	14 (29)
C(4)	0.0163 (8)	0.286 (2)	0.013 (3)	12 (5)	93 (24)	167 (47)	-1 (8)	3 (12)	7 (25)
C(5)	0.1028 (9)	0.132 (2)	-0.090 (3)	16 (5)	86 (23)	221 (57)	-6 (8)	23 (14)	11 (28)
C(6)	0.159 (1)	0.058 (2)	-0.010 (4)	20 (6)	50 (22)	344 (79)	-14 (9)	22 (17)	-30 (30)
C(7)	0.187 (1)	0.060 (2)	0.197 (3)	17 (6)	80 (25)	237 (68)	-6 (9)	8 (15)	50 (30)
C(8)	0.1589 (9)	0.138 (2)	0.332 (3)	16 (5)	70 (22)	280 (62)	-3 (8)	21 (14)	37 (30)
C(9)	0.0337 (9)	0.387 (2)	0.179 (3)	22 (6)	68 (21)	173 (53)	1 (8)	-1 (13)	-7 (27)
C(10)	0.1045 (7)	0.210 (2)	0.248 (2)	9 (4)	83 (22)	137 (48)	0 (7)	6 (11)	12 (23)
C(11)	0.0771 (8)	0.207 (2)	0.044 (2)	17 (5)	76 (22)	110 (49)	-9 (7)	16 (12)	-11 (22)
C(12)	-0.088 (1)	0.190 (3)	0.478 (3)	20 (6)	161 (35)	109 (52)	-8 (11)	3 (13)	-2 (31)
C(13)	-0.1338 (9)	0.274 (2)	0.567 (3)	20 (6)	159 (32)	303 (62)	3 (11)	46 (15)	-20 (39)
C(14)	0.210 (1)	0.389 (2)	0.259 (3)	13 (6)	112 (29)	234 (65)	-2 (9)	12 (15)	9 (35)
C(15)	0.255 (1)	0.251 (2)	0.015 (3)	29 (6)	72 (23)	229 (52)	-10 (12)	28 (15)	-34 (33)
C(16)	0.156 (1)	0.391 (2)	-0.103 (3)	23 (7)	120 (31)	226 (68)	-20 (11)	-5 (16)	-26 (36)

to-counter distance were 3.7°, 18 cm, and 23 cm, respectively. The receiving aperture at the counter was 6 × 8 mm. The counting rate never exceeded 5000 counts and no attenuators were used. No corrections

Table 2. Bond distances (Å) and bond angles (°)

Cr—ring center	1.73 (3)	C(14)—Cr—C(15)	88.6 (9)
Cr—C(14)	1.83 (2)	C(14)—Cr—C(16)	87.1 (8)
Cr—C(15)	1.85 (2)	C(15)—Cr—C(16)	89.7 (9)
Cr—C(16)	1.84 (3)	O(4)—C(15)—Cr	178.3 (21)
C(5)—C(6)	1.47 (3)	O(3)—C(14)—Cr	178.3 (19)
C(5)—C(11)	1.42 (2)	O(5)—C(16)—Cr	179.1 (18)
C(6)—C(7)	1.43 (3)	C(5)—C(6)—C(7)	120.7 (19)
C(7)—C(8)	1.46 (3)	C(6)—C(7)—C(8)	120.3 (18)
C(8)—C(10)	1.42 (2)	C(7)—C(8)—C(10)	117.3 (18)
C(10)—C(11)	1.41 (2)	C(8)—C(10)—C(11)	122.4 (17)
C(10)—C(1)	1.55 (2)	C(10)—C(11)—C(5)	121.7 (17)
C(11)—C(4)	1.55 (2)	C(11)—C(5)—C(6)	117.5 (18)
C(1)—C(9)	1.59 (2)	C(10)—C(11)—C(4)	107.4 (14)
C(4)—C(9)	1.55 (2)	C(5)—C(11)—C(4)	130.7 (16)
C(1)—C(2)	1.60 (2)	C(11)—C(10)—C(1)	107.3 (14)
C(4)—C(3)	1.61 (2)	C(8)—C(10)—C(1)	129.9 (16)
C(2)—C(3)	1.58 (3)	C(10)—C(1)—C(2)	101.4 (15)
C(2)—O(1)	1.49 (2)	C(10)—C(1)—C(9)	99.7 (14)
O(1)—C(12)	1.36 (2)	C(9)—C(1)—C(2)	99.9 (14)
C(12)—C(13)	1.56 (3)	C(1)—C(2)—C(3)	104.8 (14)
C(12)—O(2)	1.19 (2)	C(1)—C(2)—O(1)	103.4 (14)
C(14)—O(3)	1.17 (2)	C(3)—C(2)—O(1)	110.8 (15)
C(15)—O(4)	1.18 (2)	C(2)—C(3)—C(4)	102.5 (14)
C(16)—O(5)	1.17 (3)	C(3)—C(4)—C(9)	101.6 (15)
Cr—C(5)	2.26 (2)	C(9)—C(4)—C(11)	101.1 (13)
Cr—C(6)	2.24 (2)	C(3)—C(4)—C(11)	101.2 (14)
Cr—C(7)	2.26 (2)	C(4)—C(9)—C(1)	96.4 (14)
Cr—C(8)	2.27 (2)	C(2)—O(1)—C(12)	113.9 (15)
Cr—C(10)	2.23 (2)	O(1)—C(12)—O(2)	123.8 (21)
Cr—C(11)	2.24 (2)	O(1)—C(12)—C(13)	110.5 (20)
Cr—C(1)	3.48 (2)	O(2)—C(12)—C(13)	125.6 (21)
Cr—C(4)	3.47 (2)		
Cr—C(9)	3.60 (2)		
C(9)—C(14)	3.78 (3)		
C(9)—C(16)	3.62 (3)		
Cr—plane defined by O(3), O(4), O(5) 1.77 (3).			

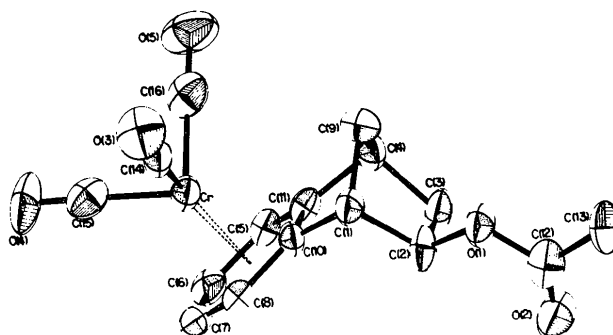


Fig. 1. An ORTEP drawing of the π -(*exo*-2-acetoxybornenyl)-*exo*-tricarbonylchromium molecule with notation consistent with text. No H atoms are shown for reasons of simplicity. Thermal ellipsoids are scaled at 50% probability.

Table 3. *R.m.s. displacements along principal axes of thermal ellipsoids (Å)*

	1	2	3
Cr	0.168 (5)	0.194 (4)	0.219 (5)
O(1)	0.167 (20)	0.240 (20)	0.259 (19)
O(2)	0.208 (23)	0.220 (24)	0.344 (22)
O(3)	0.183 (26)	0.298 (22)	0.324 (23)
O(4)	0.167 (24)	0.321 (24)	0.371 (24)
O(5)	0.213 (26)	0.271 (24)	0.410 (24)
C(1)	0.166 (32)	0.204 (29)	0.274 (29)
C(2)	0.142 (37)	0.236 (28)	0.263 (28)
C(3)	0.153 (35)	0.232 (30)	0.276 (29)
C(4)	0.162 (34)	0.202 (27)	0.228 (29)
C(5)	0.166 (32)	0.225 (30)	0.232 (30)
C(6)	0.136 (40)	0.228 (32)	0.286 (32)
C(7)	0.167 (33)	0.199 (33)	0.269 (30)
C(8)	0.164 (33)	0.201 (32)	0.265 (28)
C(9)	0.186 (31)	0.196 (31)	0.247 (29)
C(10)	0.147 (35)	0.176 (30)	0.217 (28)
C(11)	0.150 (35)	0.174 (30)	0.225 (27)
C(12)	0.157 (37)	0.218 (32)	0.301 (33)
C(13)	0.165 (32)	0.278 (28)	0.301 (30)
C(14)	0.170 (38)	0.230 (32)	0.251 (33)
C(15)	0.179 (34)	0.221 (31)	0.275 (29)
C(16)	0.168 (37)	0.255 (33)	0.291 (32)

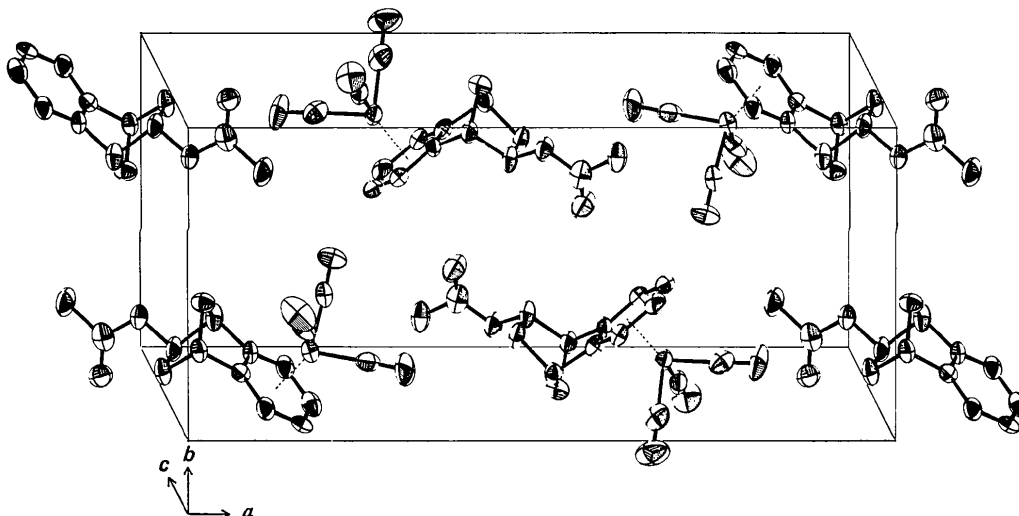


Fig. 2. An ORTEP packing diagram of the molecule in Fig. 1. The unit-cell boundary is outlined. Thermal ellipsoids as in Fig. 1.

were made for absorption. The usual Lorentz-polarization corrections were applied and the intensities reduced to structure factors.

The crystal structure was solved by routine heavy-atom methods in which the Cr atom was located from the three-dimensional Patterson function, and the remaining non-hydrogen atoms were located from electron density maps. The function minimized in the full-matrix least-squares refinement was $\sum(F_o - F_c)^2$ with unit weights. Scattering factors for Cr, C, O were from Cromer & Waber (1965) and the effects of anomalous dispersion for Cr (Cromer, 1965) were included by additions to F_c . Isotropic temperature factor refinement converged to a conventional R value of 0.103. Full anisotropic refinement for all atoms (excluding H atoms) yielded a final R and weighted R of 0.0692 and 0.0755, respectively. A final difference Fourier map showed no unusual features.* Final atomic coordinates and thermal parameters are given in Table 1. Interatomic distances, angles, and errors are listed in Table 2 and r.m.s. displacements, in Table 3.

Discussion. The structure is made up of discrete molecules with no unusual intermolecular distances, Fig. 2, nor unexpected molecular packing features. A detailed representation of an isolated molecule with nomenclature is in Fig. 1. The stereochemistry is *exo*-tricarbonylchromium and *exo*-acetoxy. The orientation of the chromium tricarbonyl fragment is such that the C atoms of the benzene ring are in a staggered configuration relative to the carbonyl groups. This is the same configuration that has been found in benzenechromium tricarbonyl (Rees & Coppens, 1972; Bailey & Dahl, 1965a) hexamethylbenzenechromium tricarbonyl (Bailey & Dahl, 1965b) phenanthrenechromium tricarbonyl (Deuschl & Hoppe, 1964; Muir & Ferguson, 1968) naphthalenechromium tricarbonyl (Kunz & Nowacki, 1967). However, an eclipsed configuration is found in methylbenzoatechromium tricarbonyl (Carter, McPhail & Sim, 1967). The molecule, excluding the acetate group, has an approximate mirror plane of symmetry passing through O(4), C(15), Cr, C(9) and bisecting the C(6)–C(7), C(11)–C(10) and C(3)–C(2) bonds. The Cr–C and C–O distances within the Cr(CO)₃ entity are normal. The Cr–C ring distances are as expected from results of similar compounds mentioned above. The benzene ring is planar, well within experimental error (± 0.01 Å). All other distances and angles are more or less normal.

The results of the torsional angle calculations suggested by Altona & Sundaralingam (1970) are shown

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31452 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. Torsional angles ($^\circ$)

Saturated five-membered ring			Unsaturated five-membered ring		
Bond	A&S*	Angle	Bond	A&S*	Angle
	notation			notation	
C(1)–C(2)	a_R	33 (1)	C(1)–C(10)	a_L	32 (1)
C(2)–C(3)	b_R	0 (1)	C(10)–C(11)	b_L	1 (1)
C(3)–C(4)	c_R	35 (1)	C(11)–C(4)	c_L	31 (1)
C(4)–C(9)	d_R	56 (1)	C(4)–C(9)	d_L	49 (1)
C(9)–C(1)	e_R	55 (1)	C(9)–C(1)	e_L	49 (1)
Six-membered boat ring					
C(1)–C(2)	f_B	69 (1)			
C(3)–C(4)	g_B	69 (1)			
C(1)–C(10)	f_B'	70 (1)			
C(4)–C(11)	g_B'	73 (1)			

* Notation introduced by Altona & Sundaralingam (1970) in their compilation of torsional angles found in existing structures of camphanes, norbornenes, and substituted norbornane skeletons.

in Table 4. As found in other norbornene structures we do not find a pseudo rotation or twist of the two fused rings relative to each other; in fact, they superimpose. Not only is the benzene ring planar, but also atoms C(1) and C(4) deviate from this plane by not more than 0.13 (1) Å.

It appears that neither of the two *exo* substituents causes distortion of the norbornene system.

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