C33	0.7917 (4)	0.1702 (3)	0.4853 (3)	0.0722 (11)
C34	0.7252 (4)	0.1686 (3)	0.5717 (3)	0.0655 (10)
C35	0.6496 (4)	0.2575 (4)	0.5955 (3)	0.0766 (12)
C36	0.6411 (4)	0.3506 (3)	0.5322 (3)	0.0637 (10)
N1	0.6486 (3)	0.5876 (2)	0.4248 (3)	0.0560 (8)
H1*A*	0.5677 (33)	0.5934 (26)	0.4302 (25)	0.053 (10)
H1*B*	0.6946 (35)	0.6220 (28)	0.4679 (25)	0.060 (11)
N2	0.2748 (3)	0.7763 (3)	0.4269 (3)	0.0711 (9)
N3	0.3287 (2)	0.6920 (3)	0.4404 (2)	0.0543 (7)
N4	0.3808 (3)	0.6062 (3)	0.4532 (3)	0.0901 (12)

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

P—N1	1.603 (3)	C23—C24	1.375 (5)
P—C11	1.788 (3)	C24—C25	1.369 (5)
P—C21	1.796 (3)	C25—C26	1.381 (5)
P—C31	1.798 (3)	C31—C36	1.375 (4)
C11—C12	1.378 (4)	C31—C32	1.383 (4)
C11—C16	1.394 (4)	C32—C33	1.382 (5)
C12—C13	1.388 (5)	C33—C34	1.352 (5)
C13—C14	1.359 (5)	C34—C35	1.361 (5)
C14—C15	1.375 (5)	C35—C36	1.387 (5)
C15—C16	1.376 (5)	N1—H1*A*	0.87 (3)
C21—C22	1.384 (4)	N1—H1*B*	0.86 (4)
C21—C26	1.389 (4)	N2—N3	1.161 (4)
C22—C23	1.387 (5)	N3—N4	1.167 (4)
N1—P—C11	106.9 (2)	C21—C22—C23	119.7 (3)
N1—P—C21	109.5 (2)	C24—C23—C22	119.9 (4)
C11—P—C21	110.12 (14)	C25—C24—C23	120.5 (3)
N1—P—C31	113.3 (2)	C24—C25—C26	120.4 (4)
C11—P—C31	109.90 (14)	C25—C26—C21	119.4 (4)
C21—P—C31	107.21 (14)	C36—C31—C32	118.2 (3)
C12—C11—C16	119.5 (3)	C36—C31—P	118.8 (2)
C12—C11—P	122.6 (3)	C32—C31—P	122.9 (2)
C16—C11—P	117.7 (2)	C33—C32—C31	120.6 (3)
C11—C12—C13	119.4 (3)	C34—C33—C32	120.5 (4)
C14—C13—C12	120.6 (3)	C33—C34—C35	119.8 (3)
C13—C14—C15	120.5 (3)	C34—C35—C36	120.5 (3)
C14—C15—C16	119.8 (4)	C31—C36—C35	120.4 (3)
C15—C16—C11	120.1 (3)	P—N1—H1*A*	115 (2)
C22—C21—C26	120.1 (3)	P—N1—H1*B*	122 (2)
C22—C21—P	120.1 (2)	H1*A*—N1—H1*B*	118 (3)
C26—C21—P	119.7 (2)	N2—N3—N4	178.6 (4)

H atoms were placed at expected positions, riding, with $U = 1.2U_{eq}$(C), except for those attached to N which were refined freely. Data collection: *DIF*4 (Stoe & Cie, 1988). Cell refinement: *DIF*4. Data reduction: local programs. Program(s) used to solve structure: *SHELXTL*/*PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL* (Sheldrick, 1994). Molecular graphics: *SHELXTL*/*PC*. Software used to prepare material for publication: *SHELXL*; local programs.

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References

Böhm, E., Dehnicke, K., Beck, J., Hiller, W., Strähle, J., Maurer, A. & Fenske, D. (1988). *Z. Naturforsch. Teil B*, **43**, 138-144.

Bracuti, A. J. & Extine, M. W. (1990). *J. Crystallogr. Spectrosc. Res.* **20**, 31-35.

Christe, K. O., Wilson, W. W., Bau, R. & Bunte, S. W. (1992). *J. Am. Chem. Soc.* **114**, 3411-3414.

Clegg, W. (1981). *Acta Cryst.* A**37**, 22-28.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876-881.

Kimura, E., Anan, H., Koike, T. & Shiro, M. (1989). *J. Org. Chem.* **54**, 3998-4000.

Lex, J. & Linke, K.-H. (1976). *Chem. Ber.* **109**, 2684-2690.

Llamas-Saiz, A. L., Foces-Foces, C., Elguero, J., Molina, P., Alajarín, M. & Vidal, A. (1991*a*). *J. Chem. Soc. Perkin Trans.* 2, pp. 1667-1676.

Llamas-Saiz, A. L., Foces-Foces, C., Elguero, J., Molina, P., Alajarín, M. & Vidal, A. (1991*b*). *J. Chem. Soc. Perkin Trans.* 2, pp. 2033-2040.

Llamas-Saiz, A. L., Foces-Foces, C., Elguero, J., Molina, P., Alajarín, M. & Vidal, A. (1992). *Acta Cryst.* C**48**, 1940-1945.

Molina, P., Alajarín, M., Lopez-Leonardo, C., Claramunt, R. M., Foces-Foces, C., Cano, F. H., Catalán, J., de Paz, J. L. G. & Elguero, J. (1989). *J. Am. Chem. Soc.* **111**, 355-363.

Molina, P., Alajarín, M., Lopez-Leonardo, C., Cano, F. H., Llamas-Saiz, A. L., Foces-Foces, C., Claramunt, R. M. & Elguero, J. (1992). *J. Chem. Soc. Perkin Trans.* 1, pp. 199-210.

Sheldrick, G. M. (1990). *SHELXTL*/*PC User's Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1994). *J. Appl. Cryst.* In preparation.

Staudinger, H. & Hauser, E. (1921). *Helv. Chim. Acta*, **4**, 861-886.

Stoe & Cie (1988). *DIF*4. *Diffractometer Control Program.* Version 7.04. Stoe & Cie, Darmstadt, Germany.

Woning, J., Daniels, L. M. & Verkade, J. G. (1990). *J. Am. Chem. Soc.* **112**, 4601-4602.

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Low-Temperature Structure of Bicyclohexylidene, $C_{12}H_{20}$

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Abstract

The two apical C_{sp^3}—C_{sp^3} bonds [mean 1.521 (2) Å] in bicyclohexylidene are significantly shorter than the other two C_{sp^3}—C_{sp^3} bonds [mean 1.530 (2) Å]. The molecule exhibits approximate C_{2h} symmetry in the solid.

Comment

Well defined oligomers of [1.1.1]propellane (Murthy, Hassenrück, Lynch & Michl, 1989; Friedli, Lynch,

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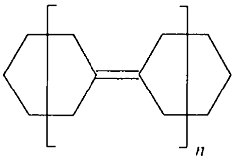
Kaszynski & Michl, 1990; Kaszynski, McMurdie & Michl, 1991; Kaszynski, Friedli & Michl, 1992) and bicyclo[2.2.2]octane (Zimmerman, King & Meinhardt, 1992) receive considerable attention as building blocks for supramolecular assemblies (Obeng, Laing, Friedli, Yang, Wang, Thulstrup, Bard & Michl, 1992). We are currently developing synthetic strategies for the preparation of oligo(cyclohexylidenes), 1(*n*) (Hoogesteger, Havenith, Zwikker & Jenneskens, 1994), using, among others, a Barton-Kellogg approach (Barton & Willis, 1972; Buter, Wassenaar & Kellogg, 1972). These oligo(cyclohexylidenes) may be thought of as a new class of molecular building blocks for the preparation of defined supramolecular assemblies. Our primary object is to gain insight into the solid-state structures of the compounds 1(*n*). A room-temperature single-crystal structure determination for bicyclohexylidene, 1(1), synthesized by Criegee, Vogel & Horger (1952), has been reported (Sasvári & Löw, 1965). Here we report a more accurate low-temperature study.



1(*n*)

The molecule is located on a crystallographic centre of symmetry. Combined with a non-crystallographic mirror plane perpendicular to the double-bond plane, this results in approximate C_{2h} symmetry. Bond distances and angles related by this pseudomirror plane are equal within their standard deviations. The bonds around C1 have values in the range expected for C_{sp^2}—C_{sp^2} and C_{sp^2}—C_{sp^3} bonds. Interestingly, the two C_{sp^3}—C_{sp^3} bonds involving C4 [C3—C4 1.519 (2), C4—C5 1.523 (3) Å] are significantly shorter than the other two C_{sp^3}—C_{sp^3} bonds [C2—C3 1.531 (2), C5—C6 1.529 (2) Å]. All of the bonds are shorter than the standard 1.54 Å. Both semi-empirical (AMI; Dewar, Zoebisch, Healy & Stewart, 1985) and *ab initio* (STO-3G, 6-31G; Hehre, Radom, von Schleyer & Pople, 1986) calculations appear to support these experimental observations. Similar results were reported by Sasvári & Löw (1965) for the room-temperature structure, although our results do not show the large difference between the two C_{sp^2}—C_{sp^3} bond distances observed in this earlier study.

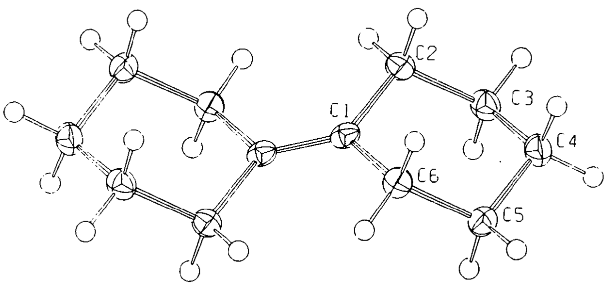


Fig. 1. A displacement ellipsoid plot at the 50% probability level for bicyclohexylidene.

Experimental

The preparation of bicyclohexylidene will be reported elsewhere (Hoogesteger, Havenith, Zwikker & Jenneskens, 1994). The crystals used for data collection were grown by sublimation.

Crystal data

$C_{12}H_{20}$
$M_r = 164.29$
Triclinic
$P\bar{1}$
$a = 5.2346$ (6) Å
$b = 6.1700$ (7) Å
$c = 8.3346$ (17) Å
$\alpha = 71.831$ (14)°
$\beta = 77.530$ (13)°
$\gamma = 74.985$ (9)°
$V = 244.34$ (7) Å^3
$Z = 1$
$D_x = 1.117$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 8.8$-$16.7°$
$\mu = 0.06$ mm^{-1}
$T = 150$ K
Needle
0.75 × 0.12 × 0.05 mm
Colourless

Data collection

Enraf-Nonius CAD-4-Turbo diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2453 measured reflections
1106 independent reflections
793 observed reflections [$I > 2.5\sigma(I)$]

$R_{\rm int} = 0.065$
$\theta_{\rm max} = 27.5°$
$h = -6 \rightarrow 6$
$k = -7 \rightarrow 7$
$l = -10 \rightarrow 10$
3 standard reflections
frequency: 60 min
intensity variation: none

Refinement

Refinement on F
$R = 0.050$
$wR = 0.064$
$S = 0.24$
793 reflections
86 parameters
Only coordinates of H atoms refined and one common $U_{\rm iso}$

$w = 1/[\sigma^2(F) + (0.03F)^2]$
$(\Delta/\sigma)_{\rm max} = 0.042$
$\Delta\rho_{\rm max} = 0.42$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.22$ e Å^{-3}
Atomic scattering factors from Cromer & Mann (1968)

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

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

	x	y	z	$U_{\rm eq}$
C1	0.9702 (3)	0.5502 (3)	0.4208 (2)	0.0180 (5)
C2	0.8563 (3)	0.8074 (3)	0.3517 (2)	0.0217 (5)
C3	0.5969 (3)	0.8486 (3)	0.2798 (2)	0.0228 (5)
C4	0.6378 (3)	0.7215 (3)	0.1439 (2)	0.0238 (5)
C5	0.7469 (3)	0.4621 (3)	0.2152 (2)	0.0222 (5)
C6	1.0051 (3)	0.4211 (3)	0.2878 (2)	0.0213 (5)

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

C1—C2	1.514 (3)	C3—C4	1.519 (2)
C1—C6	1.511 (2)	C4—C5	1.523 (3)
C1—C1^{i}	1.339 (2)	C5—C6	1.529 (2)
C2—C3	1.531 (2)		
C2—C1—C6	111.04 (13)	C2—C3—C4	111.17 (14)
C1^{i}—C1—C2	124.55 (16)	C3—C4—C5	110.42 (13)
C1^{i}—C1—C6	124.40 (17)	C4—C5—C6	111.08 (14)
C1—C2—C3	111.88 (15)	C1—C6—C5	112.27 (14)

Symmetry code: (i) $2 - x, 1 - y, 1 - z$.

The adopted spacegroup, $P\overline{1}$, is consistent with the statistical $N(z)$ test for centrosymmetry and is confirmed by the successful refinement. Data collection: *CAD*-4 *Software* (Enraf-Nonius, 1989) with local modifications. Cell refinement: *SET*4 (de Boer & Duisenberg, 1984). Data reduction: *HELENA* (Spek, 1993). Program(s) used to solve structure: *SIR*92 (Altomare, Cascarano, Giacovazzo & Guagliardi, 1993). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *PLATON*93 (Spek, 1990). Software used to prepare material for publication: *PLATON*93.

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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 71795 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1118]

References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343-350.
Barton, D. H. R. & Willis, B. J. (1972). *J. Chem. Soc. Perkin Trans.* 1, pp. 305-310.
Boer, J. L. de & Duisenberg, A. J. M. (1984). *Acta Cryst.* A**40**, C-410.
Buter, J., Wassenaar, S. & Kellogg, R. M. (1972). *J. Org. Chem.* **37**, 4045-4060.
Criegee, R., Vogel, E. & Horger, H. (1952). *Chem. Ber.* **85**, 144-152.
Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321-324.
Dewar, M. J. S., Zoebisch, E. G., Healy, E. F. & Stewart, J. J. P. (1985). *J. Am. Chem. Soc.* **107**, 3902-3909.
Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
Friedli, A. C., Lynch, V. M., Kaszynski, P. & Michl, J. (1990). *Acta Cryst.* B**46**, 377-389.
Hehre, W. J., Radom, L., von Schleyer, R. P. & Pople, J. A. (1986). *Ab Initio Molecular Orbital Theory*. New York: John Wiley.
Hoogesteger, F. J., Havenith, R. W. A., Zwikker, J. W. & Jenneskens, L. W. (1994). In preparation.
Kaszynski, P., McMurdie, N. D. & Michl, J. (1991). *J. Org. Chem.* **56**, 307-316.
Kaszynski, P., Friedli, A. C. & Michl, J. (1992). *J. Am. Chem. Soc.* **114**, 601-620.
Murthy, G. S., Hassenrück, K., Lynch, V. M. & Michl, J. (1989). *J. Am. Chem. Soc.* **111**, 7262-7264.
Obeng, Y. S., Laing, M. E., Friedli, A. C., Yang, H. C., Wang, D., Thulstrup, E. W., Bard A. J. & Michl, J. (1992). *J. Am. Chem. Soc.* **114**, 9943-9952.
Sasvári, K. & Löw, M. (1965). *Acta Cryst.* **19**, 840-848.
Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.
Spek, A. L. (1993). *HELENA. Program for Data Reduction*. Univ. of Utrecht, The Netherlands.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.
Zimmerman, H. E., King, R. K. & Meinhardt, M. B. (1992). *J. Org. Chem.* **57**, 5484-5492.

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trans-transoid-trans-transoid-trans-Tetracyclo[16.4.0.0^{2,9}.0^{10,17}]docosa-5,13-diene

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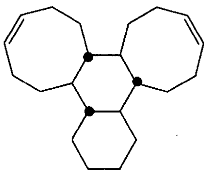
Abstract

The title compound, $C_{22}H_{34}$, is obtained by cycloaddition of one cyclohexene and two 1,5-cyclooctadiene molecules, photoassisted by copper(I) trifluoromethanesulfonate. The crystal structure contains two crystallographically independent molecules, each positioned on sites with twofold axial symmetry. The two independent (half)-molecules show only minor differences.

Comment

The monoclinic unit cell contains four molecules of the title compound, (I) (Fig. 1), each located on a twofold axis. The geometries of the two crystallographically independent half-molecules are similar. The puckering of the central six-membered ring is best described as skew-boat (Boeyens, 1978) with puckering-analysis parameters (Cremer & Pople, 1975) $Q = 0.675$ (2) [0.676 (3)] Å, $\theta = 76.4$ (2) [75.6 (3)]°, $\varphi = 150.0$ (2) [150.0 (2)]° for molecule (1) [data for molecule (2) in square brackets]. The corresponding values of $Q = 0.546$ (3) [0.538 (3)] Å, $\theta = 9.5$ (3) [7.3 (3)]°, $\varphi = 150$ (2) [150 (3)]° for the other six-membered ring indicate a chair conformation.



(I)

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