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Structure of 1,2-Bis(spiro[2.3]hex-4-ene-4-yl)ethane

BY DMITRII S. YUFIT* AND YURII T. STRUCHKOV

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov St, Moscow 117813, Russia

AND KIRILL A. LUKIN, SERGEI I. KOZHUSHKOV AND NIKOLAI S. ZEFIROV

Chemistry Department, Moscow State University, Moscow 119899, Russia

Abstract. $C_{14}H_{18}$ (1), $M_r = 186.3$, monoclinic, $P2_1/c$, $a = 9.285$ (6), $b = 5.373$ (2), $c = 11.981$ (6) Å, $\beta = 112.09$ (4)°, $V = 553.8$ (1) Å^3, $Z = 2$, $D_x = 1.12$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.6$ cm^{-1}, $F(000) = 204$, $T = 183$ K, $R = 0.050$, $wR = 0.049$ for 871 observed reflections. The molecule occupies a special position at an inversion centre. The bond lengths in the three-membered ring are undisturbed due to the opposing influence of the double-bond π-system conjugation with the Walsh molecular orbital of cyclopropane and strain due to a spiro conjunction of two small rings.

Introduction. Continuing our structural investigation of the new class of hydrocarbons, triangulanes (Zefirov, Kozhushkov, Kuznetsova, Kokoreva,

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* To whom correspondence should be addressed.

Lukin, Ugrak & Tratch, 1990) and their derivatives, we report in the present paper the results of an X-ray study of (1). The compound was obtained by the reaction of the linear triangulane 1,1-dibromotrispiro[2.0.2.1]heptane with MeLi. The details of synthesis, chemistry and spectra of (1) will be published elsewhere. Besides the unequivocal confirmation of the structure of (1), the present study seemed of interest because there were no structural data on compounds with spiro-conjugated cyclopropane (CP) and cyclobutane rings (according to the Cambridge Crystallographic Database, Release 1991).

Experimental. A single transparent colourless crystal with approximate dimensions $0.2 \times 0.25 \times 0.4$ mm was mounted on a Siemens P3/PC four-circle diffractometer (graphite-monochromated, Mo $K\alpha$ radia-

tion). Accurate cell parameters were refined from setting angles of 24 reflections with $24 \leq 2\theta \leq 25°$; two standard reflections measured every 98 reflections showed no significant variations; a $\theta/2\theta$ scan mode was used and of the 1474 reflections measured within $2 \leq 2\theta \leq 75°$ ($0 \leq h \leq 11$, $-9 \leq k \leq 6$, $-20 \leq l \leq 18$), 1364 were unique ($R_{int} = 0.069$), from which 871 with $I \geq 2\sigma$ were regarded as observed. Data were corrected for Lp factors but not for absorption and extinction. The structure was solved by direct methods and refined by full-matrix least squares, anisotropically for all non-H atoms. All H atoms were located from the difference Fourier map and refined isotropically. Final discrepancy factors were $R = 0.050$, $wR = 0.049$ for 100 refined parameters (unit weights). Maximum shift/e.s.d. in the final least-squares cycle less than 0.03, the electron density in the final difference map varied from -0.18 to $+0.24$ e Å^{-3}. The atomic scattering factors were taken from the *SHELXS*86 program package (PC version) (Robinson & Sheldrick, 1988) which was used for all calculations and plotting.

Discussion. Atomic coordinates are given in Table 1,* bond lengths and angles are listed in Table 2. A view of the molecule and the numbering scheme are shown in Fig. 1.

The molecule in the crystal occupies a special position, with an inversion centre in the middle of the ethane bridge C(1)—C(1a), giving it an *s-trans*-configuration relative to this bond. The four-membered cyclobutene ring is planar to within 0.008 Å and the dihedral angle between the planes of the three- and four-membered rings is 89.5°. The bond lengths in the cyclopropane ring (average 1.505 Å) are in good agreement with the average C—C distances for cyclopropane derivatives, 1.509 Å (Allen, 1980). The C(2)=C(3) distance is similar to that reported for cyclobutene by microwave data (Bak, Led, Nygaard, Rastrup-Andersen & Sorensen, 1969), but the C(2)—C(5) and C(3)—C(4) bond lengths of 1.498 (3) and 1.525 (3) Å, respectively, are significantly different.

This difference could result from the conjugation of the cyclobutane double-bond π-system with the Walsh $3e_A$-MO of the cyclopropane ring as observed, *e.g.* in vinylcyclopropane (VCP) (Nijveldt & Vos, 1988). The elongation of vicinal bonds and the contraction of distal bonds observed in VCP are common for CP derivatives with electron withdrawing substituents (Allen, 1980). The equivalence of

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement coefficients* (Å$^2 \times 10^3$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	9469 (2)	3982 (4)	10068 (2)	25 (1)
C(2)	8565 (2)	2705 (4)	8912 (2)	24 (1)
C(3)	8649 (3)	2559 (5)	7817 (2)	31 (1)
C(4)	7317 (3)	701 (5)	7319 (2)	33 (1)
C(5)	7218 (2)	943 (4)	8579 (2)	27 (1)
C(6)	6874 (3)	-1007 (5)	9338 (2)	32 (1)
C(7)	5775 (3)	1152 (5)	8868 (2)	33 (1)

Table 2. *Bond lengths* (Å) *and angles* (°)

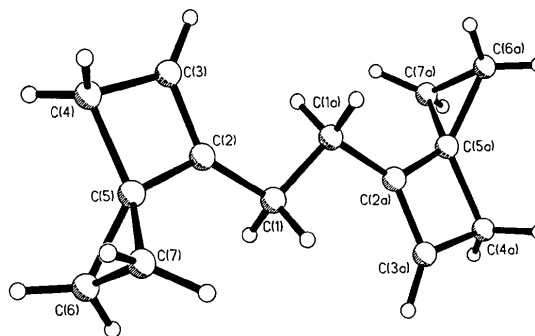|				
C(1)—C(2)	1.490 (3)	C(4)—C(5)	1.552 (3)
C(1)—C(1a)	1.522 (5)	C(5)—C(6)	1.499 (4)
C(2)—C(3)	1.344 (3)	C(5)—C(7)	1.509 (4)
C(2)—C(5)	1.498 (3)	C(6)—C(7)	1.507 (4)
C(3)—C(4)	1.525 (3)		
C(2)—C(1)—C(1a)	113.1 (2)	C(2)—C(5)—C(6)	128.9 (2)
C(1)—C(2)—C(3)	135.6 (2)	C(4)—C(5)—C(6)	129.5 (2)
C(1)—C(2)—C(5)	131.3 (2)	C(2)—C(5)—C(7)	128.1 (2)
C(3)—C(2)—C(5)	93.0 (2)	C(4)—C(5)—C(7)	127.7 (2)
C(2)—C(3)—C(4)	94.8 (2)	C(6)—C(5)—C(7)	60.1 (2)
C(3)—C(4)—C(5)	84.3 (2)	C(5)—C(6)—C(7)	60.3 (2)
C(2)—C(5)—C(4)	87.9 (2)	C(5)—C(7)—C(6)	59.6 (2)

Fig. 1. Molecular structure and numbering scheme.

bond lengths in the CP ring of (1) and the elongation of the C(2)—C(5) bond in comparison with VCP (1.478 Å) may seem to contradict the conjugation effects mentioned above. However, it should be noticed that the CP ring and the C(2)=C(3) double bond in (1) are parts of the strained, rigid bicyclic system and the spiro conjugation of CP with another small ring is known to result in significant elongation of the distal bond, which decreases the strain at the spiro atom. This effect was discussed by Boese (Boese, Miebach & De Meijere, 1991) on comparing the spiropentane and [n]rotane structures and was also observed in our previous studies of triangulane structures (Yufit, Lukin, Kozhushkov, Struchkov & Zefirov, 1991; Zefirov, Kozhushkov, Ugrak, Lukin, Kokoreva, Yufit, Struchkov, Zoellner, Boese & De Meijere, 1992). At the same time, there are no significant deviations of the CP bond distances in two

4-methylenespiro[2.3]heptane derivatives (Boese, 1992) with fixed *s-cis*-orientations of the CP rings and double bonds. The opposing influence of strain forces, leading to the distal bond elongation in the CP ring, and the conjugation of the CP molecular orbital with the double bond leading to this bond shortening results in the almost undisturbed CP ring geometry in this class of compound, as well as in molecule (1). This effect is the same for molecules with either *s-cis* or *s-trans*-orientation [*e.g.* (1)] of the double bond and CP ring.

The small lengthening of the C(2)—C(5) bond is probably also caused by the strain in the bicyclic system. The lengths of the double bonds in the vinyl substituted CP ring are not sensitive to conjugation (Allen, 1981), and therefore the absence of any elongation of the C(2)=C(3) bond distance in (1) is not unusual. The other geometrical parameters of (1) are unexceptional.

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Structure of 4,5-(Pentasulfane-1,5-diyl)-1,3-dithiole-2-thione

BY VYACHESLAV N. BAUMER, VLADIMIR A. STARODUB AND VLADIMIR P. BATULIN

Institute of Chemistry at Kharkov State University, Dzershinsky Square 4, Kharkov 310077, Ukraine

EUGENII E. LAKIN AND VALERII P. KUZNETSOV

Institute for Single Crystals of Academy of Sciences of Ukraine, Kharkov 310001, Ukraine

AND OLEG A. DYACHENKO*

Institute of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow Region 142432, Russia

Abstract. [1,3]Dithiolo[4,5-*f*]pentathiepine-7-thione, C_3S_8, $M_r = 292.5$, triclinic, $P\bar{1}$, $a = 4.4204$ (5), $b = 9.136$ (1), $c = 11.762$ (2) Å, $\alpha = 101.61$ (1), $\beta = 96.20$ (1), $\gamma = 92.28$ (1)°, $V = 461.6$ (1) Å^3, $Z = 2$, $D_x = 2.105$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.790$ mm^{-1}, $F(000) = 292$, $T = 290$ K, $R = 0.035$, $wR = 0.042$ for 1170 observed reflections. The C_3S_8 molecule in the crystal has a local *m* symmetry and shows a chair conformation of the seven-membered ring containing five S and two C atoms. The central part of this ring makes dihedral angles of 68.6° with the C_3S_5 group and 71.6° with the terminal S_3 group.

Introduction. Sulfur–organic compounds containing the 2-thioxo-1,3-dithiole-4,5-dithiolate group C_3S_5

(dmit) are used for synthesis of organic metals and superconductors such as BEDT–TTF salts and square-planar organometallics (Kaminskii, Prokhorova, Shibaeva & Yagubskii, 1984; Cassoux, Valade, Kobayashi, Kobayashi, Clark & Underhill, 1991; Shklover, Nagapetyan & Struchkov, 1990). We have carried out the synthesis of the new 4,5-poly-sulfanediyl-1,3-dithiole-2-thiones, details of which will be published elsewhere (Starodub & Baumer, 1993). X-ray structure analysis was used for characterization of each component of the mixture of reaction products. The main product of the synthesis is 4,5-(pentasulfane-1,5-diyl)-1,3-dithiole-2-thione, the structure of which is reported in this paper.

Experimental. The title compound forms thin yellow folium-shaped blocked crystals with dimensions of

* Author for correspondence.