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The Crystal Structure of 1,3,3,5-Tetramethyl-6-(1′,2′-naphtho)-bicyclo[3,2,1]octenechromium(0) Tricarbonyl

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Single crystals of the title compound, $C_{23}H_{24}O_3Cr$, were grown from a pentane solution. Crystal data are: space group $C2/c$, $a = 19{\cdot}663$ (3), $b = 14{\cdot}350$ (5), $c = 16{\cdot}443$ (3) Å, $\beta = 120{\cdot}10$ (1)°, $Z = 8$. The structure was solved by the heavy-atom method and refined by block-diagonal least-squares calculation to a weighted R value of 0·053 and an unweighted R of 0·046. 3695 reflections were measured, of which 1946 were greater than $3\sigma(I)$. Results of the analysis indicate that the cyclohexane ring is highly distorted from its normal chair form due to (1) the steric interaction of an axial methyl group with the naphthalene moiety, and (2) the strain of fusion through a five-membered ring to the naphthalene moiety. The chromium atom is complexed to ring A of the naphthalene (ring A is that fused to the aliphatic part of the molecule).

Introduction

The title compound (Fig. 1) is one of a series of bicyclic hydrocarbons and derivatives under structural investigation. Interest in this and similar compounds (*e.g.* the uncomplexed hydrocarbon) has its origin in methyl proton n.m.r. shift data (Shapiro, Gattuso & Sullivan, 1971). In particular, the axial methyl group [C(19)] is oriented near the face of the naphthalene ring A. The n.m.r. spectral data for these protons are affected by the aromatic ring currents, which in turn are affected by the presence of a metal complex. The detailed geometry of the molecule should provide a basis for understanding the spectral shifts observed. Such correlation of the structure with n.m.r. shift data will be presented elsewhere.

Experimental

Accurate cell constants were obtained by a least-squares fit to 29 2θ values measured at 20°C. The systematic absences are consistent with space groups Cc or $C2/c$. The latter, which is centrosymmetric, was chosen. The successful solution of the structure confirmed this choice. Crystal data are given in Table 1.

Table 1. *Crystal data*

$C_{23}H_{24}O_3Cr$
Space group $C2/c$
$a = 19{\cdot}663$ (3) Å
$b = 14{\cdot}350$ (5)
$c = 16{\cdot}443$ (3)
$\beta = 120{\cdot}10$ (1)°
$V = 4014$ Å^3
$\mu = 6{\cdot}17$ cm^{-1} (Mo $K\alpha$ Radiation

F.W. 400·4
Systematic absences:
hkl: $h+k=2n+1$
$h0l$: $l=2n+1$
$Z=8$
$D_c = 1{\cdot}326$ g.cm^{-3}
$D_m = 1{\cdot}328$ g cm^{-3}
Crystal size:
0·42 × 0·34 × 0·34 mm
Crystal shape:
bipyramid

Intensity data were measured on a Datex-Syntex automated four-circle diffractometer using Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$A). The radiation was monochromatized by pyrolitic graphite. Reflections with $2\theta \le 50{\cdot}0^\circ$ were scanned in the θ–2θ mode at a rate of 2·0° (in 2θ) per minute, the scan range being 2·0°. Backgrounds were measured for half the scan time at each end of the scan range. The intensities of five check reflections were measured periodically. Deviations in the intensities of these check reflections were not considered significant. A total of 3695 independent reflections was measured of which 1946 had $I \ge 3\sigma_I$ and were used in the refinement. No corrections were made for absorption effects or for secondary extinction. Neutral atom scattering factors were used (*International Tables for X-ray Crystallography*, 1974). Real and imaginary anomalous dispersion corrections were made for chromium (Cromer & Liberman, 1970).

The position of the chromium atom was found by Patterson methods. The positions of the other 26 non-hydrogen atoms were found from subsequent F_o Fourier syntheses. The quantity minimized was $\sum w|F_o - F_c|^2$ with weights w taken equal to $\sigma^{-2}(F_o)$. Initial refinements assumed isotropic thermal parameters for each atom: subsequently anisotropic thermal parameters were introduced. In the later stages of refinement, the calculated positions of the 24 hydrogen atoms were introduced assuming a C–H distance of 1·01 Å. Each was assigned an isotropic B of 4·5. These hydrogen atom positions were not refined, but new positions were calculated after each refinement. The final R index ($R = \sum|F_o - |F_c||/\sum F_o$) was 0·046, the weighted R_w $\{R_w = (\sum w|F_o - |F_c||^2/\sum wF_o^2)^{1/2}\}$ was 0·053 and the goodness of fit $\{= [\sum w|F_o - |F_c||^2/(M-S)]^{1/2}\}$ was 1·66 for $M = 1946$ observations and $S = 243$ parameters. The largest shift in the final least-squares calculation was 0.5σ, and most were of the order of 0·1σ or less. A final difference map showed a maximum electron density of 0·24 e Å^{-3}.

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The refined parameters and their estimated standard deviations are given in Table 2. A table of observed and calculated structure factors is available.*

Discussion

Fig. 1 presents a stereographic view of the completed structure and shows the chromium to be complexed to the back side of naphthalene ring *A*. Ring *A* is connected to the cyclohexane ring through a five-membered ring and is thus facing the axial methyl group containing C(19). Interatomic distances and angles are listed in Table 3.

The highly substituted cyclohexane ring is labeled with carbon atoms C(1) through C(6) as shown in Fig. 1. For the hypothetical case of an undistorted cyclohexane ring, the torsional angles along each of the six bonds would be 60·0° and the axial methyl group [C(19)] would be 2·32 Å from the plane of the naphthalene ring *A*. Two factors serve to cause large distortion in the aliphatic six-membered ring: (1) the

Table 2. *Fractional coordinates and thermal parameters*

Estimated standard deviations are given in parentheses.

The anisotropic thermal parameters U_{ij} are the mean-square amplitudes of vibration in Å. They are introduced into the structure-factor expression as $T=\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$. The U_{ij} in the table have been multiplied by 10^4.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr	0·3484 (1)	0·3666 (1)	0·2348 (1)	455 (3)	788 (5)	438 (3)	50 (9)	181 (6)	20 (9)
C(1)	0·3861 (2)	0·1476 (3)	0·3388 (3)	596 (30)	632 (35)	685 (31)	134 (52)	291 (52)	−38 (53)
C(2)	0·2977 (2)	0·1463 (3)	0·3014 (3)	584 (29)	530 (32)	716 (31)	−11 (50)	225 (50)	−100 (53)
C(3)	0·2861 (2)	0·2252 (3)	0·3562 (2)	475 (26)	503 (30)	656 (20)	14 (45)	286 (46)	−22 (48)
C(4)	0·3198 (2)	0·1916 (3)	0·4584 (3)	538 (29)	618 (33)	657 (30)	56 (50)	286 (50)	87 (53)
C(5)	0·4058 (2)	0·1557 (3)	0·5094 (3)	617 (30)	653 (36)	670 (31)	137 (52)	329 (53)	145 (53)
C(6)	0·4282 (2)	0·1098 (3)	0·4402 (3)	630 (32)	647 (37)	776 (33)	175 (52)	343 (55)	93 (55)
C(7)	0·3993 (2)	0·2521 (3)	0·3421 (2)	414 (25)	755 (35)	431 (24)	58 (47)	156 (40)	18 (48)
C(8)	0·4611 (2)	0·3009 (3)	0·3417 (3)	445 (27)	966 (39)	535 (27)	110 (54)	201 (46)	118 (58)
C(9)	0·4657 (2)	0·3953 (3)	0·3541 (3)	469 (27)	1097 (45)	554 (28)	−138 (56)	194 (46)	104 (57)
C(10)	0·4130 (2)	0·4449 (3)	0·3743 (2)	655 (32)	688 (35)	348 (23)	−124 (52)	71 (44)	39 (48)
C(11)	0·4208 (3)	0·5433 (3)	0·3953 (3)	816 (38)	842 (41)	478 (28)	−259 (62)	46 (53)	81 (57)
C(12)	0·3731 (3)	0·5854 (3)	0·4183 (3)	1095 (45)	626 (36)	534 (30)	−74 (67)	69 (61)	−14 (56)
C(13)	0·3130 (3)	0·5397 (3)	0·4222 (3)	1021 (41)	771 (40)	454 (27)	247 (65)	277 (57)	4 (55)
C(14)	0·2999 (2)	0·4467 (3)	0·3994 (3)	769 (34)	629 (33)	485 (26)	115 (54)	286 (51)	19 (49)
C(15)	0·3493 (2)	0·3963 (3)	0·3750 (2)	538 (26)	611 (32)	344 (21)	27 (46)	139 (40)	37 (42)
C(16)	0·3414 (2)	0·2976 (3)	0·3530 (2)	400 (24)	547 (29)	428 (23)	66 (43)	155 (39)	−2 (44)
C(17)	0·1992 (2)	0·2507 (3)	0·3122 (3)	455 (27)	726 (36)	821 (34)	50 (52)	297 (51)	75 (59)
C(18)	0·4140 (3)	0·0821 (4)	0·5811 (4)	885 (42)	871 (41)	962 (42)	277 (69)	497 (73)	312 (71)
C(19)	0·4634 (2)	0·2343 (3)	0·5650 (3)	643 (33)	896 (41)	620 (31)	89 (60)	234 (53)	38 (60)
C(20)	0·4119 (3)	0·0938 (4)	0·2789 (3)	1039 (47)	938 (44)	871 (40)	436 (75)	491 (75)	48 (71)
C(21)	0·3444 (2)	0·2953 (3)	0·1411 (3)	542 (30)	947 (40)	571 (29)	122 (58)	220 (49)	21 (59)
C(22)	0·2405 (2)	0·3756 (3)	0·1608 (3)	590 (29)	934 (41)	510 (26)	61 (59)	232 (47)	−27 (58)
C(23)	0·3582 (2)	0·4685 (3)	0·1744 (3)	669 (33)	926 (42)	585 (30)	100 (60)	346 (54)	18 (59)
O(1)	0·3414 (2)	0·2512 (2)	0·0802 (2)	845 (26)	1285 (34)	691 (23)	117 (49)	344 (41)	−193 (47)
O(2)	0·1737 (1)	0·3811 (2)	0·1129 (2)	489 (20)	1392 (36)	785 (24)	153 (45)	117 (36)	79 (49)
O(3)	0·3669 (2)	0·5329 (2)	0·1390 (2)	1265 (34)	931 (29)	892 (27)	127 (50)	676 (54)	194 (47)

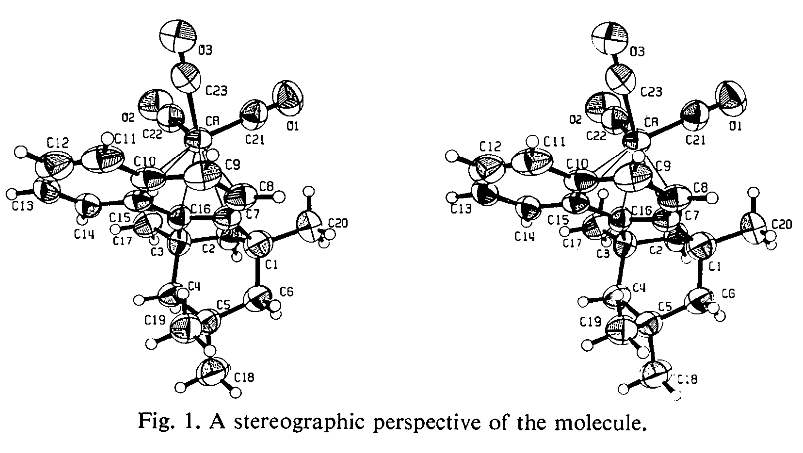

Fig. 1. A stereographic perspective of the molecule.

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Table 3. *Interatomic distances and angles with estimated standard errors in parentheses*

Cr——C(7)	2·245 (5) Å	C(21)–Cr——C(22)	86·3 (2)°
Cr——C(8)	2·231 (4)	C(21)–Cr——C(23)	87·9 (3)
Cr——C(9)	2·190 (4)	C(22)–Cr——C(23)	89·1 (2)
Cr——C(10)	2·284 (4)	C(2)—C(1)—C(6)	108·4 (5)
Cr——C(15)	2·336 (5)	C(2)—C(1)—C(7)	99·6 (4)
Cr——C(16)	2·245 (5)	C(2)—C(1)—C(20)	114·5 (4)
Cr——C(21)	1·818 (6)	C(6)—C(1)—C(7)	108·6 (4)
Cr——C(22)	1·847 (4)	C(6)—C(1)—C(20)	110·4 (4)
Cr——C(23)	1·831 (6)	C(7)—C(1)—C(20)	114·7 (5)
C(1)—C(2)	1·526 (7)	C(1)—C(2)—C(3)	103·3 (3)
C(1)—C(6)	1·542 (7)	C(2)—C(3)—C(4)	107·4 (4)
C(1)—C(7)	1·518 (7)	C(2)—C(3)—C(16)	99·4 (5)
C(1)—C(20)	1·524 (10)	C(2)—C(3)—C(17)	111·0 (3)
C(2)—C(3)	1·534 (8)	C(4)—C(3)—C(16)	109·1 (3)
C(3)—C(4)	1·542 (7)	C(4)—C(3)—C(17)	111·1 (5)
C(3)—C(16)	1·525 (7)	C(16)–C(3)—C(17)	117·9 (4)
C(3)—C(17)	1·528 (7)	C(3)—C(4)—C(5)	116·8 (5)
C(4)—C(5)	1·551 (7)	C(4)—C(5)—C(6)	112·1 (4)
C(5)—C(6)	1·557 (9)	C(4)—C(5)—C(18)	108·1 (5)
C(5)—C(18)	1·531 (9)	C(4)—C(5)—C(19)	111·0 (4)
C(5)—C(19)	1·533 (7)	C(6)—C(5)—C(18)	108·2 (4)
C(7)—C(8)	1·405 (8)	C(6)—C(5)—C(19)	110·6 (5)
C(7)—C(16)	1·400 (8)	C(18)–C(5)—C(19)	106·7 (4)
C(8)—C(9)	1·365 (8)	C(1)—C(6)—C(5)	116·5 (4)
C(9)—C(10)	1·426 (8)	C(1)—C(7)—C(8)	128·7 (5)
C(10)–C(11)	1·445 (7)	C(1)—C(7)—C(16)	109·3 (4)
C(10)–C(15)	1·439 (8)	C(7)—C(8)—C(9)	119·1 (3)
C(11)–C(12)	1·321 (10)	C(8)—C(9)—C(10)	121·9 (5)
C(12)–C(13)	1·380 (10)	C(9)—C(10)–C(11)	122·8 (5)
C(13)–C(14)	1·376 (7)	C(9)—C(10)–C(15)	119·8 (4)
C(14)–C(15)	1·422 (8)	C(11)–C(10)–C(15)	117·4 (5)
C(15)–C(16)	1·450 (6)	C(10)–C(11)–C(12)	120·6 (6)
C(21)–O(1)	1·162 (7)	C(11)–C(12)–C(13)	122·9 (5)
C(22)–O(2)	1·147 (5)	C(12)–C(13)–C(14)	119·8 (6)
C(23)–O(3)	1·161 (7)	C(13)–C(14)–C(15)	120·6 (5)
		C(10)–C(15)–C(14)	118·5 (4)
		C(10)–C(15)–C(16)	117·1 (5)
		C(14)–C(15)–C(16)	124·3 (5)
		C(3)—C(16)–C(7)	109·1 (4)
		C(3)—C(16)–C(15)	130·2 (8)
		C(7)—C(16)–C(15)	119·7 (4)
		Cr——C(21)–O(1)	178·7 (5)
		Cr——C(22)–O(2)	178·3 (5)
		Cr——C(23)–O(3)	177·6 (4)

steric interaction of the axial methyl group with the naphthalene moiety, and (2) the strain of fusion through atoms C(1) and C(3) to ring *A* of naphthalene. The distortion is evident by examining the experimentally determined torsional angles in Fig. 2. A flattening (decrease from 60·0°) is noted in the region of C(4) C(5) and C(6) (remote from naphthalene) and a steepening (increase from 60·0°) in the region of C(1), C(2) and C(3) (attached to the naphthalene). A second torsional angle is given directly below the first and refers to a similar structure (Towns, Godwin & Shapiro, 1973) in which the molecule is identical except for the absence of the metal complex and substitution of a bromine atom for the methyl group containing C(20) (formula $C_{19}H_{21}Br$).

In the present work the distance of C(19) from the best least-squares plane containing the atoms of naphthalene ring *A* is 3·13 Å, an increase of about 0·8 Å compared with the hypothetical case of an undistorted cyclohexane ring. The corresponding distance in the uncomplexed structure ($C_{19}H_{21}Br$) is 3·08 Å, a small but significant difference.

Another measure of the distortion is found in the dihedral angles between various least-squares planes containing atoms of the cyclohexane ring. Table 4 lists the planes and the dihedral angles they make with one another. The first value refers to this structure and the second to $C_{19}H_{21}Br$. For an undistorted ring the angles between the plane containing atoms C(1),

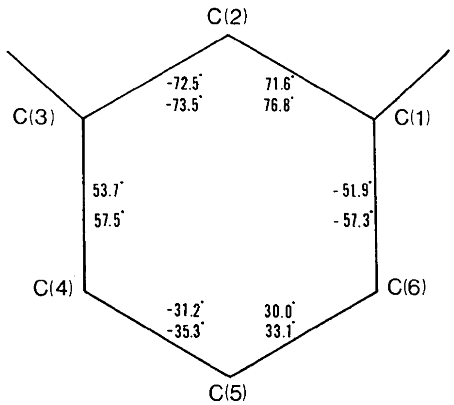

Fig. 2. Torsion angles in the cyclohexane ring for this structure (first angle) and the structure of Towns *et al.* (1973) (second number). The torsion angle *W*(*IJKL*) is defined as the angle between the vector *JI* and the vector *KL* when viewed along *JK*. The sign of *W* is positive if *JI* is to be rotated clockwise into *KL* and negative if anticlockwise.

Table 4. *Dihedral angles between various least-squares planes for this structure,* $C_{23}H_{24}O_3Cr$, *and the structure of* $C_{19}H_{21}Br$ (*Towns et al.*, 1973)

Plane	C(1), C(2), C(3)	C(4), C(5), C(6)	C(1), C(3), C(4), C(6)
C(1), C(2), C(3)	–	37·8°* 36·4†	115·0° 112·8
C(4), C(5), C(6)	–	–	152·9 149·3
C(1), C(3), C(7), C(16)	136·1° 136·1	98·3 99·7	108·8 111·1

* $C_{23}H_{24}O_3Cr$
† $C_{19}H_{21}Br$

C(3), C(4) and C(6) and the planes containing atoms C(1), C(2), C(3) and C(4), C(5), C(6) should both be 125·5°. The measured values are respectively 115·0 and 152·9° for this structure and 112·8 and 149·3° for $C_{19}H_{21}Br$. The overall comparison of this structure with the uncomplexed one indicates a small but significant increase in the distortion of the cyclohexane ring.

The chromium atom is calculated to be 1·757 Å out of the plane of ring *A*. The six individual metal aromatic carbon atom distances differ significantly from one another, the longest distances being those to C(10) and C(15). These are the atoms shared between rings *A* and *B*. A similar situation has also been observed in other structures, *e.g.* the chromium tricarbonyl naphthalene complex (Kunz & Nowacki, 1967). In this case the chromium–carbon atom distances corresponding to C(7), C(8), C(9), C(10), C(15) and C(16) are respectively 2·191, 2·219, 2·214, 2·337, 2·306 and 2·186 Å. The corresponding values in the chromium tricarbonyl phenanthroline complex are 2·210, 2·206, 2·208, 2·289, 2·289 and 2·212 Å respectively (Muir & Ferguson, 1968). A check on intermolecular contacts showed that all were 3·50 Å or greater with the exception of an O(1)···O(1) contact of 3·22 Å and an O(3)···C(13) contact of 3·34 Å.

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The Crystal Structure of Sodium Chloride Dihydrate

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Crystals of $NaCl.2H_2O$ are monoclinic, probable space group $P2_1/c$, with $a=6{\cdot}3313$ (5), $b=10{\cdot}1178$ (9), $c=6{\cdot}5029$ (6) Å, $\beta=114{\cdot}407$ (7)° and $Z=4$ at 105 K. 26 of the 'forbidden' reflexions were observed, but a complete structure determination in space group $P2_1/c$ led to an R index of 0·0193 and a goodness-of-fit of 2·15 for 2833 reflexions (53 variable parameters). $NaCl.2H_2O$ is isomorphous with the corresponding bromide. The observed differences between the two structures can be rationalized on the basis of the difference in ionic radii of 0·15 Å between a bromide and a chloride ion. The electron-density distribution in a water molecule is discussed and the lack of lobes in the electron distribution from the two lone-pair electrons is pointed out.

Introduction

Mitscherlich (1829) (the discoverer of isomorphism) found it easy to grow large single crystals of sodium chloride dihydrate, and he performed the first crystallographic study of this hydrate and the related dihydrates of NaBr and NaI. $NaCl.2H_2O$ is the only compound formed in the $NaCl–H_2O$ system, and it melts under its own vapour pressure at −0·1 °C (Gmelin, 1973). No phase transformation in the solid state has been detected.

The crystal structure of this simple ionic hydrate has never been determined, but it is known to be isomorphous with the corresponding cyanide (Le Bihan, 1958) and bromide, both stable at room temperature. The crystal structure of the bromide was determined by Culot, Piret & Van Meerssche (1962) and independently by Haaf & Carpenter (1964) from X-ray diffraction data. The structure has recently been refined from neutron diffraction data by Tellgren, Pedersen, Tegenfeldt & Olovsson (1974). Sodium iodide dihydrate forms a closely related structure (Verbist, Piret & Van Meerssche, 1970).

Infrared studies by Schiffer & Hornig (1969) and Ford & Falk (1969) and n.m.r. studies by Rockelmann

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