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1,5-Dibromocycloocta-1,5-diene

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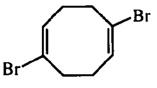
Abstract

The molecule of the title compound, $C_8H_{10}Br_2$, lies on a crystallographic twofold axis. The eight-membered ring has a twist-boat conformation in which the two olefin planes form a dihedral angle of 74.7 (1)° with one another. The C—Br distance is 1.928 (3) Å and the C═C distance is 1.314 (3) Å.

Comment

1,5-Dibromocycloocta-1,5-diene, (I), is a key intermediate in the preparation of the highly reactive 1,5-cyclooctadiyne. The crystal structure of the title compound was determined in order to confirm its identity, as well as to determine the conformation of its eight-membered ring.



(I)

The molecular structure of (I) is shown in Fig. 1. The molecule lies on a crystallographic twofold axis. The cyclooctadiene ring has a twist-boat conformation, identical to that of *syn*-3,7-dibromocycloocta-1,5-diene, which also lies on a twofold axis in the crystal (MacKenzie, MacNicol, Mills, Raphael, Wilson & Zabkiewicz, 1972). The mean difference in the four endocyclic torsion angles defining the eight-membered ring conformation is 1.7° when comparing the structure of (I) with that of MacKenzie *et al.* This is less than the uncertainties of their determination, which was based on film data. There is also excellent agreement with the twist-boat conformation found for unsubstituted cycloocta-1,5-diene by gas-phase electron diffraction (Hagen, Hedberg & Hedberg, 1982). The mean endocyclic torsion-angle deviation when (I) is compared with unsubstituted cycloocta-1,5-diene is 2.7°, well within the limits of error of that experiment.

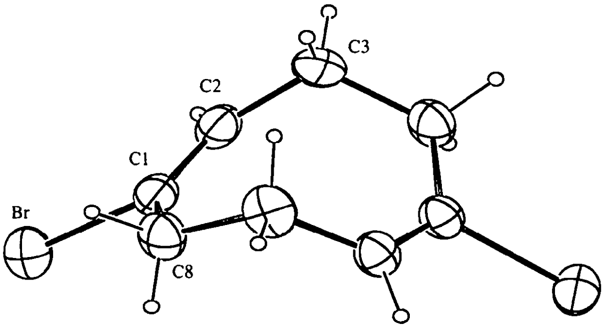


Fig. 1. The molecular structure of (I) shown with 40% probability ellipsoids and H atoms of arbitrary radius.

The five atoms defining the olefin plane (C_4Br) are coplanar within a maximum deviation of 0.013 (4) Å (for C3). This plane is tilted at an angle of 37.4 (1)° to the **b** direction and, thus, the two olefin planes related by the twofold axis form a dihedral angle of 74.7 (1)°. This angle is identical to the value of 74° reported for *syn*-3,7-dibromocycloocta-1,5-diene (MacKenzie *et al.*, 1972).

The C—Br distance in (I) is longer than expected. The standard value for C_{sp^2}—Br distances found by Allen, Kennard, Watson, Brammer, Orpen & Taylor (1987) is 1.883 Å and the upper quartile is 1.894 Å. Kaftory (1983) finds an average value of 1.888 Å for bromoolefins. Our distance is thus 0.043 (3) Å longer than the expected value. We have, however, found a number of well determined structures containing the C═C—Br moiety for which the C—Br distances agree well with ours. Examples are 1.922 (5) Å in 11-bromo-

endo-9-chloro-7-ethoxybicyclo[5.3.1]undec-1(11)-ene (Wijsman, de Wolf, Bickelhaupt, Kooijman & Spek, 1992), 1.924 (5) and 1.931 (4) Å in (*E*)-1,2-diphenyl-2-(4-tolyl)vinyl bromide (Luo, Barton, Robertson, Lee & Wanigasekera, 1987), 1.927 (5) Å in 1-anisyl-2,2-diphenylvinyl bromide and 1.923 (3) Å in 9-(α-bromoanisylidene)anthrone (Kaftory, Apeloig & Rappoport, 1985). Notably, 4,10-dibromo-1,7-methano[12]annulene (Mugnoli & Simonetta, 1976), which also has the C═C—Br unit as part of an eight-membered ring, has a C—Br distance of 1.931 (3) Å, in excellent agreement with the present value.

The packing is illustrated in Fig. 2. Each Br atom forms two contacts of 3.763 (1) Å to Br atoms related to it by the 2_1 axis (at $\frac{3}{2} - x, y \pm \frac{1}{2}, \frac{3}{2} - z$). This distance compares well with a value of 3.70 Å, which is twice the van der Waals radius of bromine (Bondi, 1964).

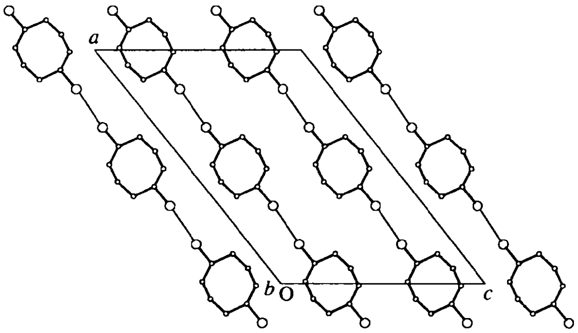


Fig. 2. Projection of the structure in the symmetry direction, illustrating the Br···Br contacts.

Experimental

The title compound was prepared by double dehydrohalogenation of 1,2,5,6-tetrabromocyclooctane with excess 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in hexane at 343 K. Crystals were grown by recrystallization from pentane.

Crystal data

$C_8H_{10}Br_2$
$M_r = 266.0$
Monoclinic
$C2/c$
$a = 18.8917 (8)$ Å
$b = 4.6858 (3)$ Å
$c = 12.7916 (8)$ Å
$\beta = 127.95 (1)°$
$V = 892.8 (3)$ Å^3
$Z = 4$
$D_x = 1.980$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12–16°$
$\mu = 9.0$ mm^{-1}
$T = 298$ K
Prism
0.33 × 0.28 × 0.20 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scans (North, Phillips, & Mathews, 1968)
$T_{min} = 0.107$, $T_{max} = 0.164$
3175 measured reflections
1548 independent reflections

1239 observed reflections [$I > 0$]
$R_{int} = 0.037$
$\theta_{max} = 32°$
$h = 0 \rightarrow 28$
$k = -6 \rightarrow 6$
$l = -19 \rightarrow 15$
3 standard reflections
frequency: 120 min
intensity decay: −0.2%

Refinement

Refinement on F
$R = 0.069$
$wR = 0.038$
$S = 1.128$
1239 reflections
67 parameters
H atoms refined isotropically
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0004F_o^4]$
$(\Delta/\sigma)_{max} = 0.003$

$\Delta\rho_{max} = 1.07$ e Å^{-3}
$\Delta\rho_{min} = -1.06$ e Å^{-3}
Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: $1.06 (8) \times 10^{-6}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	y	z	U_{eq}
Br	0.66801 (2)	0.48532 (8)	0.73984 (3)	0.0556 (1)
C1	0.5866 (2)	0.2413 (7)	0.7417 (2)	0.0400 (9)
C2	0.5086 (2)	0.1867 (8)	0.6273 (2)	0.0423 (9)
C3	0.4344 (2)	−0.0017 (8)	0.5999 (3)	0.051 (1)
C8	0.6275 (2)	0.1448 (9)	0.8800 (3)	0.048 (1)

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

Br—C1	1.928 (3)	C3—C8^i	1.507 (6)
C1—C2	1.314 (3)	C3—H3*A*	0.96 (2)
C1—C8	1.500 (4)	C3—H3*B*	1.02 (3)
C2—C3	1.504 (5)	C8—H8*A*	0.97 (4)
C2—H2	0.99 (3)	C8—H8*B*	0.99 (3)
Br—C1—C2	117.4 (3)	C1—C2—C3	128.4 (3)
Br—C1—C8	110.9 (2)	C2—C3—C8^i	113.7 (3)
C2—C1—C8	131.7 (3)	C1—C8—C3^i	116.6 (2)
C8—C1—C2—C3	−1.2 (7)	C1—C2—C3—C8^i	84.3 (5)
C2—C1—C8—C3^i	−11.7 (6)	C2—C3—C8^i—C1^i	−63.8 (4)

Symmetry code: (i) $1 - x, y, \frac{3}{2} - z$.

The crystal was sealed in a capillary to prevent sublimation. The largest features in the final difference map were within 1 Å of the bromine position. The structure was solved by Patterson and Fourier methods.

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD*-4 *Operations Manual.* Data reduction: *PROCESS* in *MolEN* (Fair, 1990). Program(s) used to refine structure: *LSFM* in *MolEN.* Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CIF IN* in *MolEN.*

The purchase of the diffractometer was made possible by a National Science Foundation chemical instrumentation grant, which we gratefully acknowledge. The chemical synthesis was supported by a grant from the NSF (CHE-912284).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1224). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1,2-Diphenyl-3-benzylguanidine Hydrochloride

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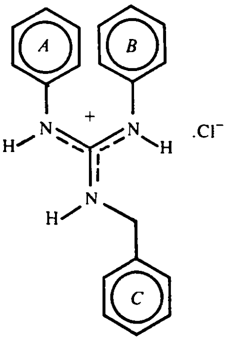
Abstract

In the title compound, 3-benzyl-1,2-diphenylguanidinium chloride $C_{20}H_{20}N_3^+.Cl^-$, the guanidine moiety is protonated. Steric strain due to the phenyl substituents leads to distortions of the guanidine skeleton. All three guanidinium N—H groups donate hydrogen bonds to symmetry-related chloride ions.

Comment

The conformation of the title compound, (1), as observed in the crystal structure is shown in Fig. 1. Since (1) has been crystallized as a hydrochloride, the guanidine moiety is protonated (*i.e.* N7, N9 and N10 all carry one H atom each). The three guanidinium C—N bond lengths are almost identical [1.337 (2), 1.337 (2) and 1.332 (2) Å for C8—N7, C8—N9 and C8—N10, respectively]; this is in agreement with the previously reported structure of a related substituted guanidinium salt (Sudha *et al.*, 1996) and contrasts with related uncharged molecules, where the guanidine C—N bonds are unequal, with a defined C=N double bond (Sudha *et al.*, 1995*a*,*b*).



(1)

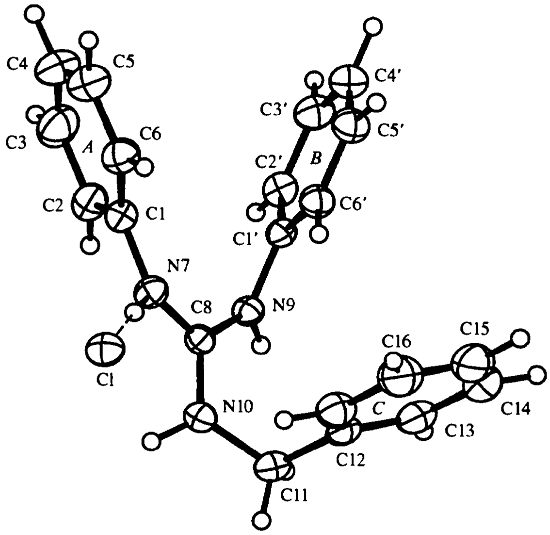


Fig. 1. The molecular structure and atomic labelling of the title compound. Displacement ellipsoids are drawn at the 30% probability level.