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 $U_{\rm iso}({\rm H})$ = $1.2U_{\rm eq}$(parent C atom). The largest density in the final difference Fourier map of compound (2) is $1.02\,{\rm e\,Å^{-3}}$ 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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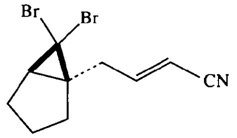
Abstract

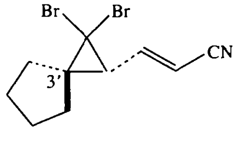
The X-ray crystal structure of the title compound, $C_{10}H_{11}Br_2N$, reveals that the three- and five-membered rings are fused to one another in a spiro fashion and that there is an *E* arrangement of substituents about the carbon–carbon double bond.

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 ring-fused cyclopropane was the commercially available (Aldrich) 1-cyclopenteneacetonitrile, which was hydrolyzed to the corresponding acid under literature conditions (Corey, Ueda & Ruden, 1975). The acid so-formed was reduced to the corresponding alcohol which was, in turn, acetylated. The acetate obtained in this manner was then subjected to reaction with dibromocarbene (generated under phase-transfer conditions), but spectroscopic analysis of the only isolable adduct suggested a spiro relationship between the five-membered ring and the newly installed cyclopropane moiety. This outcome implied that double-bond migration, from an endo- to an exocyclic position, had occurred prior to the carbene-addition step. In order to prove that this migration had indeed taken place, the oily dibromocarbene adduct was hydrolyzed to the alcohol which could then be converted, under standard conditions, to the corresponding aldehyde. Since both the alcohol and aldehyde were also oils, the latter was subjected to Wadsworth–Emmons reaction with diethyl cyanomethylphosphonate which resulted in the formation of a 1:1 mixture of the expected (*E*)- and (*Z*)-α,β-unsaturated nitriles. The chromographically less mobile isomer, (2), proved to be a crystalline solid and was subjected to single-crystal X-ray analysis.



(1)



(2)

The present work provides the first crystal structure of a 2,2-dibromospiro[2.4]heptane that is not fused to an additional ring (see Castellano, Brocksom & Ceschi, 1994). There are no short or interesting intermolecular contacts below 3.60 Å.

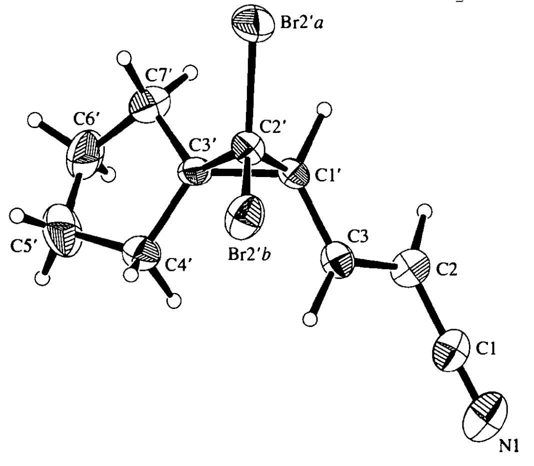


Fig. 1. View of the title compound showing the labelling of all non-H atoms. Displacement ellipsoids are shown at 20% probability levels. H atoms are shown as circles of arbitrary radii.

Experimental

Reaction of a 1,2-dimethoxyethane solution of the appropriate aldehyde (see above) with the sodium salt of diethyl cyanomethylphosphonate provided a 1:1 mixture of (2) and the corresponding *Z* isomer, which were separated from one another by HPLC (μ-porasil semi-preparative column, 1:9 ethyl acetate/hexane elution, 2 ml min^{-1} flow rate). The solid obtained by concentration of the chromatographically less mobile fraction was recrystallized (solvent) to give the title compound, (2), as colourless plates (m.p. 336–337 K).

Crystal data

$C_{10}H_{11}Br_2N$
$M_r = 305.01$
Monoclinic
$P2_1/a$
$a = 12.268\,(2)$ Å
$b = 7.520\,(2)$ Å
$c = 12.338\,(2)$ Å
$\beta = 91.86\,(1)^\circ$
$V = 1137.6\,(4)$ Å^3
$Z = 4$
$D_x = 1.781$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 28.8$–32.2°
$\mu = 8.781$ mm^{-1}
$T = 295\,(1)$ K
Plate
0.20 × 0.12 × 0.04 mm
Colourless

Data collection

Rigaku AFC-6*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical based on azimuthal (ψ) scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.552$, $T_{\max} = 0.704$
1942 measured reflections
1848 independent reflections

1053 reflections with $I > \sigma(I)$
$R_{\rm int} = 0.028$
$\theta_{\max} = 60.05^\circ$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 8$
$l = -13 \rightarrow 13$
3 standard reflections every 150 reflections intensity decay: 37.19%

Refinement

Refinement on *F*
$R = 0.0774$
$wR = 0.0563$
$S = 2.107$
1053 reflections
119 parameters
H atoms not refined
$w = 4F_o^2/[\sigma^2(F_o^2) + (0.02F_o^2)^2]$
$(\Delta/\sigma)_{\max} = 0.0003$

$\Delta\rho_{\max} = 0.70$ e Å^{-3}
$\Delta\rho_{\min} = -0.63$ e Å^{-3}
Extinction correction: Zachariasen (1968) type 2 Gaussian isotropic
Extinction coefficient: $2\,(3) \times 10^{-7}$
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Br2′*a*—C2′	1.94 (1)	C2′—C3′	1.52 (1)
Br2′*b*—C2′	1.87 (1)	C2—C3	1.32 (1)
N1—C1	1.13 (1)	C3′—C4′	1.51 (1)
C1—C2	1.41 (2)	C3′—C7′	1.50 (1)
C1′—C2′	1.49 (1)	C4′—C5′	1.52 (2)
C1′—C3	1.49 (1)	C5′—C6′	1.47 (2)
C1′—C3′	1.54 (1)	C6′—C7′	1.49 (2)
N1—C1—C2	180 (2)	C1′—C3—C2	122 (1)
C2′—C1′—C3	119.4 (9)	C1′—C3′—C2′	58.3 (7)
C2′—C1′—C3′	60.1 (7)	C1′—C3′—C4′	122.0 (9)
C3—C1′—C3′	120.3 (9)	C1′—C3′—C7′	118 (1)

Br2'*a*—C2'—Br2'*b*	111.4 (6)	C2'—C3'—C4'	121 (1)
Br2'*a*—C2'—C1'	115.5 (7)	C2'—C3'—C7'	123 (1)
Br2'*a*—C2'—C3'	115.6 (8)	C4'—C3'—C7'	108 (1)
Br2'*b*—C2'—C1'	123.8 (8)	C3'—C4'—C5'	105 (1)
Br2'*b*—C2'—C3'	120.8 (8)	C4'—C5'—C6'	106 (1)
C1'—C2'—C3'	61.6 (7)	C5'—C6'—C7'	106 (1)
C1—C2—C3	122 (1)	C3'—C7'—C6'	105 (1)

The θ-scan width used was $(1.40 + 0.30\tan\theta)^\circ$ at a speed of $16^\circ\ \text{min}^{-1}$ (in ω). The weak reflections were rescanned a maximum of four times and the counts accumulated to ensure good counting statistics. Stationary background counts were made on each side of the reflection with a 2:1 ratio of peak to background counting time. H atoms were located from difference maps and then fixed at ideal positions with C—H = 0.96 Å and $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$. A linear correction factor was applied to account for substantial crystal decay. The structure was solved by Patterson methods using the program *PATTY* (Beurskens *et al.*, 1992) and expanded using Fourier techniques (*DIRDIF*; Beurskens *et al.*, 1992). Refinement was carried out using full-matrix least-squares techniques. All calculations were performed using *TEXSAN* (Molecular Structure Corporation, 1995).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN*. Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: OA1016). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Antazoline

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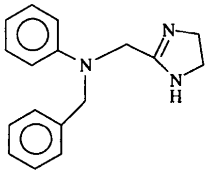
Abstract

The crystal structure of the title compound, 4,5-dihydro-*N*-phenyl-*N*-(phenylmethyl)-1*H*-imidazole-2-methanamine, $C_{17}H_{19}N_3$, is composed of independent molecules of the free base with normal molecular dimensions. There is an intermolecular N—H···N hydrogen bond between the imidazole ring N atoms linking the molecules into a chain structure [N···N 2.965 (4) Å].

Comment

The crystal structures of antazoline hydrochloride (Bertolasi, Borea & Gilli, 1982) and bis(antazoline)dichlorozinc(II) (Parvez & Rusiewick, 1995) have been reported. The crystal structure of the free base, antazoline, (1), which is an anti-allergic drug effective on H1 receptors is reported in this paper.



(1)

The phenyl rings were constrained to be regular hexagons, with $\text{C—C}_{\text{aromatic}}$ 1.395 Å and C—C—C 120.0°. The remaining molecular dimensions in (1) are normal and are identical within 3σ values to the dimensions reported for its hydrochloride salt (Bertolasi, Borea & Gilli, 1982), except the N3—C15 distance of 1.351 (4) Å in (1) which is clearly a C_{sp^2}—N single bond.

The imidazole ring in (1) is essentially planar [maximum deviation 0.033 (3) Å] and lies at angles of 79.47 (14) and 113.29 (14)° with respect to the planes of the C1–C6 and C8–C13 phenyl rings, respectively; the mean-planes angle between the two phenyl rings is 95.72 (13)°. The corresponding mean-planes angles in the Zn complex are 92.4 (9), 47.7 (12) and 86.6 (11)° in one half and 84.9 (9), 89.7 (10) and 99.5 (12)° in the other half of the molecule. The mean-planes angles in (1) are also different from the corresponding