Refinement

Refinement on F^2
$R(F) = 0.0528$
$R(F^2) = 0.1459$
$S = 1.179$
2379 reflections
195 parameters
H atoms were geometrically constrained
$w = 1/[\sigma^2(F_o^2) + (0.1104P)^2$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 0.453$ e Å^{-3}
$\Delta\rho_{min} = -0.325$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
S2	0.0234 (1)	0.1694 (1)	0.7178 (1)	0.045 (1)
O2	0.0878 (2)	0.2108 (2)	0.8075 (2)	0.059 (1)
O1	0.0280 (2)	0.2702 (2)	0.6279 (2)	0.047 (1)
O3	0.0460 (2)	0.0497 (2)	0.6752 (2)	0.064 (1)
C5	−0.0494 (2)	0.3726 (3)	0.6365 (2)	0.039 (1)
C4	−0.1101 (2)	0.3427 (3)	0.7299 (3)	0.040 (1)
C3	−0.1156 (3)	0.1971 (3)	0.7393 (2)	0.038 (1)
C6	0.0054 (2)	0.4980 (1)	0.6461 (2)	0.040 (1)
C7	0.1058 (2)	0.5110 (2)	0.6998 (2)	0.057 (1)
C8	0.1502 (2)	0.6304 (2)	0.7162 (2)	0.068 (1)
C9	0.0943 (2)	0.7368 (2)	0.6788 (2)	0.066 (1)
C10	−0.0061 (2)	0.7238 (2)	0.6251 (2)	0.065 (1)
C11	−0.0505 (2)	0.6044 (2)	0.6088 (2)	0.052 (1)
C12	−0.1972 (1)	0.1442 (2)	0.6541 (1)	0.041 (1)
C13	−0.1723 (2)	0.0931 (2)	0.5605 (2)	0.060 (1)
C14	−0.2532 (2)	0.0580 (3)	0.4852 (1)	0.076 (1)
C15	−0.3591 (2)	0.0741 (3)	0.5036 (2)	0.077 (1)
C16	−0.3841 (1)	0.1252 (2)	0.5972 (2)	0.068 (1)
C17	−0.3031 (2)	0.1603 (2)	0.6725 (2)	0.053 (1)
C18	−0.1334 (2)	0.1474 (2)	0.8461 (1)	0.042 (1)
C19	−0.1593 (2)	0.2285 (2)	0.9244 (2)	0.057 (1)
C20	−0.1745 (2)	0.1808 (2)	1.0220 (2)	0.068 (1)
C21	−0.1638 (2)	0.0520 (2)	1.0413 (1)	0.067 (1)
C22	−0.1380 (2)	−0.0292 (2)	0.9630 (2)	0.062 (1)
C23	−0.1228 (2)	0.0185 (2)	0.8654 (2)	0.050 (1)

Table 2. *Selected geometric parameters* (Å, °)

S2—O2	1.418 (3)	C5—C6	1.496 (3)
S2—O3	1.421 (3)	C5—C4	1.524 (5)
S2—O1	1.583 (2)	C4—C3	1.548 (4)
S2—C3	1.825 (3)	C3—C18	1.514 (3)
O1—C5	1.470 (4)	C3—C12	1.538 (3)
O2—S2—O3	118.1 (2)	C18—C3—C4	115.4 (2)
O2—S2—O1	109.44 (14)	C12—C3—C4	109.7 (2)
O3—S2—O1	107.0 (2)	C18—C3—S2	108.3 (2)
O2—S2—C3	107.9 (2)	C12—C3—S2	114.7 (2)
O3—S2—C3	115.7 (2)	C4—C3—S2	95.5 (2)
O1—S2—C3	96.24 (13)	C7—C6—C5	121.4 (2)
C5—O1—S2	111.6 (2)	C11—C6—C5	118.3 (2)
O1—C5—C6	110.8 (2)	C13—C12—C3	124.9 (2)
O1—C5—C4	107.2 (2)	C17—C12—C3	114.9 (2)
C6—C5—C4	112.5 (2)	C19—C18—C3	121.0 (2)
C5—C4—C3	107.4 (3)	C23—C18—C3	119.0 (2)
C18—C3—C12	112.2 (2)		

Data collection: *CAD*-4 *Software* (Enraf-Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1994). Molecular graphics: *PLUTON* (Spek, 1991). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1085). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A C_{20} 2:3 Formaldehyde–Cyclohexanone Adduct

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Abstract

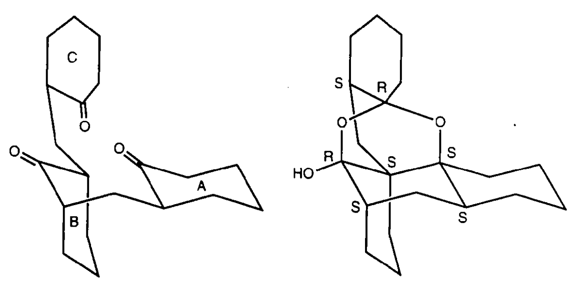
The structure of the base-catalyzed condensation product of cyclohexanone and formaldehyde, (±)-(4aα,6β,9aβ,10aβ,14aβ,15aR*,17S*)-hexadecahydro-14a,6,9a-(epoxymetheno)benzo[b]benzo[2,3]cycloocta-[1,2-e]pyran-17-ol, $C_{20}H_{30}O_3$, reported by Plesek & Munk [*Collect. Czech. Chem. Commun.* (1957), **22**, 1596–1602; *Chem. Listy* (1957), **51**, 633–638], is confirmed to be a 2:3 adduct of formaldehyde to cyclohexanone, being formed by a sequence of aldol and Michael reactions followed by intramolecular ketal and hemi-ketal formation.

Comment

Although more than half a dozen different products have been obtained from the condensation of cyclohexanone with formaldehyde, the product depending on the catalyst, reaction conditions and ratio of reactants (Olsen, 1953; Colonge, Dreux & Delplace, 1956; Mounet, Huet & Dreux, 1971), the structure of the most complex product has remained elusive until recently. A crystalline condensation product, formed by heating the reactants with alcoholic NaOH, was reported in 1957 (Plesek & Munk, 1957) and given the empirical formula

$C_{19}H_{28}O_3$, based on elemental analysis, without structural assignment. The same compound was reported later by Tilichenko (1966), who corrected the empirical formula to $C_{20}H_{30}O_3$ but proposed a structure which was inconsistent with later ^{13}C NMR studies by Akimova, Kosenko & Tilichenko (1991). These same NMR studies led to a revised assignment which has been confirmed by our X-ray structure results. In addition, our X-ray structure study of the title compound reveals details of stereochemistry not provided by IR and NMR data.

The structure is formally derived from the triketone (Fig. 1*a*) by intramolecular aldol, ketal and hemi-ketal formation. The numbering scheme (Fig. 2, Table 1) relates the C atoms in the structure to the *A*, *B* or *C* cyclohexanone ring in the triketone by using *a*, *b* or *c* designations in the C-atom labels. The structure contains seven chiral centers; the *R*/*S* designations are shown in



(*a*) (*b*)

Fig. 1. (*a*) An oriented drawing of the formal triketone precursor showing ring labels *A*, *B* and *C*, and (*b*) a structural drawing of the adduct showing the *R*/*S* configurations for the seven chiral C centers in this enantiomer.

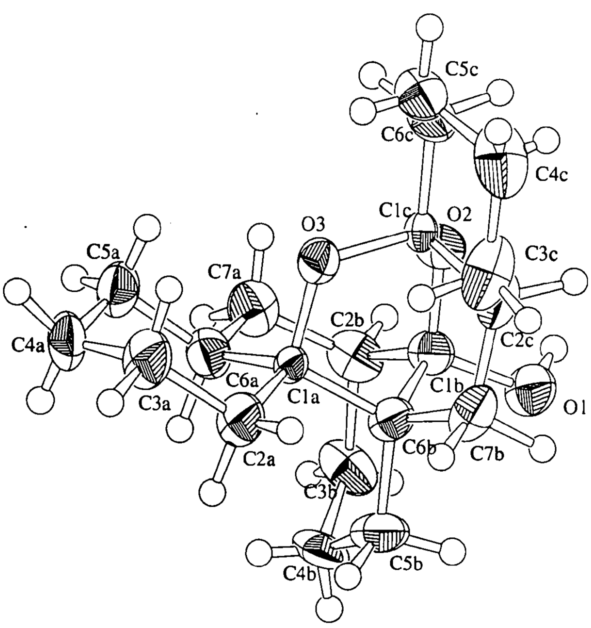


Fig. 2. An *ORTEP* (Johnson, 1976) drawing (50% probability ellipsoids) of the 2:3 formaldehyde–cyclohexanone adduct.

Fig. 1(*b*). An *ORTEP* diagram (Johnson, 1976) of the molecular structure is shown in Fig. 2.

The lengths of the five C—O single bonds range from 1.405 to 1.450 Å and average 1.427 Å. All C atoms are sp^3 hybridized and should exhibit bond lengths and angles commenusurate with this hybridization. Thus, the lengths of the 23 C—C single bonds range from 1.489 to 1.557 Å and average 1.531 Å. The 48 bond angles involving C and O range from 106.1 to 117.0° and average 110.6°.

Pairs of enantiomers are associated through hydrogen bonding into dimers which occupy the inversion center. Thus, there are two hydrogen bonds per dimer; the OH group in one enantiomer is hydrogen bonded to a ketal O atom in its partner, and similarly for the symmetry-related OH···O pair. The intermolecular O(1)···O(2) contact distance of 2.821 (2) Å indicates a modest hydrogen-bonding interaction (Vinogradov & Linnell, 1971). The observed O(1)—H(1) distance is 1.01 Å and the H(1)···O(2) distance is 1.82 Å with an O(1)—H(1)···O(2) intermolecular angle of 171°.

Experimental

The condensation product was prepared as reported (Plesek & Munk, 1957). The IR spectrum showed intense OH absorption at 3360–3420 cm^{-1} but no carbonyl absorption between 1500 and 2000 cm^{-1}. The ^{1}H NMR spectrum (60 MHz) showed overlapping multiplets at δ 1.4, 1.6–1.7, 1.9 and 2.3 p.p.m., as well as a singlet at δ 2.3 p.p.m., which disappeared upon addition of D_2O, but no signals further downfield. The ^{13}C NMR spectrum (Akimova, Kosenko & Tilichenko, 1991) confirmed the absence of carbonyl C atoms; only two signals appeared downfield of the solvent ($CHCl_3$) signal at 93.29 and 95.26 p.p.m.

Crystal data

$C_{20}H_{30}O_3$	Cu $K\alpha$ radiation
M_r = 318.46	λ = 1.5418 Å
Monoclinic	Cell parameters from 25 reflections
$P2_1/n$	θ = 20.0–40.0°
a = 12.947 (1) Å	μ = 0.646 mm^{-1}
b = 7.385 (1) Å	T = 296.2 K
c = 17.817 (1) Å	Needle
β = 95.965 (8)°	0.45 × 0.30 × 0.20 mm
V = 1694.2 (3) Å^3	Colorless
Z = 4	
D_x = 1.248 Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffractometer	θ_{max} = 74.90°
$\omega/2\theta$ scans	h = 0 → 15
Absorption correction: none	k = 0 → 9
2636 measured reflections	l = −21 → 20
2636 independent reflections	3 standard reflections monitored every 120 reflections
1968 observed reflections [$I > 3\sigma(I)$]	intensity variation: −0.68%

Refinement

Refinement on F
$R = 0.048$
$wR = 0.056$
$S = 4.160$
1968 reflections
209 parameters
H-atom parameters not refined
Weighting scheme based on measured e.s.d.'s (*TEXSAN*; Molecular Structure Corporation, 1992)
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.16$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}
Atomic scattering factors from Cromer Waber (1974) for non-H atoms and Stewart, Davidson Simpson (1965) for H atoms

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
O(1)	−0.0119 (1)	0.1955 (2)	0.9365 (1)	3.67 (4)
O(2)	0.1313 (1)	0.0897 (2)	1.01215 (9)	2.97 (3)
O(3)	0.2955 (1)	0.2066 (2)	1.00363 (9)	2.82 (3)
C(1a)	0.2712 (2)	0.2419 (2)	0.9237 (1)	1.90 (4)
C(2a)	0.3479 (2)	0.3886 (3)	0.9027 (2)	3.71 (6)
C(3a)	0.4604 (2)	0.3297 (3)	0.9211 (2)	4.22 (7)
C(4a)	0.4834 (2)	0.1500 (4)	0.8839 (2)	4.15 (8)
C(5a)	0.4062 (2)	0.0061 (3)	0.9036 (2)	3.81 (6)
C(6a)	0.2947 (2)	0.0664 (3)	0.8813 (1)	3.32 (5)
C(7a)	0.2164 (2)	−0.0848 (3)	0.8932 (2)	3.76 (6)
C(1b)	0.0918 (2)	0.1396 (2)	0.9367 (1)	2.85 (5)
C(2b)	0.1029 (2)	−0.0246 (3)	0.8858 (2)	3.57 (5)
C(3b)	0.0569 (3)	0.0199 (4)	0.8064 (2)	3.97 (7)
C(4b)	0.1019 (3)	0.1914 (4)	0.7728 (2)	3.86 (7)
C(5b)	0.1137 (2)	0.3479 (3)	0.8296 (2)	3.96 (6)
C(6b)	0.1551 (2)	0.3006 (2)	0.9110 (1)	2.86 (4)
C(7b)	0.1383 (2)	0.4598 (2)	0.9639 (2)	3.64 (5)
C(1c)	0.2094 (2)	0.2115 (2)	1.0459 (1)	1.71 (4)
C(2c)	0.1634 (2)	0.4028 (3)	1.0465 (2)	3.53 (5)
C(3c)	0.2415 (2)	0.5293 (3)	1.0920 (2)	4.66 (7)
C(4c)	0.2734 (3)	0.4605 (5)	1.1695 (3)	5.10 (10)
C(5c)	0.3214 (3)	0.2693 (4)	1.1674 (2)	3.74 (8)
C(6c)	0.2437 (2)	0.1403 (3)	1.1239 (2)	3.59 (6)

Table 2. *Selected geometric parameters* (Å, °)

O(1)—C(1b)	1.405 (3)	C(1b)—C(2b)	1.529 (3)
O(2)—C(1b)	1.436 (3)	C(1b)—C(6b)	1.540 (3)
O(2)—C(1c)	1.437 (2)	C(2b)—C(3b)	1.512 (4)
O(3)—C(1a)	1.450 (3)	C(3b)—C(4b)	1.541 (4)
O(3)—C(1c)	1.409 (3)	C(4b)—C(5b)	1.534 (5)
C(1a)—C(2a)	1.542 (3)	C(5b)—C(6b)	1.533 (4)
C(1a)—C(6a)	1.546 (3)	C(6b)—C(7b)	1.536 (3)
C(1a)—C(6b)	1.557 (3)	C(7b)—C(2c)	1.533 (4)
C(2a)—C(3a)	1.522 (4)	C(1c)—C(2c)	1.533 (3)
C(3a)—C(4a)	1.526 (4)	C(1c)—C(6c)	1.509 (4)
C(4a)—C(5a)	1.525 (4)	C(2c)—C(3c)	1.544 (3)
C(5a)—C(6a)	1.523 (4)	C(3c)—C(4c)	1.489 (6)
C(6a)—C(7a)	1.537 (3)	C(4c)—C(5c)	1.545 (5)
C(7a)—C(2b)	1.528 (4)	C(5c)—C(6c)	1.536 (4)
C(1b)—O(2)—C(1c)	113.4 (1)	C(1b)—C(2b)—C(3b)	109.3 (2)
C(1a)—O(3)—C(1c)	114.6 (2)	C(2b)—C(3b)—C(4b)	114.5 (2)
O(3)—C(1a)—C(2a)	106.6 (2)	C(3b)—C(4b)—C(5b)	112.2 (3)
O(3)—C(1a)—C(6a)	107.2 (1)	C(4b)—C(5b)—C(6b)	117.0 (2)
O(3)—C(1a)—C(6b)	107.5 (2)	C(1a)—C(6b)—C(1b)	106.1 (1)
C(2a)—C(1a)—C(6a)	107.8 (2)	C(1a)—C(6b)—C(5b)	116.0 (2)
C(2a)—C(1a)—C(6b)	113.9 (2)	C(1a)—C(6b)—C(7b)	108.7 (2)
C(6a)—C(1a)—C(6b)	113.5 (2)	C(1b)—C(6b)—C(5b)	108.2 (2)
C(1a)—C(2a)—C(3a)	111.9 (2)	C(1b)—C(6b)—C(7b)	107.2 (2)
C(2a)—C(3a)—C(4a)	112.4 (2)	C(5b)—C(6b)—C(7b)	110.3 (2)
C(3a)—C(4a)—C(5a)	110.1 (2)	C(6b)—C(7b)—C(2c)	110.4 (2)
C(4a)—C(5a)—C(6a)	111.3 (2)	O(2)—C(1c)—O(3)	108.8 (2)
C(1a)—C(6a)—C(5a)	110.3 (2)	O(2)—C(1c)—C(2c)	108.8 (2)
C(1a)—C(6a)—C(7a)	112.0 (2)	O(2)—C(1c)—C(6c)	107.1 (2)
C(5a)—C(6a)—C(7a)	111.8 (2)	O(3)—C(1c)—C(2c)	110.9 (2)
C(6a)—C(7a)—C(2b)	114.8 (2)	O(3)—C(1c)—C(6c)	108.0 (2)
O(1)—C(1b)—O(2)	109.0 (2)	C(2c)—C(1c)—C(6c)	113.0 (2)
O(1)—C(1b)—C(2b)	112.3 (2)	C(7b)—C(2c)—C(1c)	106.9 (2)
O(1)—C(1b)—C(6b)	108.1 (1)	C(7b)—C(2c)—C(3c)	113.6 (2)
O(2)—C(1b)—C(2b)	107.8 (2)	C(1c)—C(2c)—C(3c)	109.2 (2)
O(2)—C(1b)—C(6b)	109.1 (2)	C(2c)—C(3c)—C(4c)	112.6 (3)
C(2b)—C(1b)—C(6b)	110.5 (2)	C(3c)—C(4c)—C(5c)	111.3 (3)
C(7a)—C(2b)—C(1b)	109.1 (2)	C(4c)—C(5c)—C(6c)	109.5 (3)
C(7a)—C(2b)—C(3b)	115.1 (2)	C(1c)—C(6c)—C(5c)	111.4 (2)

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SIR*88 (Burla *et al.*, 1989). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*. Other crystallographic calculations were performed using *MolEN* (Fair, 1990).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete H-atom geometry and torsion angles, as well as a packing diagram, have been deposited with the IUCr (Reference: CR1137). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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