

A molecule with a C_1 -homobasketane framework

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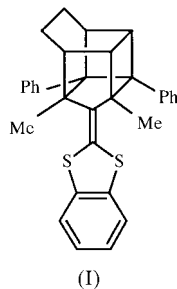
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The title compound, 6-(1,3-benzodithiol-2-ylidene)-5,7-dimethyl-1,2-diphenylpentacyclo[5.4.0.0^{2,5}.0^{3,11}.0^{4,8}]undecane, $C_{32}H_{28}S_2$, with a C_1 -homobasketane framework, crystallizes in the $P\bar{1}$ space group with one molecule in the asymmetric unit. The two cyclobutane rings in the cage are in a puckered conformation. Due to the enhanced through-bond interaction of the phenyl π systems involving a strained σ bond, the (Ph)C—C(—Ph) bond length is significantly extended, to 1.610 (3) Å.

Comment

There is considerable interest in the chemistry of highly strained polycyclic 'cage' compounds and their application to solar energy storage (Osawa & Yonemitsu, 1992). Trishomocubanes, which are one type of cubane homologue, result from the introduction of three methylene groups into the cubane framework and have 14 isomers (Marchand, 1989). Among these, X-ray crystal structures of only four types of isomer have been reported. We have recently synthesized the title trishomocubane, the C_1 -homobasketane derivative, (I), with a 1,3-dithiole moiety as the redox part, and we present here the X-ray analysis of (I). To the best of our knowledge, this is the first example of the crystal structure determination of a molecule with a C_1 -homobasketane framework.



Compound (I) crystallizes in the $P\bar{1}$ space group with one molecule in the asymmetric unit. The molecular structure of (I) is shown in Fig. 1 and selected geometric parameters are

listed in Table 1. The two cyclobutane rings in the cage are in puckered conformations. The torsion angles in the rings are -13.1 (2)° for C2—C3—C7—C6 and -20.1 (2)° for C3—C4—C8—C7. The deviations of C6 and C4 from the planes defined by the other three atoms are 0.35 (1) and 0.56 (1) Å, respectively. The bridging bond shared with the two cyclobutane rings [C3—C7 1.550 (3) Å] is almost the same length as the bonds in cyclobutanes (1.554 Å; Allen *et al.*, 1987) and cubane [1.551 (3) Å; Fleischer, 1964].

The two phenyl groups are nearly oriented in a face-to-face conformation. The twist angles of the ring planes (Hounshell *et al.*, 1977) to the C3—C4 bond are -88.3 (3) and 93.8 (3)° for the C21—C26 phenyl ring, and 62.2 (3) and -121.7 (2)° for the C27—C32 phenyl ring. The angle between the least-squares planes of the two phenyl groups is 75.3 (4)°.

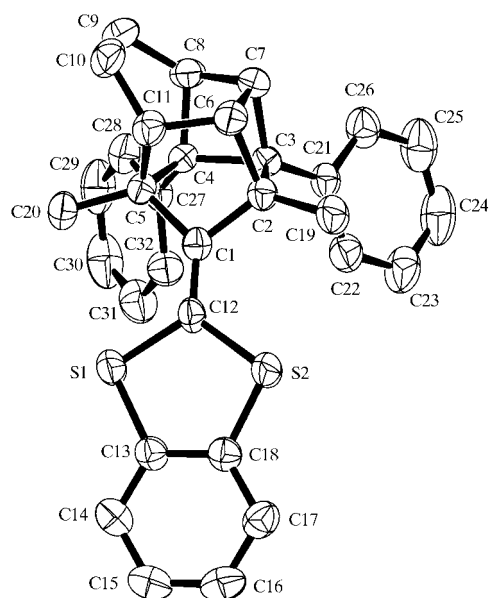


Figure 1

The molecular structure of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

The most remarkable features of the molecular structure of (I) are the considerably long C3—C4 [1.610 (3) Å] and C4—C5 [1.592 (3) Å] bonds. Harano *et al.* (1981) have proposed that elongation of (Ph)C—C(—Ph) bonds in 1,2-diphenyl-11-azapentacyclo[5.5.0.0^{2,5}.0^{3,12}.0^{4,8}]dodec-9-en-6-one derivatives, which have the same face-to-face conformation of the phenyl groups as in (I), is caused by the enhanced through-bond interaction of the phenyl π systems involving a strained σ bond. Thus, this effect brings about the elongation of the C3—C4 bond in (I).

Experimental

Compound (I) was synthesized by a Wittig–Horner reaction of 5,7-dimethyl-1,2-diphenylpentacyclo[5.4.0.0^{2,5}.0^{3,11}.0^{3,8}]undecan-6-one (Tezuka *et al.*, 1976) with 2-dimethoxyphosphinyl-4,5-benzo-1,3-dithiole (Akiba *et al.*, 1978; Moore & Bryce, 1991). Recrystallization from dichloromethane–ethanol afforded colourless crystals of (I) suitable for X-ray analysis.

Crystal data

$C_{32}H_{28}S_2$	$Z = 2$
$M_r = 476.66$	$D_x = 1.314 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.7467 (12) \text{ \AA}$	Cell parameters from 25 reflections
$b = 14.2911 (18) \text{ \AA}$	$\theta = 14.7\text{--}15.0^\circ$
$c = 9.2122 (11) \text{ \AA}$	$\mu = 0.241 \text{ mm}^{-1}$
$\alpha = 94.091 (11)^\circ$	$T = 296 (2) \text{ K}$
$\beta = 95.769 (11)^\circ$	Prismatic, colourless
$\gamma = 70.809 (9)^\circ$	$0.25 \times 0.25 \times 0.20 \text{ mm}$
$V = 1204.7 (3) \text{ \AA}^3$	

Data collection

Rigaku AFC-7R diffractometer	$h = 0 \rightarrow 12$
$\omega/2\theta$ scans	$k = -17 \rightarrow 18$
5854 measured reflections	$l = -11 \rightarrow 11$
5529 independent reflections	3 standard reflections
3128 reflections with $I > 2\sigma(I)$	every 150 reflections
$R_{\text{int}} = 0.022$	intensity decay: 0.29%
$\theta_{\text{max}} = 27.5^\circ$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0495P)^2 + 0.2116P]$
$R[F^2 > 2\sigma(F^2)] = 0.042$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.122$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 0.998$	$\Delta\rho_{\text{max}} = 0.28 \text{ e \AA}^{-3}$
5529 reflections	$\Delta\rho_{\text{min}} = -0.25 \text{ e \AA}^{-3}$
419 parameters	
All H-atom parameters refined	

All H atoms were located in the difference Fourier map and were refined isotropically, giving C–H distances in the range 0.85 (3)–1.05 (3) Å and $U_{\text{iso}}(\text{H})$ in the range 0.036 (6)–0.084 (10) Å².

Data collection and cell refinement: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); data reduction: *TEXSAN* (Molecular Structure Corporation, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1587). Services for accessing these data are described at the back of the journal.

Table 1

Selected geometric parameters (Å, °).

C1–C2	1.521 (3)	C5–C11	1.556 (3)
C1–C5	1.531 (3)	C6–C11	1.515 (3)
C2–C3	1.560 (3)	C6–C7	1.561 (4)
C2–C6	1.579 (3)	C7–C8	1.532 (3)
C3–C7	1.550 (3)	C8–C9	1.522 (4)
C3–C4	1.610 (3)	C9–C10	1.522 (4)
C4–C8	1.561 (3)	C10–C11	1.527 (4)
C4–C5	1.592 (3)		
C2–C1–C5	98.42 (17)	C11–C6–C2	104.63 (19)
C1–C2–C3	102.99 (17)	C7–C6–C2	91.41 (18)
C1–C2–C6	105.14 (18)	C8–C7–C3	91.12 (17)
C3–C2–C6	86.06 (17)	C8–C7–C6	110.3 (2)
C7–C3–C2	92.55 (17)	C3–C7–C6	87.04 (17)
C7–C3–C4	85.66 (16)	C9–C8–C7	118.8 (2)
C2–C3–C4	103.21 (16)	C9–C8–C4	116.3 (2)
C8–C4–C5	109.99 (18)	C7–C8–C4	88.01 (17)
C8–C4–C3	87.88 (16)	C8–C9–C10	108.9 (2)
C5–C4–C3	102.43 (16)	C9–C10–C11	110.8 (2)
C1–C5–C11	99.84 (17)	C6–C11–C10	112.4 (2)
C1–C5–C4	101.40 (16)	C6–C11–C5	100.12 (18)
C11–C5–C4	105.02 (18)	C10–C11–C5	114.9 (2)
C11–C6–C7	109.3 (2)		

References

- Akiba, K., Ishikawa, K. & Inamoto, N. (1978). *Bull. Chem. Soc. Jpn.*, **51**, 2674–2683.
- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Fleischer, E. B. (1964). *J. Am. Chem. Soc.* **86**, 3889–3890.
- Harano, K., Ban, T., Yasuda, M., Osawa, E. & Kanematsu, K. (1981). *J. Am. Chem. Soc.* **103**, 2310–2317.
- Hounshell, W. D., Dougherty, D. A., Hummel, J. P. & Mislow, K. J. (1977). *J. Am. Chem. Soc.* **99**, 1916–1924.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Marchand, A. P. (1989). *Chem. Rev.* **89**, 1011–1033.
- Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1995). *TEXSAN*. Version 1.7-2. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Moore, A. J. & Bryce, M. R. (1991). *Synthesis*, pp. 26–28.
- Osawa, E. & Yonemitsu, O. (1992). Editors. *Carbocyclic Cage Compounds*. Weinheim: VCH.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Tezuka, T., Yamashita, Y. & Mukai, T. (1976). *J. Am. Chem. Soc.* **98**, 6051–6052.