

1,3,3,5-Tetramethyl-6-(1',2'-naphtho)-bicyclo[3,2,1]octene

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Abstract. $C_{20}H_{24}$: $P2_1/a$, $a=23.482$ (5), $b=7.845$ (3), $c=8.825$ (2) Å, $\beta=92.06$ (1)°, $Z=4$, F.W. 264.4, $V=1625$ Å³, $D_c=1.079$ g cm⁻³, $D_m=1.08$ g cm⁻³, $\mu=0.65$ cm⁻¹ (Mo $K\alpha$ radiation), crystal size $0.5 \times 0.5 \times 0.6$ mm, systematic absences; $h0l$; $h=2n+1$ and $0k0$; $k=2n+1$. Diffractometer data, 2122 reflections measured, 1172 with $I \geq 3\sigma_I$. $R=0.055$. The structure consists of a tetramethyl-substituted cyclohexane ring joined to the 1,2-positions of naphthalene *via* a five-membered ring. The geometrical details of this structure are to be used in conjunction with n.m.r. spectral shift data.

Introduction. Accurate cell dimensions were determined by least-squares calculations, comparing the observed and calculated values of 2θ for 19 reflections. The 2θ values for these reflections and the subsequent intensity measurements were obtained using a Datex-Syntex automated diffractometer equipped with a Mo X-ray tube [$\lambda(K\alpha)=0.71069$ Å] and a pyrolytic graphite monochromator. For the intensity measurements, 2122 independent reflections were scanned by the $\theta-2\theta$ technique out to a $\sin \theta/\lambda$ limit of 0.5385 or $\theta=22.5^\circ$. The scan rate was $2.0^\circ \text{ min}^{-1}$ and the scan range was set at 2.0° . The background was determined by counting for half the scan time, respectively, at the lower and upper limits of the 2θ scan range. A group of five check reflections was measured periodically to monitor the crystal alignment and deterioration. A steady decrease was noted for the intensities of these check reflections, the values dropping by about 32% from start to finish. Group scale factors, calculated from a weighted average of the five check reflections were applied to the intensity measurements to correct for crystal deterioration. A correction was also applied for the effects of coincidence counting ($\tau=5.18 \times 10^{-7}$ counts⁻¹) (Sletten, Sletten & Jensen, 1969). The standard deviation of an intensity measurement, σ_I , was obtained from the equation, $\sigma_I^2 = \sigma_I^2(\text{count}) + K^2[S + B1 + B2]^2$, where S , $B1$ and $B2$ are the observed counts for the scan and two backgrounds respectively, σ_I (count) is the standard deviation derived purely from counting statistics, and K is an empirically determined instrumental stability constant ($K=0.01$). 1172 reflections had $I \geq 3\sigma_I$ and these were used in the

subsequent analysis. No corrections were made for absorption or secondary extinction. Scattering factors for neutral C and H were taken from *International Tables for X-ray Crystallography* (1974).

Normalized structure factors were calculated and the 292 reflections with $|E| \geq 1.25$ were used in the phasing program *MULTAN* (Germain, Main & Woolfson, 1971) to generate Σ_2 relationships. *MULTAN* was allowed to choose phases for three origin defining reflections and variable phases (0 and π) for four other reflections. 16 starting sets were possible for the tangent refinement, and each was used to generate phases for the remaining 286 reflections. An E map was calculated for the set with the highest figure of merit (1.16) as defined by Germain, Main & Woolfson (1971), but a structural solution was not evident. The set with the next highest figure of merit (1.14) was used to compute an E map and the largest peaks could readily be assembled to construct the molecule (20 C atoms).

The structure was refined by block-diagonal least-squares calculations, the quantity minimized being $\sum w|F_o - F_c|^2$ with the weight w equal to $\sigma^{-2}(F_o)$. The 20 C atoms were refined with anisotropic temperature factors. After six cycles of refinement ($R=14\%$), calculated positions and isotropic B 's of 4.5 for each of the 24 H atoms were introduced into the refinement, but these parameters were not allowed to vary. Two more cycles of refinement were completed with the fixed H atoms included, followed by a structure factor calculation with the same omitted. A difference Fourier map gave reasonable positions for all the H atoms and accounted for the 24 highest peaks. The final cycles of refinement were done using the observed peak positions and isotropic B 's of 4.5 for the H atoms. The final R value, defined as $\sum |F_o - |F_c|| / \sum F_o$ was 0.055 and the weighted R value, defined as $(\sum w|F_o - |F_c||^2 / \sum wF_o^2)^{1/2}$ was 0.044. The goodness of fit $\{ = [\sum w|F_o - |F_c||^2 / (M - S)]^{1/2} \}$ was 2.76 for $M=1172$ reflections and $S=181$ parameters. All parameter shifts in the last cycle of refinement were less than 1σ and most were of the order of 0.1σ . A final difference Fourier map showed a maximum electron density of $0.19 \text{ e } \text{Å}^{-3}$.

The refined parameters and their estimated standard deviations are listed in Table 1. Also included in this Table are the fractional coordinates for the H atoms.

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Table 1. *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 \AA^2 . 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 .

	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0.5917 (1)	0.7374 (5)	0.9969 (3)	552 (26)	639 (30)	376 (23)	80 (52)	15 (39)	-42 (51)
C(2)	0.5878 (1)	0.5462 (5)	0.9896 (4)	514 (27)	697 (33)	743 (30)	7 (52)	-30 (46)	282 (56)
C(3)	0.6144 (1)	0.5065 (4)	0.8361 (4)	547 (27)	308 (25)	742 (29)	11 (45)	17 (46)	-24 (50)
C(4)	0.5701 (1)	0.5592 (5)	0.7125 (4)	524 (27)	596 (31)	679 (29)	-114 (50)	-47 (46)	-177 (53)
C(5)	0.5481 (1)	0.7440 (4)	0.7206 (3)	448 (24)	558 (29)	509 (25)	-18 (49)	-56 (40)	-3 (51)
C(6)	0.5454 (1)	0.8094 (4)	0.8855 (4)	468 (25)	569 (29)	553 (26)	43 (48)	89 (42)	52 (49)
C(7)	0.6504 (1)	0.7632 (4)	0.9365 (3)	449 (25)	498 (27)	358 (22)	28 (47)	-23 (38)	43 (47)
C(8)	0.6873 (1)	0.9024 (4)	0.9591 (3)	643 (29)	491 (29)	504 (26)	37 (51)	-111 (44)	-151 (49)
C(9)	0.7372 (1)	0.9060 (5)	0.8850 (4)	569 (28)	546 (30)	703 (29)	-161 (51)	-124 (46)	-32 (54)
C(10)	0.7520 (1)	0.7750 (2)	0.7873 (3)	443 (26)	758 (33)	416 (24)	-14 (52)	-62 (40)	90 (52)
C(11)	0.8046 (1)	0.7776 (5)	0.7094 (4)	574 (29)	876 (36)	641 (29)	-64 (58)	-63 (58)	80 (62)
C(12)	0.8185 (1)	0.6530 (6)	0.6152 (4)	474 (28)	1531 (48)	603 (29)	77 (64)	36 (47)	53 (70)
C(13)	0.7818 (1)	0.5207 (6)	0.5872 (4)	775 (35)	1318 (48)	784 (35)	301 (70)	0 (55)	-386 (73)
C(14)	0.7311 (1)	0.5091 (5)	0.6589 (4)	515 (29)	865 (38)	848 (33)	48 (57)	33 (50)	-235 (62)
C(15)	0.7145 (1)	0.6344 (4)	0.7625 (3)	432 (25)	539 (28)	427 (24)	69 (47)	-33 (38)	-50 (49)
C(16)	0.6638 (1)	0.6314 (4)	0.8429 (3)	420 (24)	393 (25)	420 (23)	29 (44)	-18 (38)	29 (45)
C(17)	0.5839 (1)	0.8108 (6)	1.1556 (4)	696 (32)	1327 (48)	591 (29)	79 (58)	36 (51)	-12 (66)
C(18)	0.4873 (1)	0.7523 (5)	0.6491 (4)	707 (31)	887 (38)	835 (32)	10 (63)	-87 (52)	-139 (68)
C(19)	0.5842 (1)	0.8621 (5)	0.6285 (4)	828 (33)	813 (36)	552 (27)	-69 (61)	-125 (49)	206 (58)
C(20)	0.6275 (1)	0.3161 (5)	0.8267 (6)	664 (33)	623 (35)	1812 (52)	-55 (60)	277 (71)	-10 (75)

Table 1 (*cont.*)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(2A)	0.612	0.490	1.052	4.5
H(2B)	0.553	0.501	0.977	4.5
H(4A)	0.583	0.530	0.616	4.5
H(4B)	0.538	0.490	0.714	4.5
H(6A)	0.545	0.925	0.875	4.5
H(6B)	0.509	0.766	0.936	4.5
H(8)	0.678	0.988	1.029	4.5
H(9)	0.757	1.002	0.906	4.5
H(11)	0.820	0.886	0.728	4.5
H(12)	0.856	0.655	0.562	4.5
H(13)	0.788	0.433	0.546	4.5
H(14)	0.705	0.411	0.645	4.5
H(17A)	0.609	0.755	1.230	4.5
H(17B)	0.546	0.770	1.179	4.5
H(17C)	0.589	0.926	1.155	4.5
H(18A)	0.465	0.683	0.697	4.5
H(18B)	0.488	0.694	0.562	4.5
H(18C)	0.474	0.864	0.656	4.5
H(19A)	0.581	0.846	0.533	4.5
H(19B)	0.624	0.871	0.661	4.5
H(19C)	0.574	0.971	0.609	4.5
H(20A)	0.597	0.266	0.849	4.5
H(20B)	0.663	0.298	0.857	4.5
H(20C)	0.644	0.294	0.736	4.5

A table of observed and calculated structure factors is available.*

Discussion. Fig. 1 is a stereographic projection of the completed molecular structure. The molecule is identical to that of the hydrocarbon part of $C_{23}H_{24}O_3Cr$ (Pettersen, Cullen, Pearce, Shapiro & Shapiro, 1974). The purpose of examining these structures is to note detailed changes in the molecular geometry, both for intrinsic structural interest and as an attempt to correlate the structural differences with n.m.r. spectral data. It is well known that complexation with $Cr(CO)_3$ will cause profound changes in both proton and carbon-13 n.m.r. chemical shifts, including both the shifts of those atoms in the plane of the aromatic ring and those removed from this plane (Trahanov-

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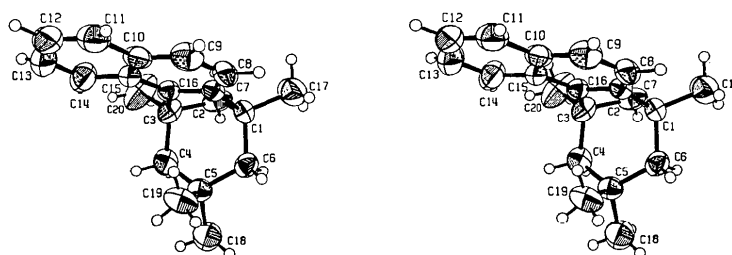


Fig. 1. A stereographic perspective of the molecule.

sky, Kowalski & Avery, 1974; Thoennes, Wilkins & Trahanovsky, 1974). For example, the C(19) methyl proton n.m.r. shift data are, respectively, $\delta_{\text{H}} = -0.38$ and $\delta_{\text{H}} = -0.08$ [$\delta(\text{TMS}) = 0.00$] for $\text{C}_{20}\text{H}_{24}$ and $\text{C}_{23}\text{H}_{24}\text{O}_3\text{Cr}$, indicating markedly increased proton shielding in the former. The distance of C (19) from the best least-squares plane containing the ten naphthalene atoms is 3.06 Å for $\text{C}_{20}\text{H}_{24}$ and 3.13 Å for $\text{C}_{23}\text{H}_{24}\text{O}_3\text{Cr}$.* The decrease (0.07 Å) in the C (19)-naphthalene plane distance between the two molecules cannot account for the large observed chemical shift difference on the basis of calculated tables of ring current shielding for proton shifts (Haigh & Mallion, 1972). The chromium tricarbonyl group obviously affects the ring current causing these shifts by withdrawing electron density from the aromatic ring in a manner which awaits detailed elucidation on the basis of the present, and other, structural and spectroscopic data.

The naphthalene ring (ring *A*) associated with the $\text{Cr}(\text{CO})_3$ group in the complex is expanded slightly with respect to the same ring *A* in $\text{C}_{20}\text{H}_{24}$. The corresponding bond distances in the complex are:

C(7)–C(8)	1.405 (8) Å	C(9)–C(10)	1.426 (8) Å
C(7)–C(16)	1.400 (8)	C(10)–C(15)	1.439 (8)
C(8)–C(9)	1.365 (8)	C(15)–C(16)	1.450 (6)

The conformation of the substituted cyclohexane ring is nearly the same for both structures. Torsion angles for this ring are listed in Table 2 and may be compared with other similar structures (Pettersen, Cullen, Pearce, Shapiro & Shapiro, 1974). Table 3 lists the interatomic distances for the hydrocarbon structure. There are no intermolecular carbon-carbon contacts less than 3.70 Å. A supplementary table of valency angles has been deposited along with the structure factor tables.

* Maximum deviations of the ten naphthalene atoms contained in the best least-squares planes are 0.032 Å [C(16)] for $\text{C}_{20}\text{H}_{24}$ and 0.069 Å [C(16)] for $\text{C}_{23}\text{H}_{24}\text{O}_3\text{Cr}$. The respective r.m.s. deviations are 0.017 and 0.049 Å.

Table 2. Cyclohexane ring torsion angles for $\text{C}_{20}\text{H}_{24}$ *

C(6)–C(1)–C(2)–C(3)	74.4 (3)°
C(1)–C(2)–C(3)–C(4)	–73.9 (3)
C(2)–C(3)–C(4)–C(5)	54.3 (4)
C(3)–C(4)–C(5)–C(6)	–32.9 (4)
C(4)–C(5)–C(6)–C(1)	32.5 (4)
C(5)–C(6)–C(1)–C(2)	–55.1 (3)

* The torsion angle $W(\text{JJKL})$ 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 3. Interatomic distances for $\text{C}_{20}\text{H}_{24}$

Bond	Distance	Bond	Distance
C(1)–C(2)	1.504 (6) Å	C(7)–C(8)	1.403 (5) Å
C(1)–C(6)	1.545 (5)	C(7)–C(16)	1.368 (5)
C(1)–C(7)	1.510 (5)	C(8)–C(9)	1.363 (5)
C(1)–C(17)	1.531 (5)	C(9)–C(10)	1.394 (6)
C(2)–C(3)	1.542 (6)	C(10)–C(11)	1.436 (5)
C(3)–C(4)	1.535 (5)	C(10)–C(15)	1.424 (5)
C(3)–C(16)	1.518 (5)	C(11)–C(12)	1.331 (6)
C(3)–C(20)	1.528 (6)	C(12)–C(13)	1.367 (7)
C(4)–C(5)	1.542 (6)	C(13)–C(14)	1.371 (6)
C(5)–C(6)	1.546 (5)	C(14)–C(15)	1.406 (6)
C(5)–C(18)	1.542 (5)	C(15)–C(16)	1.409 (5)
C(5)–C(19)	1.513 (6)		

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Dichlorobis(pyridine)zinc(II) – a Redetermination

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Abstract. Dichlorobispyridinezinc(II), $\text{C}_{10}\text{H}_{10}\text{N}_2\text{Cl}_2\text{Zn}$, *M.W.* 294.50, monoclinic, $P2_1/c$, $a = 8.580$ (3), $b = 17.677$ (11), $c = 8.397$ (5) Å, $\beta = 101.42$ (4)°; $V = 1248.4$ (1.2) Å³; $d_m = 1.56$, $d_c = 1.567$ g cm⁻³ for $Z = 4$. The final *R* was 0.047 for the 1266 reflections used in

the analysis. The Zn atom is in the center of an approximately tetrahedral arrangement of the two Cl atoms [Zn–Cl is 2.215 (2) and 2.228 (2) Å] and the two N atoms [Zn–N is 2.046 (5) and 2.052 (6) Å] from the pyridine rings. The pyridine rings pack in two differ-