C4—C14	1.544 (4)	C17—C18	1.484 (3)
C5—C6	1.392 (3)	C17—O	1.219 (3)
C5—C10	1.386 (3)		
C2—C1—C9	111.3 (2)	C5—C6—C16	119.8 (2)
C2—C1—C11	108.7 (2)	C7—C6—C16	124.0 (2)
C2—C1—C12	109.0 (2)	C6—C7—C8	120.7 (2)
C9—C1—C11	110.9 (2)	C6—C7—C17	121.6 (2)
C9—C1—C12	107.9 (2)	C8—C7—C17	117.7 (2)
C11—C1—C12	109.0 (2)	C7—C8—C9	122.5 (2)
C1—C2—C3	115.2 (2)	C1—C9—C8	122.7 (2)
C2—C3—C4	110.5 (2)	C1—C9—C10	121.4 (2)
C3—C4—C10	108.3 (2)	C8—C9—C10	115.6 (2)
C3—C4—C13	111.5 (2)	C4—C10—C5	111.7 (2)
C3—C4—C14	117.5 (2)	C4—C10—C9	125.4 (2)
C10—C4—C13	109.9 (2)	C5—C10—C9	122.8 (2)
C10—C4—C14	100.3 (2)	C4—C14—C15	105.5 (2)
C13—C4—C14	108.8 (2)	C5—C15—C14	102.7 (2)
C6—C5—C10	121.9 (2)	C7—C17—C18	118.9 (2)
C6—C5—C15	128.7 (2)	C7—C17—O	121.2 (2)
C10—C5—C15	109.3 (2)	C18—C17—O	119.8 (2)
C5—C6—C7	116.2 (2)		

Table 3. *Distances from the best plane through the phenyl ring* (Å)

	Ring atoms	Attached atoms
C5	0.012 (3)	0.134 (4)
C6	0.019 (2)	0.081 (4)
C7	−0.021 (2)	−0.021 (3)
C8	−0.000 (2)	-
C9	0.026 (2)	0.253 (3)
C10	−0.036 (2)	−0.080 (4)

The crystals were recrystallized by slow evaporation from ethanol. The structure was determined by direct methods (*SIMPEL*; Schenk & Hall, 1990). H-atom positions were calculated on the basis of standard geometry. Full-matrix least-squares refinement on *F*, anisotropic for non-H atoms and isotropic for H atoms.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71502 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1068]

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Acta Cryst. (1994). C**50**, 267–269

2,2′-Biadamantane

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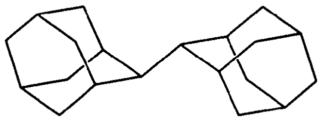
Abstract

The structure of 2,2′-biadamantane, $C_{20}H_{30}$, (space group *C*2/*c*) has been determined by single-crystal diffractometry. The central C—C linkage was found to be 1.542 (2) Å and is perfectly staggered (crystallographic center of symmetry). The bridging induces a small distortion of the adamantane moieties [average C—C 1.533 (5) Å, average C—C—C 109.6 (6)°].

Comment

Few structures of compounds involving the 2,2′-biadamantane skeleton are known (*e.g.* Watson & Nagl, 1988; Hess & Vos, 1977; Slebocka-Tilk, Ball & Brown, 1985). While investigating mechanistic aspects of a modified Barbier reaction (Mielke, 1993) we obtained the parent hydrocarbon 2,2′-biadamantane (I) (van Zorge, Strating



(I)

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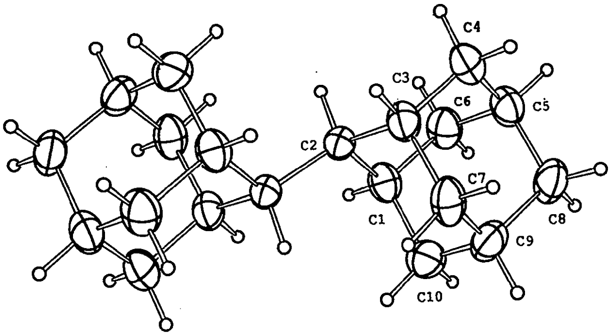

Fig. 1. *ORTEPII* (Johnson, 1976) plot of 2,2′-biadamantane with thermal ellipsoids shown at the 50% probability level. H atoms are drawn as unlabeled spheres of arbitrary size.

& Wynberg, 1970) which was recrystallized from tetrahydrofuran to give high quality crystals [spectroscopic data: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.9-1.7 (*m*, 26 H), 1.5-1.4 (*m*, 4 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 27.9, 28.1, 28.3, 31.7, 38.5, 39.7, 42.5; mass spectrum, *m*/*z* (relative intensity) 270 (M^+, 30), 135 (100)]. The determination of the geometry of 2,2′-biadamantane should reveal structural information about the extent of distortion induced by linking the highly symmetrical adamantane substructures, as well as insight into the conformation of the hydrocarbon in the solid state.

The observed long central C—C bridge [C2—C2′ 1.542 (2) Å] is in accord with the general rule that higher C substitution increases the length of C—C single bonds (Stoicheff, 1962). For comparison, a value of 1.578 (2) Å was determined in the isomeric 1,1′-biadamantane for the analogous C bridge (Alden, Kraut & Traylor, 1968). The linkage of the two adamantane substructures induces a weak deformation of the cages. The bond lengths decrease with distance from the junction [the bond lengths range from 1.525 (2) to 1.543 (2) Å, with an average value of 1.533 (5) Å, in the adamantane substructure]. Furthermore, the tetrahedral geometry around C2 is also distorted [C1—C2—C2′ 113.9 (1), C2′-C2—C3 113.7 (1)°]. The other C—C—C angles in the adamantane unit are normal [109.6 (6)° average]. The molecule sits on a crystallographic center of symmetry; hence, the conformation of the bridge is *anti* and perfectly staggered. Finally, it should be noted that although molecular-mechanics calculations (*PCModel*; Serena Software, 1990) and semi-empirical calculations (*AM*1; Dewar, Zoebisch, Healy & Stewart, 1985) correctly predict the *anti* conformation, neither method reproduces the length of the central C—C bond very well (C2—C2′: *PCModel* 1.556 Å; *AM*1 1.528 Å).

Experimental

Crystal data

$C_{20}H_{30}$
M_r = 270.46
Monoclinic
$C2/c$
a = 9.306 (2) Å
b = 9.184 (2) Å
c = 18.506 (4) Å
β = 103.19 (2)°
V = 1539 (1) Å^3
Z = 4

D_x = 1.17 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 10-17°
μ = 0.060 mm^{-1}
T = 294 K
Plate
0.15 × 0.15 × 0.10 mm
Colorless

Data collection

Enraf-Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical
T_{min} = 0.96, T_{max} = 0.99
1705 measured reflections
1599 independent reflections
829 observed reflections [$I > 3.0\sigma(I)$]

R_{int} = 0.036
θ_{max} = 25.97°
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 11$
$l = -22 \rightarrow 22$
3 standard reflections
frequency: 60 min
intensity variation: 1.32%

Refinement

Refinement on F
R = 0.037
wR = 0.050
S = 1.514
829 reflections
152 parameters
H atoms refined isotropically
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$
$(\Delta/\sigma)_{max}$ = 0.001

$\Delta\rho_{max}$ = 0.13 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}
Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: 0.36 (3) × 10^{-5}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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}
C1	0.1042 (2)	0.3107 (2)	0.05741 (8)	0.0372 (4)
C2	0.2024 (1)	0.2096 (2)	0.02264 (7)	0.0313 (4)
C3	0.2926 (1)	0.1142 (2)	0.08550 (7)	0.0362 (4)
C4	0.1874 (2)	0.0236 (2)	0.12034 (9)	0.0468 (4)
C5	0.0887 (2)	0.1235 (2)	0.15393 (8)	0.0442 (4)
C6	−0.0004 (2)	0.2195 (2)	0.09258 (9)	0.0450 (5)
C7	0.3881 (2)	0.2086 (2)	0.14608 (9)	0.0437 (4)
C8	0.1847 (2)	0.2185 (2)	0.21370 (9)	0.0492 (5)
C9	0.2895 (2)	0.3099 (2)	0.17907 (8)	0.0468 (5)
C10	0.1988 (2)	0.4062 (2)	0.11810 (8)	0.0448 (4)

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

C1—C2	1.543 (2)	C4—C5	1.527 (2)
C1—C6	1.536 (2)	C5—C6	1.525 (2)
C1—C10	1.534 (2)	C5—C8	1.527 (2)
C2—C2′	1.542 (2)	C7—C9	1.529 (2)
C2—C3	1.543 (2)	C8—C9	1.533 (3)
C3—C4	1.535 (2)	C9—C10	1.528 (2)
C3—C7	1.531 (2)		
C2—C1—C6	109.9 (1)	C4—C5—C6	108.6 (1)
C2—C1—C10	110.7 (1)	C4—C5—C8	109.4 (1)
C6—C1—C10	108.3 (1)	C6—C5—C8	109.8 (1)

C1—C2—C2′	113.9 (1)	C1—C6—C5	110.0 (1)
C1—C2—C3	107.4 (1)	C3—C7—C9	109.7 (1)
C2′—C2—C3	113.7 (1)	C5—C8—C9	109.4 (1)
C2—C3—C4	109.6 (1)	C7—C9—C8	109.3 (1)
C2—C3—C7	110.9 (1)	C7—C9—C10	109.8 (1)
C4—C3—C7	108.6 (1)	C8—C9—C10	109.2 (1)
C3—C4—C5	110.2 (1)	C1—C10—C9	109.7 (1)

Backgrounds were obtained from analysis of the scan profile (Blessing, Coppens & Becker, 1974). As a result of high local symmetry in 2,2′-biadamantane, solution of the structure with direct methods (*MULTAN*80; Main *et al.*, 1980) caused difficulties. The set with the fourth highest ranking combined figure of merit (2.105) gave a recognizable partial solution which was completed by Fourier methods. *PCModel* and *AM*1 calculations were carried out on 486PC and Stardent Titan 3040 computers, respectively. Data collection: *CAD*-4 (Enraf-Nonius, 1977). Cell refinement: *CAD*-4. Data reduction: *MolEN PROCESS* (Fair, 1990). Program(s) used to solve structure: direct methods in *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *MolEN LSFM*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN CIFIN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71538 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1078]

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Acta Cryst. (1994). C**50**, 269–271

Structure du 5-Méthyl-2-thioxo-1,2,3,4-tétrahydro-7*H*-pyrano[2,3-*d*]pyrimidine-4,7-dione Méthanol Solvaté, $C_8H_6N_2O_3S.CH_4O$

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Abstract

The title compound, containing the bicyclic ring system TPPM, is solvated by a methanol molecule. The bicycle is planar; the dihedral angle between the pyrimidine and the pyran rings is 3.6 (2)°. The C—S bond length is shorter than that found in the thioglycoside that contains a TPPM moiety [Tomas, Nguyen-Huy, Viossat, Esanu & Rolland (1993). *Acta Cryst.* C**49**, 626–628]. In the crystal, several hydrogen bonds link the TPPM and the CH_3OH molecules giving rise to zigzag chains.

Commentaire

La synthèse du 5-méthyl-2-thioxo-1,2,3,4-tétrahydro-7*H*-pyrano[2,3-*d*]pyrimidine-4,7-dione (appelé plus loin TPPM) a été décrite par Ridi (1950). Par ailleurs, nous avons récemment synthétisé et décrit la structure cristalline du 5-méthyl-2-[(2,3,4-tri-*O*-acétyl-β-D-arabinopyranosyl)thio]-3,4-dihydro-7*H*-pyrano[2,3-*d*]pyrimidine-4,7-dione caractérisée par la présence d'une liaison thioarabinosique via l'atome de soufre (Tomas, Nguyen-Huy, Viossat, Esanu & Rolland, 1993). Il nous a paru alors opportun

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