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1,1'-Diphenyl-1,1'-bicyclopropyl and 1,1'-Diphenyl-1,1'-bicyclobutyl

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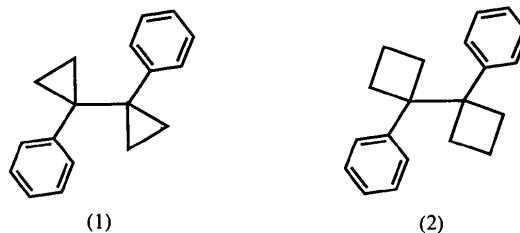
Abstract

The molecules of 1,1'-diphenyl-1,1'-bicyclopropyl, $C_{18}H_{18}$, and 1,1'-diphenyl-1,1'-bicyclobutyl, $C_{20}H_{22}$, each possess a crystallographic centre of symmetry. Both molecules adopt the *trans* conformation. The cyclopropyl rings are approximately symmetric while the cyclobutyl rings are slightly folded.

Comment

The study of steric influences is of increasing importance not only in organic chemistry. Studies of the relationships between structure and activity of drugs attest to intermolecular effects as one of the reasons for the high selectivity of biochemical and recognition processes, which have been described, *inter alia*, as docking processes between an active substance and its receptor (Yalkowsky, Sinkuk & Valvani, 1980). During a study of the relationship between thermal stability, strain and structure in a series of 1,1'-diphenyl-1,1'-bicycloalkyls (C_4 – C_8), Bernlöhner, Beckhaus, Lindner & Rüchardt (1984) determined the crystal structure of 1,1'-diphenyl-1,1'-bicyclooctyl and found it to have a *trans* conformation. Using MM2 calculations, they concluded that the bicycloheptyl and -hexyl compounds would have the *trans* conformation but that the -pentyl and

-butyl compounds would adopt the *gauche* form. We have recently investigated the structures and conformational equilibrium of 1,1'-diphenyl-1,1'-bicycloheptyl, -hexyl and -pentyl (Zhang, Xu, Koh, Lam & Huang, 1993). In view of our interest in diphenylethane derivatives, we decided to investigate the structures of other members of the 1,1'-diphenyl-1,1'-bicycloalkyl family of compounds to provide the experimental structural data which had hitherto been lacking. In this paper, we report the crystal structures of 1,1'-diphenyl-1,1'-bicyclopropyl, (1), and 1,1'-diphenyl-1,1'-bicyclobutyl, (2).



Molecule (1) is centrosymmetric and takes the *trans* conformation in the crystal, as in 1,1'-bicyclopropyl (Eraker & Rømming, 1967). This contrasts with 1-nitro-1'-nitroso-1,1'-bicyclopropyl, 1,1'-dinitro-1,1'-bicyclopropyl (Kai *et al.*, 1982) and 1,1'-dicyano-1,1'-bicyclopropyl (Schrumpp & Jones, 1987), which each exist as the *gauche* rotamer. The C(12)—C(11)—C(1) plane makes an angle of $86.9(2)^\circ$ with the plane through the central C atoms C(11), C(1) and C(1a). The central C(1)—C(1a) bond is longer than the corresponding bonds in 1,1'-bicyclopropyl (Eraker & Rømming, 1967) and the other substituted bicyclopropyls (Schrumpp & Jones, 1987; Kai *et al.*, 1982). The length of the central C—C bond appears not to be correlated with a single parameter, but to be influenced by several factors, *e.g.* conjugation between the two cyclopropane moieties, steric factors and electronic effects of the substituents at C(1) and C(1a).

The bond angles around the two central C atoms reveal evidence of intramolecular stress, the angle C(12)—C(11)—C(16) showing the largest deviation from 120° of any of the internal phenyl ring angles.

Molecule (2) is situated at a centre of symmetry with approximate C_{2h} symmetry and adopts the *trans* conformation. The C(12)—C(11)—C(1) plane is orientated at an angle of $90.8(2)^\circ$ to the C(11)—C(1)—C(1a) plane. The cyclobutyl rings are slightly folded forming a 'butterfly'-type square with C(3) bending away from the phenyl ring attached to C(1). The dihedral angle between the C(2)—C(1)—C(4) and C(2)—C(3)—C(4) planes is $17.5(2)^\circ$. This contrasts with 1,1'-dinitro-1,1'-bicyclobutyl which exists as a *gauche* conformer in the crystalline state and has approximately planar cyclobutane rings (Kai *et al.*, 1982). The central C(1)—C(1a) bond is much longer than in (1). This is consistent with

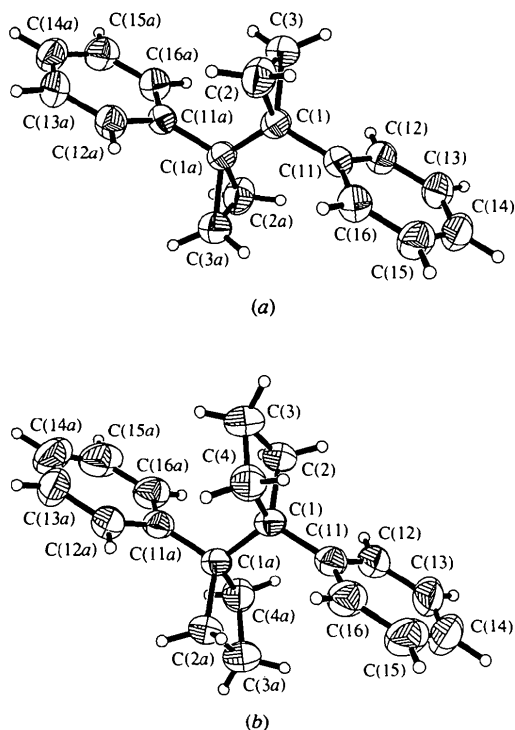


Fig. 1. ORTEP (Johnson, 1965) plots of (a) compound (1), and (b) compound (2), with ellipsoids at the 50% probability level.

The AMI calculations also failed to reproduce the greater stability of the *trans* form as observed in X-ray results. Analysis of the optimized geometries showed that although the *trans* and *gauche* conformers have similar bond lengths and angles, in the *trans* arrangement the interatomic distance (~ 2.6 Å) between the β -H atoms on the cycloalkyl rings and the nearest C atoms of the vicinal phenyl groups is 1.4 Å smaller than that in the *gauche* form. As the π -electron clouds could extend 1.5–2.0 Å beyond the plane of the ring, this implies that in the *trans* conformer the β -H atoms on the cycloalkyl rings would be strongly interacting with the π -electron clouds. However, it should be borne in mind that AMI calculations strictly refer to the situation in the gas phase and it is highly probable that the gas phase geometry may differ from that imposed by the solid state.

Experimental

1,1'-Diphenyl-1,1'-bicyclopropyl, (1), was synthesized in two steps from 2,3-diphenyl-1,3-butadiene, according to the method described by Beckhaus, Schoch & Röchardt (1976). The compound was purified by silica column chromatography with petroleum ether:benzene (6:1) as the eluant. M.p. 331–332 K (literature m.p. 330–331 K; Beckhaus, Schoch & Röchardt, 1976). Single crystals for X-ray measurements were obtained from ethanol under dry ice/ethanol temperature. 1,1'-Diphenyl-1,1'-bicyclobutyl, (2), was prepared by the coupling of 1-phenylcyclobutanol with titanium trichloride and lithium aluminium hydride (McMurry, 1975). 1-Phenylcyclobutanol was obtained in quantitative yield by the reaction of cyclobutanone with phenylmagnesium bromide. Compound (2) was purified by silica column chromatography using hexane:ethyl acetate (3.5:0.5) as eluant. M.p. 377–378 K (literature m.p. 377–378 K; Beckhaus, Schoch & Röchardt, 1976). Over a period of several months, well formed crystals were grown from a mixture of hexane/benzene solution.

Compound (1)

Crystal data

C₁₈H₁₈
 $M_r = 234.3$
 Monoclinic
 $P2_1/n$
 $a = 7.679(2)$ Å
 $b = 5.891(1)$ Å
 $c = 14.800(3)$ Å
 $\beta = 91.28(3)^\circ$
 $V = 669.4(3)$ Å³
 $Z = 2$
 $D_x = 1.163$ Mg m⁻³

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 15 reflections
 $\theta = 2.8$ – 12.8°
 $\mu = 0.065$ mm⁻¹
 $T = 298$ K
 Plate
 $0.40 \times 0.30 \times 0.30$ mm
 Colourless

Data collection

Siemens R3m/V diffractometer
 ω scans
 Absorption correction: none

$R_{int} = 0.0316$
 $\theta_{max} = 24^\circ$
 $h = 0 \rightarrow 9$
 $k = 0 \rightarrow 7$
 $l = -17 \rightarrow 17$

the increased steric crowding expected on expansion of the ring. Table 5 summarizes the values of the central C—C bond lengths and C(2)—C(1)—C(*n*) angles ($n = 3$ – 8) in various 1,1'-disubstituted-1,1'-bicycloalkyl compounds. The central C—C bond length increases as the crowding around the two central C atom increases. The bond length is shortest for $n = 3$ and reaches a maximum length at $n = 7$. Further increase in ring size shows no effect on the central C—C bond length. Replacing the phenyl rings with nitro or cyano groups causes angle C(2)—C(1)—C(*n*) to widen relative to those of the 1,1'-diphenyl-1,1'-bicycloalkyl series. This degree of widening, however, decreases as n gets smaller. Bernlöhr *et al.* (1984) have calculated the energies of the rotamers of some 1,1'-diphenyl-1,1'-bicycloalkyl compounds ($n = 4$ – 8) using an empirical force field (EFF) combined with the MM2 force field. Their calculations showed that in 1,1'-diphenyl-1,1'-bicyclobutyl, the *gauche* conformer is more stable than the *trans*. Our semi-empirical molecular orbital calculations carried out using AMPAC5.0 (1994) with AMI parametrization (Dewar, Zoisbisch, Healey & Stewart, 1985) show that the energy difference between the *gauche* and *trans* conformation ($\Delta E = E_g - E_t$) are -2.31 and -6.86 kJ mol⁻¹ in (1) and (2), respectively. From the Boltzmann distribution, the *gauche* populations would be 83.6 and 96.9% at 298 K.

1270 measured reflections
1178 independent reflections
720 observed reflections
[$F > 4\sigma(F)$]

3 standard reflections
monitored every 97
reflections
intensity variation: $\pm 1.5\%$

$V = 1500 (2) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.162 \text{ Mg m}^{-3}$

Prism
 $0.50 \times 0.50 \times 0.40 \text{ mm}$
Colourless

RefinementRefinement on F $R = 0.0397$ $wR = 0.0473$ $S = 1.24$

720 reflections

83 parameters

H-atom parameters not refined

 $w = 1/[\sigma^2(F) + 0.0006F^2]$ $(\Delta/\sigma)_{\max} = 0.010$ $\Delta\rho_{\max} = 0.16 \text{ e \AA}^{-3}$ $\Delta\rho_{\min} = -0.12 \text{ e \AA}^{-3}$

Extinction correction:

$$F^* = F[1 + (0.002\chi \times F^2/\sin 2\theta)]^{-1/4}$$

Extinction coefficient:

$$\chi = 0.0016 (10)$$

Atomic scattering factors

from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV)

Data collection

Siemens R3m/V diffractometer

 ω scans

Absorption correction:

none

1182 measured reflections

1182 independent reflections

818 observed reflections

[$F > 4\sigma(F)$] $\theta_{\max} = 24^\circ$ $h = 0 \rightarrow 12$ $k = 0 \rightarrow 8$ $l = 0 \rightarrow 19$

3 standard reflections

monitored every 97

reflections

intensity variation: $\pm 1.5\%$ **Refinement**Refinement on F $R = 0.0354$ $wR = 0.0437$ $S = 1.37$

818 reflections

92 parameters

H-atom parameters not refined

 $w = 1/[\sigma^2(F) + 0.0004F^2]$ $(\Delta/\sigma)_{\max} = 0.002$ $\Delta\rho_{\max} = 0.11 \text{ e \AA}^{-3}$ $\Delta\rho_{\min} = -0.10 \text{ e \AA}^{-3}$

Extinction correction:

$$F^* = F[1 + (0.002\chi \times F^2/\sin 2\theta)]^{-1/4}$$

Extinction coefficient:

$$\chi = 0.0021 (3)$$

Atomic scattering factors

from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (1)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
C(1)	-0.0722 (2)	0.0412 (3)	0.0306 (1)	0.041 (1)
C(2)	-0.2581 (3)	0.0109 (4)	-0.0006 (1)	0.061 (1)
C(3)	-0.1794 (3)	0.2435 (4)	0.0000 (1)	0.059 (1)
C(11)	-0.0376 (2)	0.0229 (3)	0.1311 (1)	0.040 (1)
C(12)	0.0482 (3)	0.1953 (3)	0.1784 (1)	0.048 (1)
C(13)	0.0775 (3)	0.1806 (4)	0.2706 (1)	0.057 (1)
C(14)	0.0223 (3)	-0.0070 (4)	0.3178 (1)	0.059 (1)
C(15)	-0.0620 (3)	-0.1799 (4)	0.2721 (1)	0.059 (1)
C(16)	-0.0914 (3)	-0.1659 (4)	0.1796 (1)	0.050 (1)

Table 2. Selected geometric parameters (\AA , $^\circ$) for (1)

C(1)—C(2)	1.501 (3)	C(1)—C(3)	1.512 (3)
C(1)—C(11)	1.508 (3)	C(1)—C(1 ¹)	1.527 (4)
C(2)—C(3)	1.497 (3)		
C(2)—C(1)—C(3)	59.6 (1)	C(2)—C(1)—C(11)	116.1 (2)
C(3)—C(1)—C(11)	115.8 (2)	C(2)—C(1)—C(1 ¹)	118.6 (2)
C(3)—C(1)—C(1 ¹)	118.1 (2)	C(11)—C(1)—C(1 ¹)	116.6 (2)
C(1)—C(2)—C(3)	60.6 (1)	C(1)—C(3)—C(2)	59.8 (1)
C(1)—C(11)—C(12)	121.0 (2)	C(1)—C(11)—C(16)	121.2 (2)
C(3)—C(1)—C(1 ¹)—C(2 ¹)	111.3 (2)		
C(2)—C(1)—C(1 ¹)—C(11 ¹)	33.6 (2)		
C(11)—C(1)—C(1 ¹)—C(3 ¹)	35.1 (2)		
C(1 ¹)—C(1)—C(11)—C(12)	86.9 (2)		
C(1 ¹)—C(1)—C(3)—C(2)	108.4 (2)		
C(1 ¹)—C(1)—C(2)—C(3)	-107.6 (2)		

Symmetry code: (i) $-x, -y, -z$.**Compound (2)****Crystal data** $\text{C}_{20}\text{H}_{22}$ $M_r = 262.4$

Orthorhombic

Pbca $a = 11.20 (1) \text{ \AA}$ $b = 7.627 (7) \text{ \AA}$ $c = 17.56 (1) \text{ \AA}$ Mo $K\alpha$ radiation $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 20 reflections

 $\theta = 5.0\text{--}19.2^\circ$ $\mu = 0.065 \text{ mm}^{-1}$ $T = 298 \text{ K}$ Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
C(1)	0.5116 (1)	0.0397 (2)	0.4595 (1)	0.041 (1)
C(2)	0.4624 (2)	0.2303 (2)	0.4500 (1)	0.055 (1)
C(3)	0.5878 (2)	0.3030 (2)	0.4607 (1)	0.071 (1)
C(4)	0.6393 (2)	0.1188 (2)	0.4511 (1)	0.056 (1)
C(11)	0.4760 (2)	-0.0846 (2)	0.3961 (1)	0.047 (1)
C(12)	0.3612 (2)	-0.0815 (2)	0.3650 (1)	0.057 (1)
C(13)	0.3282 (2)	-0.1960 (3)	0.3074 (1)	0.079 (1)
C(14)	0.4091 (3)	-0.3151 (3)	0.2795 (1)	0.095 (1)
C(15)	0.5230 (3)	-0.3191 (3)	0.3081 (1)	0.086 (1)
C(16)	0.5571 (2)	-0.2043 (2)	0.3659 (1)	0.063 (1)

Table 4. Selected geometric parameters (\AA , $^\circ$) for (2)

C(1)—C(2)	1.564 (3)	C(1)—C(4)	1.559 (3)
C(1)—C(11)	1.514 (3)	C(1)—C(1 ¹)	1.569 (3)
C(2)—C(3)	1.522 (3)	C(3)—C(4)	1.528 (3)
C(2)—C(1)—C(4)	87.3 (1)	C(2)—C(1)—C(11)	114.3 (1)
C(4)—C(1)—C(11)	114.5 (1)	C(2)—C(1)—C(1 ¹)	113.4 (2)
C(4)—C(1)—C(1 ¹)	112.8 (2)	C(11)—C(1)—C(1 ¹)	112.4 (2)
C(1)—C(2)—C(3)	90.0 (1)	C(2)—C(3)—C(4)	90.0 (1)
C(1)—C(4)—C(3)	90.0 (1)	C(1)—C(11)—C(12)	121.3 (2)
C(1)—C(11)—C(16)	121.3 (2)		
C(2)—C(1)—C(1 ¹)—C(4 ¹)	82.7 (2)		
C(4)—C(1)—C(1 ¹)—C(11 ¹)	48.7 (2)		
C(11)—C(1)—C(1 ¹)—C(2 ¹)	48.5 (2)		
C(1 ¹)—C(1)—C(11)—C(12)	90.8 (2)		
C(1 ¹)—C(1)—C(2)—C(3)	101.4 (2)		
C(1 ¹)—C(1)—C(4)—C(3)	-102.0 (2)		

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

Table 5. Central inter-ring C—C bond lengths (Å) and carbocyclic ring angles C(2)—C(1)—C(n) (°) at the central C(1) atom in the solid state of various 1,1'-(R)(R)-1,1'-bicycloalkyl molecules

Carbocyclic ring	n	R = nitro	R = cyano	R = phenyl
	3	1.476 (3)*	1.501 (4)†	1.527 (4)¶
	4	1.508 (9)*	—	1.569 (3)¶
	5	1.486 (4)†	1.537 (5)§	1.575 (5)**
	6	1.579 (3)†	1.582 (10)§	1.627 (5)**
	7	1.601 (9)†	1.591 (6)§	1.630 (5)**
	8	—	—	1.622††
	3	59.1 (1)*	58.6 (2)†	59.6 (1)¶
	4	89.0 (2)*	—	87.3 (1)¶
	5	105.4 (3)†	101.9 (2)§	98.9 (3)**
	6	110.2 (1)†	108.9 (4)§	105.5 (2)**
	7	113.2 (6)†	111.4 (3)§	108.0 (4)**
	8	—	—	107.6††

* Kai *et al.* (1982); † Lam, Huang & Hambley (1990); ‡ Schrupf & Jones (1987); § Koh, Huang & Sim (1992); ¶ this work; ** Zhang *et al.* (1993); †† Bernlöhr *et al.* (1984).

The structures of (1) and (2) were solved by direct methods using XS (SHELXTL-Plus; Siemens, 1989) and refined by full-matrix least-squares analysis using XLS (SHELX76; Sheldrick, 1976; SHELXS86; Sheldrick, 1985). Data were reduced using the above-mentioned programs. C atoms were refined anisotropically whereas H atoms were placed at calculated positions with fixed isotropic displacement parameters.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1191). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 400–403

Bis(methylthio)ethylenedithiotetrafulvalene

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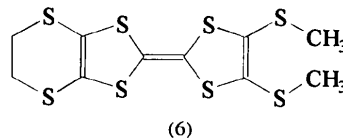
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Abstract

The title compound {alternative nomenclature: 2-[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiine}, C₁₀H₁₀S₈, is a molecular crystal with typical values for bond distances and angles. The molecules form columns along the *c* axis. The intermolecular S··S distances indicate the presence of van der Waals interactions between the columns.

Comment

Many charge-transfer complexes based on donors containing the tetrathiafulvalene (TTF) unit have been reported (Bechgaard *et al.*, 1981; Bender *et al.*, 1984; Karpova, Konovalikhin, Dyachenko, Lyubovskaya & Zhilyaeva, 1992; Mori *et al.*, 1990; Qian *et al.*, 1988; Shibaeva, Kaminskii & Yagubskii, 1985). We have prepared a new organic compound, (6), which is a derivative of TTF.



The bond distances and angles at S are dependent on the hybridization state of the C atom to which S is bound, so that S—C_{sp³} is longer than S—C_{sp²} and the angles are wider in the case of an sp²-hybridized C