(Fig. 2). The dihedral angle between the pyridine rings is 61.3°, in good agreement with the value for the La^{III} complex (Al-Karaghouli, Day & Wood, 1978). The central C—C distance is also similar to that in the La^{III} complex, but the N—O distance is shorter by 0.03 Å. There are no unusual short intermolecular distances.

Experimental

The title compound was prepared according to the method of Kanno, Yamamoto, Murahashi, Utsuno & Fujita (1991) and recrystallized from methanol.

Crystal data

$C_{12}H_{12}N_2O_2$
$M_r = 216.24$
Monoclinic
$C2/c$
$a = 11.232\ (4)$ Å
$b = 9.175\ (3)$ Å
$c = 10.444\ (4)$ Å
$\beta = 107.09\ (3)°$
$V = 1028.8\ (7)$ Å^3
$Z = 4$
$D_x = 1.396$ Mg m^{-3}
$D_m = 1.38$ Mg m^{-3}
D_m measured by flotation in a mixture of benzene and carbon tetrachloride

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 23 reflections
$\theta = 14.3–17.5°$
$\mu = 0.097$ mm^{-1}
$T = 298$ K
Needle
0.40 × 0.30 × 0.25 mm
Colourless

Data collection

MAC Science MXC3 diffractometer
$2\theta/\omega$ scans
Absorption correction: none
1328 measured reflections
1087 independent reflections
948 reflections with $I > 1.25\sigma(I)$

$R_{\rm int} = 0.027$
$\theta_{\rm max} = 26.43°$
$h = -14 \rightarrow 13$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 13$
3 standard reflections every 100 reflections intensity decay: < 2%

Refinement

Refinement on F
$R = 0.0572$
$wR = 0.0585$
$S = 1.590$
948 reflections
73 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o) + 0.0005F_o^2]$

$(\Delta/\sigma)_{\rm max} = 0.0025$
$\Delta\rho_{\rm max} = 0.26$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.29$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

O1—N1	1.301 (2)	C2—C3	1.391 (2)
N1—C1	1.370 (2)	C3—C4	1.387 (2)
N1—C5	1.362 (2)	C3—C6	1.494 (3)
C1—C1^{i}	1.482 (2)	C4—C5	1.361 (2)
C1—C2	1.375 (2)		
O1—N1—C1	120.8 (2)	C1—C2—C3	122.1 (2)
O1—N1—C5	120.4 (2)	C2—C3—C4	115.7 (2)
C1—N1—C5	118.8 (2)	C2- C3—C6	121.4 (2)
N1—C1—C1^{i}	117.3 (2)	C4—C3—C6	122.8 (2)
N1—C1—C2	120.0 (2)	C3—C4—C5	122.1 (2)
C1^{i}—C1—C2	122.6 (2)	N1—C5—C4	121.1 (2)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

The space group was finally determined from the Wilson plot. The structure was solved by direct methods and refined by full-matrix least-squares calculations using *CRYSTAN* (Gilmore & Brown, 1988). H atoms were found from the difference Fourier map at the final stage and were restricted to their parent atoms with C—H distances of 0.96 Å and the corresponding equivalent isotropic displacement parameters.

Data collection: MXC software (MAC Science Co. Ltd, 1989). Cell refinement: MXC software. Data reduction: *CRYSTAN*. Program(s) used to solve structure: *CRYSTAN*. Molecular graphics: *ORTEP* (Johnson, 1965) and *CRYSTAN*. Software used to prepare material for publication: *CRYSTAN*.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: OH1103). 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. (1997). C**53**, 499-504

meso-2,2,2′,2′-Tetrachloro-1,1′-diphenyl-1,1′-bicyclopropyl and *meso*-2,2,2′,2′-Tetrabromo-1,1′-diphenyl-1,1′-bicyclopropyl

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Abstract

Molecules of *meso*-2,2,2′,2′-tetrachloro-1,1′-diphenyl-1,1′-bicyclopropyl, $C_{18}H_{14}Cl_4$, (1), and *meso*-2,2,2′,2′-tetrabromo-1,1′-diphenyl-1,1′-bicyclopropyl, $C_{18}H_{14}Br_4$, (2), adopt *gauche* conformations. Compound (1) produced two types of crystals upon recrystallization. The phenyl rings of the two forms of compound (1), as well as those of compound (2), are in a nearly perpendicular orientation. All three structures have unsymmetrical

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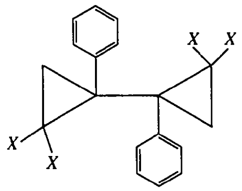
cyclopropane rings, with the shortest C—C bond being between the rings at the point of phenyl substitution.

Comment

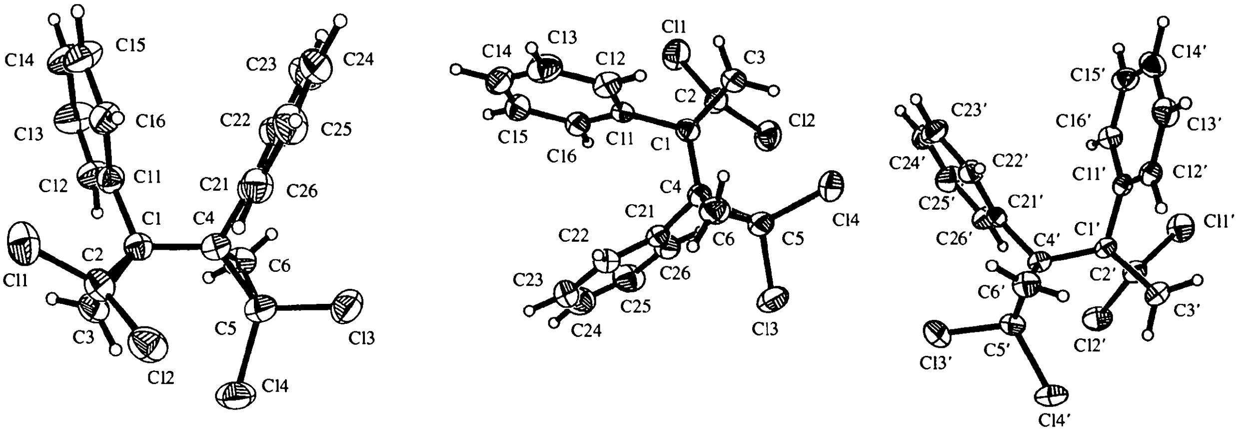
The unique ability of the cyclopropyl system to conjugate with other groups has long been recognized (Eastman & Freeman, 1955; Bartell, Guillory & Parks, 1965; de Meijere, 1979). Spectroscopic and chemical studies of various substituted cyclopropanes have shown that the cyclopropyl group is similar to a double bond in many respects (Tidewell, 1987) and substitution may cause major changes in the geometry of the cyclopropane ring. The case of bicyclopropyl is more complicated. The solid-state configuration was shown (Eraker & Rømming, 1967) by X-ray diffraction to be the *trans* form which is the most favoured rotamer from steric considerations. The shortness of the central C—C bond, 1.487 (4) Å, suggests that conjugative interactions occur between the rings. We have recently investigated the structure of 1,1′-diphenyl-1,1′-bicyclopropyl (Lam, Koh & Huang, 1996) and found that it too has a *trans* conformation. In order to understand more fully these substitution effects, we have investigated other members of the 1,1′-diphenyl-1,1′-bicyclopropyl family of compounds. In this paper, we report the crystal structures of *meso*-2,2,2′,2′-tetrachloro-1,1′-diphenyl-1,1′-bicyclopropyl, (1) and *meso*-2,2,2′,2′-tetrabromo-1,1′-diphenyl-1,1′-bicyclopropyl, (2). Compound (1) produced two types of crystals after recrystallization; (1*a*) crystallized in the space group $P2_1/n$, while (1*b*) was orthorhombic in space group *Pbca*. The structures of the molecules in the two types of crystal are very similar in terms of bond lengths and angles. Their molecular conformations are also almost identical as can be seen in Figs. 1(*a*) and (*b*). The orthorhombic form has a higher density and is better packed; there are two crystallographically different molecules in the unit cell [see Fig. 1(*b*)]. Both molecules in the orthorhombic form are packed in a staggered manner such that a Cl atom of one molecule is wedged between the phenyl rings of its neighbours.



(1) X=Cl
(2) X=Br

In both phases, (1) adopts the *gauche* conformation with a weighted mean for the Ph—C1—C4—Ph torsion angle of 57.4 (5)°. This contrasts with *meso*-2,2,2′,2′-tetrachlorobicyclopropyl (Aroney, Calderbank & Stootman, 1974) and 1,1′-diphenyl-1,1′-bicyclopropyl (Lam, Koh & Huang, 1996), both of which exist as the *trans* rotamer. The central C—C bond averages 1.532 (6) Å, compared with 1.487 (4) Å in bicyclopropyl and 1.481 (4) Å in *meso*-2,2,2′,2′-tetrachloro-3,3,3′,3′-tetramethylbicyclopropyl (Rømming & Sydnes, 1976). The length of the central C—C bond does not appear 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 C1 and C4.

The bond angles around the two central C atoms show evidence of intramolecular stress, the angles C12—C11—C16 and C22—C21—C26 having the largest deviation from 120° of any of the internal phenyl ring angles. Apart from the distortion in the internal phenyl bond angles, the orientation of both the phenyl rings also displays evidence of intramolecular stress. According to



(*a*) (*b*)

Fig. 1. *ORTEP* (Johnson, 1965) plots of (*a*) compound (1*a*) and (*b*) compound (1*b*) with ellipsoids at the 35% probability level. There are two crystallographically different molecules in the unit cell of compound (1*b*).

the molecular orbital model of Hoffmann & Davidson (1971), π substituents favour the bisected conformation [Fig. 2(*a*)] over the perpendicular orientation [Fig. 2(*b*)] because in the former orientation, one of the degenerate pairs of HOMOs of the cyclopropane ring conjugates with the LUMO of the π substituent. However, in compound (1), both phenyl rings adopt a nearly perpendicular conformation with respect to the central C—C bond, the torsion angles C4—C1—C11—C16 and C1—C4—C21—C26 being −85.2 (5) and 73.9 (5)°, respectively. Since these angles are not precisely 90°, some overlap between the orbitals is possible. The presence of π interaction is further borne out by the structures of the cyclopropyl rings. Examination of the cyclopropyl structures indicates that the rings are unsymmetrical with unequal C—C bond lengths. The bond between the cyclopropyl rings at the point of phenyl substitution is distinctly shorter than the two bonds adjacent to the point of substitution. Although the differences in bond lengths between the adjacent and inter-ring bonds are not extreme, they are significant and of an order of magnitude comparable with various previously observed cases where the cyclopropyl ring enters into π-type conjugation with its π-interacting substituents (Schrumpf & Jones, 1987; Kai *et al.*, 1982; Lauher & Ibers, 1975, and references cited therein). Furthermore, comparison of the two cyclopropyl rings in compound (1*b*) shows that the difference in bond lengths between the adjacent and inter-ring bonds is greater when the phenyl substituent deviates more from the perpendicular orientation. This result is consistent with the molecular orbital model for the cyclopropyl system.

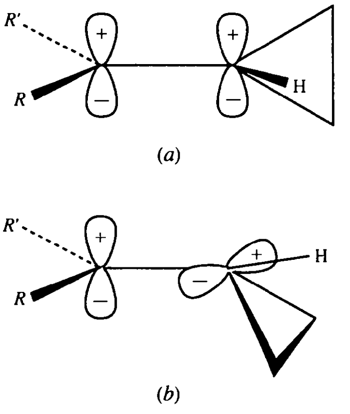


Fig. 2. Hoffmann & Davidson's (1971) molecular orbital model of π substituents in (*a*) the bisected conformation and (*b*) the perpendicular orientation.

The Cl—C bond lengths average 1.760 (4) Å, slightly longer than in 1,1-dichlorocyclopropane [1.734 (2) Å] (Flygare, Narath & Gwinn, 1962), but, within the accuracy of the determinations, the same as in 1,1-dichloro-2,2-diphenylcyclopropane [1.754 (2) Å] (Lauher & Ibers, 1975). The Cl—C—Cl bond angle, 109.4 (2)°, is almost ideally tetrahedral.

Compound (2) does not possess crystallographic symmetry and adopts a *gauche* conformation with a Ph—C1—C4—Ph torsion angle of 64.1 (6)° (Fig. 3). This contrasts with *anti-cis,cis*-2,2′-dibromobicyclopropyl (Schrumpf & Süsse, 1972) and *meso*-2,2,2′2′-tetrabromobicyclopropyl (Aroney, Calderbank & Stootman, 1974), both of which exist in the *trans* form. As in compound (1), the phenyl groups in compound (2) are in nearly perpendicular orientations with respect to the central C—C bond, the torsion angles C4—C1—C11—C16 and C1—C4—C21—C26 being −81.4 (7) and 77.8 (7)°, respectively. The cyclopropyl rings are also unsymmetrical, indicating the presence of π interactions between the cyclopropyl rings and the phenyl substituents. The three ring C—C bonds average 1.516 (8) Å in length, which is not significantly longer than the average value of 1.498 (6) Å in 1,1-dibromo-2,2-diphenylcyclopropane (Lauher & Ibers, 1975).

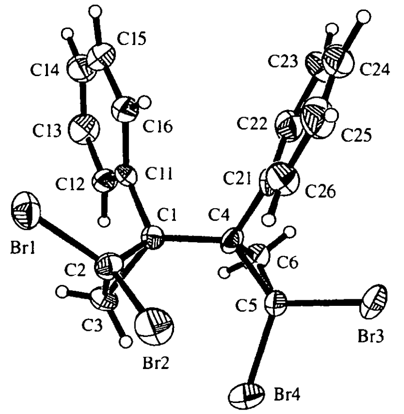


Fig. 3. *ORTEP* plot of compound (2) with ellipsoids at the 35% probability level.

The effects of bromine substitution are evident. The Br atoms interact primarily through the σ bond and have an equal effect on all the bond lengths in the cyclopropane ring. The average ring C—C bond lengths are 1.481 (2) Å in *anti-cis,cis*-2,2′-dibromobicyclopropyl (Schrumpf & Süsse, 1972) and 1.516 (8) Å in compound (2). Increasing substitution lengthens the mean bond distance, perhaps because the electronegative Br atoms withdraw electron density from the ring.

We have also carried out semi-empirical molecular orbital calculations to determine the relative energies of the *gauche* and *trans* rotamers for both compounds using the program *AMPAC* (Semichem. Inc., 1994). *AM*1 parameterization (Dewar, Zoebisch, Healey & Stewart, 1985) was used and full-geometry optimization was performed for each incremental value of the ethane C—C torsion angle. Torsion angles are defined by the atoms C11—C1—C4—C21 according to the convention of

Klyne & Prelog (1960). The variation of the energy of *meso*-2,2,2′,2′-tetrachloro-1,1′-diphenylbicyclopropyl as a function of the torsion angle is shown in Fig. 4. The torsion angles of the *gauche* rotamers of lowest energy were calculated as 58 and 56° in compounds (1) and (2). The energy differences between the *gauche* and *trans* conformations ($\Delta E = E_g - E_t$) are -11.99 and -20.15 kJ mol^{-1} in compounds (1) and (2), respectively. From the Boltzmann equation, this corresponds to an exclusive *gauche* population in both compounds. The results thus obtained are in broad agreement with the experimental data.

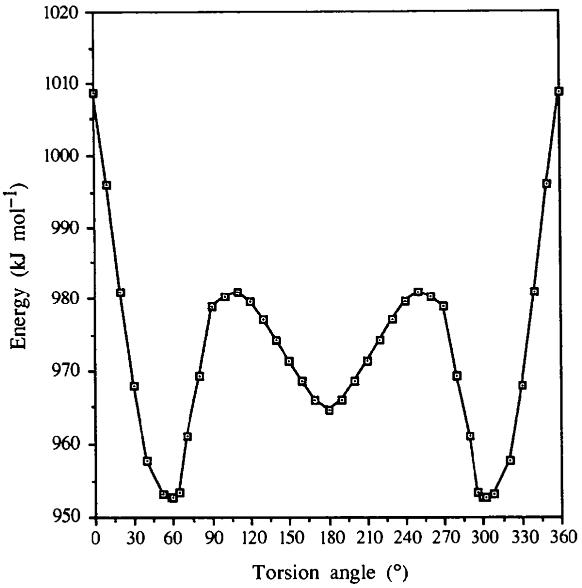


Fig. 4. Energy of *meso*-2,2,2′,2′-tetrachloro-1,1′-diphenyl-1,1′-bicyclopropyl as a function of the central torsional angle, as determined by *AM*1 calculations (Dewar, Zoebisch, Healey & Stewart, 1985).

Experimental

meso-2,2,2′,2′-Tetrachloro-1,1′-diphenyl-1,1′-bicyclopropyl, (1), and *meso*-2,2,2′,2′-tetrabromo-1,1′-diphenyl-1,1′-bicyclopropyl, (2), were synthesized from 2,3-diphenyl-1,3-butadiene according to the method described by Beckhaus, Schoch & Rüchardt (1976). Both compounds were purified by silica column chromatography with petroleum ether–benzene (6:1) as the eluant. Compound (1) had a melting point of 400–401 K [literature value 399 K (Kuhn, Marschall & Weyerstahl, 1977)]. Recrystallization of this product from ethanol gave transparent rods of the monoclinic form (1*a*), while the orthorhombic form was obtained from ethyl acetate/hexane. In each case, a crystal suitable for structure determination was obtained. Compound (2) had a melting point of 459–460 K; ^{1}H NMR ($CDCl_3$): 2.03 (*d*, J = 8.2 Hz, 2 *syn*-3-H), 2.94 (*d*, J = 8.2 Hz, 2 *anti*-3-H), 7.13–7.25 (*m*, 10 phenyl H). Analysis calculated for $C_{18}H_{14}Br_4$: C 39.32, H 2.56, Br 58.12%. Found: C 39.52, H 2.64, Br 58.30%. Single crystals for X-ray measurements were grown from a mixture of hexane/ethyl acetate solution. To our knowledge, compound (2) has not been previously reported.

Compound (1*a*)

Crystal data

$C_{18}H_{14}Cl_4$
$M_r = 372.09$
Monoclinic
$P2_1/n$
$a = 8.814\ (6)$ Å
$b = 9.992\ (9)$ Å
$c = 19.774\ (18)$ Å
$\beta = 91.60\ (7)°$
$V = 1741\ (3)$ Å^3
$Z = 4$
$D_x = 1.420$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 3.5$–$11.0°$
$\mu = 0.673$ mm^{-1}
$T = 293\ (2)$ K
Rod
0.30 × 0.25 × 0.25 mm
Colourless

Data collection

Siemens *R*3*m*/*V* diffractometer
ω scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.834$, $T_{\max} = 0.845$
3512 measured reflections
3087 independent reflections

2185 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0291$
$\theta_{\max} = 25.05°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 11$
$l = -23 \rightarrow 23$
2 standard reflections every 98 reflections intensity decay: 2.5%

Refinement

Refinement on F
$R = 0.0489$
$wR(F^2) = 0.0711$
$S = 1.09$
3087 reflections
199 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o) + 0.0021F_o^2]$

$(\Delta/\sigma)_{\max} = 0.006$
$\Delta\rho_{\max} = 0.37$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (1a)*

Cl1—C2	1.765 (4)	C1—C4	1.534 (5)
Cl2—C2	1.765 (4)	C2—C3	1.476 (5)
Cl3—C5	1.762 (4)	C4—C5	1.540 (5)
Cl4—C5	1.759 (4)	C4—C6	1.527 (5)
C1—C2	1.517 (5)	C5—C6	1.474 (5)
C1—C3	1.517 (5)		
C2—C1—C3	58.2 (2)	C16—C11—C12	118.1 (3)
C2—C1—C11	118.6 (3)	C1—C4—C5	126.7 (3)
C2—C1—C4	122.8 (3)	C5—C4—C6	57.5 (2)
C1—C2—C3	60.9 (2)	C4—C5—C6	60.8 (2)
C1—C3—C2	60.9 (2)	C22—C21—C26	118.6 (3)
C3—C1—C2—Cl1	−109.5 (3)	C4—C1—C11—C16	−85.4 (4)
C11—C1—C2—Cl1	−6.1 (4)	C2—C1—C4—C5	64.6 (4)
C4—C1—C2—Cl1	137.2 (3)	C11—C1—C4—C21	58.6 (3)
C4—C1—C2—C3	−113.3 (3)		

Compound (1*b*)

Crystal data

$C_{18}H_{14}Cl_4$
$M_r = 372.09$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Orthorhombic
Pbca
$a = 14.119$ (5) Å
$b = 11.617$ (4) Å
$c = 41.81$ (3) Å
$V = 6859$ (5) Å^3
$Z = 16$
$D_x = 1.441$ Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
$\theta = 5.7\text{–}11.0°$
$\mu = 0.683$ mm^{-1}
$T = 293$ (2) K
Prism
0.40 × 0.40 × 0.25 mm
Colourless

Data collection

Siemens *R3m/V* diffractometer
ω scans
Absorption correction: none
6176 measured reflections
4940 independent reflections
3135 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.0272$
$\theta_{\rm max} = 25.05°$
$h = -1 \rightarrow 16$
$k = -9 \rightarrow 1$
$l = -1 \rightarrow 49$
2 standard reflections every 98 reflections intensity decay: 2.5%

Refinement

Refinement on F
$R = 0.0464$
$wR(F^2) = 0.0421$
$S = 1.06$
4940 reflections
398 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o)]$
$(\Delta/\sigma)_{\rm max} = 0.013$

$\Delta\rho_{\rm max} = 0.23$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.24$ e Å^{-3}
Extinction correction: $F^* = F[1 + 0.002\chi \times F^2/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.000052 (7)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å, °) for (1b)*

Cl1—C2	1.761 (4)	Cl1′—C2′	1.766 (4)
Cl2—C2	1.761 (4)	Cl2′—C2′	1.762 (4)
Cl3—C5	1.755 (4)	Cl3′—C5′	1.752 (4)
Cl4—C5	1.762 (4)	Cl4′—C5′	1.762 (4)
C4—C5	1.536 (6)	C4′—C5′	1.534 (5)
C4—C6	1.526 (6)	C4′—C6′	1.517 (6)
C1—C4	1.529 (6)	C1′—C4′	1.532 (5)
C5—C6	1.469 (7)	C5′—C6′	1.477 (6)
C1—C2	1.505 (6)	C1′—C2′	1.509 (6)
C1—C3	1.521 (5)	C1′—C3′	1.526 (5)
C2—C3	1.472 (6)	C2′—C3′	1.473 (6)
C5—C4—C6	57.3 (3)	C5′—C4′—C6′	57.9 (3)
C5—C4—C1	126.9 (3)	C5′—C4′—C1′	126.7 (3)
C6—C4—C1	116.1 (3)	C6′—C4′—C1′	116.5 (3)
C5—C4—C21	115.5 (3)	C5′—C4′—C21′	115.8 (3)
C6—C4—C21	118.2 (4)	C6′—C4′—C21′	117.1 (3)
C1—C4—C21	112.2 (3)	C1′—C4′—C21′	112.1 (3)
Cl4—C5—C4	125.2 (3)	C4′—C5′—C6′	60.5 (3)
Cl3—C5—C4	117.5 (3)	C4′—C6′—C5′	61.6 (3)
C4—C6—C5	61.6 (3)	C4′—C1′—C2′	123.4 (3)
C4—C1—C2	123.5 (3)	C2′—C1′—C3′	58.1 (3)
C2—C1—C3	58.2 (3)	Cl1′—C2′—C1′	119.7 (3)
Cl2—C2—C1	121.0 (3)	Cl2′—C2′—C1′	120.9 (3)
Cl1—C2—C1	120.7 (3)	C1′—C2′—C3′	61.5 (3)
C1—C3—C2	60.4 (3)	C1′—C3′—C2′	60.4 (3)
C26—C21—C22	117.8 (4)	C26′—C21′—C22′	117.7 (4)
C16—C11—C12	118.9 (4)	C16′—C11′—C12′	118.4 (3)
C6—C4—C5—Cl4	−107.5 (4)	C6′—C4′—C5′—Cl3′	108.1 (3)
C6—C4—C5—Cl3	108.7 (4)	C6′—C4′—C5′—Cl4′	−106.2 (4)
C1—C4—C5—Cl4	−7.5 (7)	C1′—C4′—C5′—Cl3′	−150.9 (3)
C1—C4—C5—Cl3	−151.4 (4)	C1′—C4′—C5′—Cl4′	−5.3 (6)
C1—C4—C5—C6	100.0 (5)	C1′—C4′—C5′—C6′	100.9 (4)
C21—C4—C5—Cl4	144.1 (4)	C21′—C4′—C5′—Cl3′	1.1 (5)
C21—C4—C5—Cl3	0.3 (6)	C21′—C4′—C5′—Cl4′	146.7 (3)
C5—C4—C1—C2	64.6 (6)	C5′—C4′—C1′—C2′	60.8 (5)
C5—C4—C1—C11	−149.5 (4)	C21′—C4′—C1′—C11′	55.4 (4)
C21—C4—C1—C2	−87.8 (5)	C5′—C4′—C21′—C26′	−81.2 (5)
C21—C4—C1—C11	58.1 (5)	C4′—C1′—C2′—Cl1′	141.4 (3)
C5—C4—C21—C26	−79.1 (5)	C4′—C1′—C2′—Cl2′	−2.3 (5)
C4—C1—C2—Cl2	−5.6 (5)	C4′—C1′—C2′—C3′	−111.1 (4)
C4—C1—C2—Cl1	139.5 (3)	C3′—C1′—C2′—Cl1′	−107.6 (3)
C4—C1—C2—C3	−112.5 (4)	C11′—C1′—C2′—Cl1′	−4.0 (5)
C3—C1—C2—Cl1	−107.9 (4)	C11′—C1′—C2′—Cl2′	−147.7 (3)
C11—C1—C2—Cl1	−4.4 (5)	C4′—C1′—C11′—C16′	−86.3 (4)
C4—C1—C11—C16	−83.9 (5)	C2′—C1′—C11′—C16′	63.2 (5)

Compound (2)

Crystal data

$C_{18}H_{14}Br_4$
$M_r = 549.9$
Triclinic
$P\bar{1}$
$a = 8.432$ (2) Å
$b = 9.586$ (2) Å
$c = 11.187$ (2) Å
$\alpha = 87.19$ (2)°
$\beta = 85.51$ (2)°
$\gamma = 78.87$ (2)°
$V = 884.0$ (3) Å^3
$Z = 2$
$D_x = 2.066$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10\text{–}20°$
$\mu = 9.099$ mm^{-1}
$T = 293$ (2) K
Block
0.40 × 0.30 × 0.20 mm
Colourless

Data collection

Siemens *R3m/V* diffractometer
ω scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\rm min} = 0.071$, $T_{\rm max} = 0.162$
3075 measured reflections
2866 independent reflections

2229 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0569$
$\theta_{\rm max} = 25.05°$
$h = 0 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -13 \rightarrow 13$
2 standard reflections every 98 reflections intensity decay: 2.5%

Refinement

Refinement on F
$R = 0.0421$
$wR(F^2) = 0.0645$
$S = 0.92$
2866 reflections
200 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o) + 0.0034F_o^2]$
$(\Delta/\sigma)_{\rm max} = 0.003$

$\Delta\rho_{\rm max} = 1.02$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.49$ e Å^{-3}
Extinction correction: $F^* = F[1 + 0.002\chi \times F^2/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0010 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (2)*

Br1—C2	1.919 (6)	C1—C11	1.517 (9)
Br2—C2	1.927 (6)	C2—C3	1.488 (8)
Br3—C5	1.925 (7)	C4—C5	1.536 (8)
Br4—C5	1.926 (7)	C4—C6	1.528 (8)
C1—C2	1.513 (9)	C4—C21	1.505 (9)
C1—C3	1.544 (9)	C5—C6	1.484 (9)
C1—C4	1.531 (8)		
C2—C1—C3	58.2 (4)	C1—C4—C21	112.3 (5)
C2—C1—C4	124.7 (5)	C5—C4—C21	115.8 (5)
C2—C1—C11	116.8 (5)	Br3—C5—Br4	108.8 (3)
Br1—C2—Br2	110.4 (3)	Br3—C5—C4	116.9 (5)
Br1—C2—C1	120.0 (4)	Br4—C5—C4	127.5 (5)

Br2—C2—C1	121.3 (4)	C4—C5—C6	60.8 (4)
C1—C2—C3	61.9 (4)	C12—C11—C16	118.5 (6)
C1—C3—C2	59.9 (4)	C22—C21—C26	116.6 (6)
C1—C4—C5	127.0 (6)	C24—C25—C26	118.9 (7)
C1—C4—C6	115.5 (5)	C21—C26—C25	122.6 (7)
C5—C4—C6	57.9 (4)		
C3—C1—C2—Br1	−110.3 (5)	C4—C1—C11—C16	−81.4 (7)
C3—C1—C2—Br2	104.5 (5)	C1—C4—C5—Br3	−153.5 (5)
C4—C1—C2—C3	−113.4 (7)	C1—C4—C5—Br4	−6.0 (8)
C11—C1—C2—Br1	−8.8 (7)	C1—C4—C5—C6	99.4 (7)
C11—C1—C2—Br2	−154.1 (4)	C21—C4—C5—Br3	−0.3 (7)
C11—C1—C2—C3	101.5 (6)	C21—C4—C5—Br4	147.3 (5)
C11—C1—C3—C2	−108.4 (5)	C5—C4—C21—C22	103.3 (7)
C2—C1—C4—C5	71.0 (8)	C5—C4—C21—C26	−79.3 (7)
C2—C1—C4—C21	−83.0 (7)	C4—C21—C22—C23	177.4 (6)
C11—C1—C4—C5	−141.9 (6)	C22—C23—C24—C25	−2.0 (1.3)
C11—C1—C4—C21	64.1 (6)	C23—C24—C25—C26	1.5 (1.3)

The structures of (1*a*), (1*b*) and (2) were solved by direct methods using *XS* in *SHELXTL-Plus* (Siemens, 1990) and refined by full-matrix least squares using *XLS* in *SHELXTL-Plus*. Non-H atoms were refined anisotropically, whereas H atoms were placed at calculated positions with $U_{iso}(H) = 1.2U_{eq}$(parent C atom). The largest density in the final difference Fourier map of compound (2) is 1.02 e Å^{-3} at a distance of 0.89 Å from the Br2 atom.

For all compounds, data collection: *P3/P4-PC Diffractometer Program* (Siemens, 1991); cell refinement: *P3/P4-PC Diffractometer Program*; data reduction: *XDISK* and *XEMP* (Siemens, 1989*a*,*b*); molecular graphics: *XP* in *SHELXTL-Plus* and *ORTEP* (Johnson, 1965); software used to prepare material for publication: *XPUB* in *SHELXTL-Plus*.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BM1102). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(*E*)-3-(2,2-Dibromospiro[2.4]heptan-1-yl)propenenitrile

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Abstract

The X-ray crystal structure of the title compound, $C_{10}H_{11}Br_2N$, reveals that the three- and five-membered rings are fused to one another in a spiro fashion and that there is an *E* arrangement of substituents about the carbon–carbon double bond.

Comment

Internal nucleophilic capture of allylic cations generated by silver-ion induced electrocyclic ring-opening of *gem*-dihalogenocyclopropanes has provided a useful means of forming certain heterocyclic compounds (Banwell & Reum, 1991). In seeking to extend our own work (Banwell & Wu, 1994) in this area to the synthesis of spirocycles related to perhydrohistrionicotoxin (Winkler, Bowen & Liotta, 1995), we required compound (1). The starting point for our planned preparation of this

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