Acta Cryst. (1979). B35, 1505–1507

Structure and Stereochemistry of a 2,4,6-Trimethyl-1,3,5-triazabicyclo[3.1.0]hexane Isomer

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(*Received* 16 *June* 1978; *accepted* 7 *February* 1979)

Abstract. $C_6H_{13}N_3$, monoclinic, $C2/c$, $a = 21{\cdot}43 \pm 0{\cdot}05$, $b = 4{\cdot}537 \pm 0{\cdot}01$, $c = 16{\cdot}49 \pm 0{\cdot}03$ Å, $\beta = 108{\cdot}0 \pm 0{\cdot}1°$, $Z = 8$, $D_c = 1{\cdot}108$, $D_m = 1{\cdot}10$ Mg m^{-3}, $V = 1524{\cdot}8$ Å^3. The molecule has a distorted boat-shaped bicyclic structure consisting of a diaziridine ring fused at N—N to an almost planar five-membered triazolidine ring. The triazolidine methyl groups have the *trans* configuration and the diaziridine methyl group is exocyclic. Within the diaziridine ring, the N—N distance is 1·510 (6) Å and the average C—N distance is 1·452 (7) Å; at C the ring angle is 62·6 (4)° and at N 59·3 (3) and 58·1 (3)°.

Introduction. The compound, prepared as described by Nielsen, Moore, Atkins, Mallory, DiPol & Laberge (1976) was converted into small colorless crystals using hexane as solvent (m.p. 386–387 K). A needle-shaped crystal was encapsulated in a thin quartz tube to prevent sublimation.

Intensities out to $6° \le 2\theta \le 80°$ (Cu $K\alpha$) were collected from a block-shaped crystal, mounted along the b axis (0·01 × 0·01 × 0·01 mm) on an automated General Electric diffractometer equipped with pulse-height selection and a scintillation counter. Total intensities T_c were measured by the moving-crystal–moving-counter (4° min^{-1}) scan method with stationary-crystal–stationary-counter background counts (B_1 and B_2) taken at the beginning and end of each count. F values were obtained by subtraction of the appropriate background and application of Lorentz–polarization corrections. Equivalent intensities were averaged. 370 reflections had a net average $I > 4\sigma_{\rm av}$ (where $\sigma^2 = T_c$ + total background) and were considered observed and used in the subsequent structure determination. Locations for ring N and C atoms were found from a three-dimensional Patterson diagram. Fourier techniques and least-squares structure-factor calculations (Busing, Martin & Levy, 1962) were then used to find and refine all nine C and N atoms to $R = 0{\cdot}111$. A difference Fourier synthesis at this stage clearly revealed the positions of the 12 H atoms attached to C atoms. These were adjusted slightly to give better tetrahedral coordination around C and given an isotropic temperature factor of 5·0 Å^2. Further refinement of C and N using anisotropic temperature factors stopped when $R = 0{\cdot}070$ and $wR = 0{\cdot}082$. A difference Fourier map at this stage gave a rather imprecise location for the 13th H atom. Its coordinates were adjusted slightly and the least-squares refinement allowed to proceed as before. Significant refinement ceased at $R = 0{\cdot}062$, $wR = 0{\cdot}074$. During the final cycles of refinement the weighting scheme was: for $F \ge 35$, $w = 35/F_o$, and for $F < 35$, $w = 1$; this was chosen to maintain fairly similar values of mean $w\Delta^2$ for ranges of increasing F_o. Final atomic coordinates are given in Table 1, and bond lengths in Table 2.

Fig. 1 illustrates the molecular configuration and the atomic numbering. Fig. 2 shows how the molecules pack.†

Discussion. The investigation of the stereochemistry and mechanism of the diaziridine synthesis by Schmitz (1959, 1961, 1963, 1964), leading to the preparation of a new series of 2,4,6-trisubstituted 1,3,5-triazabicyclo[3.1.0]hexanes (1), was undertaken to confirm the proposed reaction paths and stereochemistry leading to the crystalline products.

Diaziridine rings have been investigated widely, but only a few crystal structures have been reported (Mastryukov, Dorofeeva & Vilkov, 1974; Dyachenko, Atovmyan, Aldoshin, Polyakov & Kustyanovskii, 1976; Nabeya, Tamura, Kodama & Iwakula, 1973). The present investigation is the first to describe a bicyclic diaziridine structure linked through the N—N bond. 2,4,6-Trimethyl-1,3,5-triazabicyclo[3.1.0]hexane is optically active with C(1), C(2), and C(3) (Fig. 1)

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34263 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0567-7408/79/061505-03$01.00

Table 1. *Atomic fractional coordinates* (×10^4) *with estimated standard deviations in parentheses*

	x	*y*	*z*
C(1)	570 (3)	2221 (13)	1788 (4)
C(2)	1661 (3)	1308 (13)	2539 (4)
C(3)	1371 (3)	2089 (13)	990 (4)
C(4)	−44 (3)	937 (16)	1168 (4)
C(5)	1825 (3)	3030 (15)	3368 (4)
C(6)	1580 (3)	3262 (16)	267 (4)
N(1)	1009 (2)	−4 (10)	2311 (3)
N(2)	1676 (2)	3370 (11)	1834 (3)
N(3)	966 (2)	3930 (10)	1336 (3)
H(1)	−317	2638	772
H(2)	88	−696	799
H(3)	−355	163	1507
H(4)	1900	1635	3869
H(5)	2270	4272	3447
H(6)	1463	4525	3396
H(7)	1865	1818	50
H(8)	1169	3846	−236
H(9)	1877	5112	426
H(10)	414	3637	2201
H(11)	2032	−388	2642
H(12)	1379	−246	976
H(13)	986	−1969	1928

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with estimated standard deviations*

Diaziridine ring			
C(3)–N(3)	1·443 (7)	N(2)–C(3)–N(3)	62·6 (4)
C(3)–N(2)	1·462 (7)	C(3)–N(3)–N(2)	59·3 (3)
N(2)–N(3)	1·510 (6)	N(3)–N(2)–C(3)	58·1 (3)
C(3)–C(6)	1·495 (8)	C(6)–C(3)–N(2)	117·5 (6)
		C(6)–C(3)–N(3)	118·3 (6)
Five-membered ring			
N(2)–C(2)	1·500 (7)	N(3)–C(1)–N(1)	106·9 (5)
C(2)–N(1)	1·458 (7)	C(1)–N(1)–C(2)	105·0 (5)
N(1)–C(1)	1·464 (7)	N(1)–C(2)–N(2)	107·7 (5)
C(1)–N(3)	1·506 (7)	C(2)–N(2)–N(3)	105·5 (5)
C(1)–C(4)	1·512 (8)	N(2)–N(3)–C(1)	105·7 (5)
C(2)–C(5)	1·519 (9)	C(4)–C(1)–N(1)	113·5 (6)
		C(4)–C(1)–N(3)	111·7 (6)
		C(5)–C(2)–N(2)	108·8 (6)
		C(5)–C(2)–N(1)	112·1 (6)
Others			
		C(3)–N(3)–C(1)	113·4 (5)
		C(3)–N(2)–C(2)	112·3 (5)

asymmetric. Enantiomorphic pairs are produced by the centers of symmetry in the space group *C*2/*c*. The orientation of the methyl substituents on the fused twisted boat-shaped ring is *trans–exo*. The ^{13}C NMR and steric constraints of this form as compared to *cis–exo* and *cis–endo* isomers were discussed by Nielsen *et al.* (1976). The molecule has a distorted boat-shaped six-membered ring consisting of a diaziridine ring fused at N–N to an almost planar triazolidine ring. The diaziridine ring carbon and the NH nitrogen form the 'prow' and 'stern' of the boat. The five-membered ring is almost planar with C(1), N(1), C(2), N(2), C(3), and N(3) deviating −0·115, 0·187, −0·161, 0·036, 1·286, and 0·088 Å (see numbering in Fig. 1) from the best mean plane through it. The dihedral angle between this plane and that of the diaziridine ring is 99·6°. Within the diaziridine ring the average C–N value is 1·452 Å and that of the common N–N 1·510 (6) Å. Angles at C(3), N(2), and N(3) are 62·6 (4), 58·1 (3), and 59·3 (3)° respectively. The five-membered ring has four C–N values ranging from 1·458 (7) to 1·506 (7) Å with angles ranging from 105·1 to 113·4°. The three exocyclic C(methyl)–C(ring) distances range from 1·495 to 1·519 (9) Å.

Within the diaziridine ring the average C–N value is 1·452 Å, which lies close to and between the values of 1·479, 1·434, and 1·482 Å found in 3-methyldiaziridine (2) (Mastryukov *et al.*, 1974) (determined by electron diffraction), (−)-(1*R*,2*S*)-1-(*s*)-α-phenylethylcarbamoyl-2-methyl-3,3-pentamethylenediaziridine (3) (Dyachenko *et al.*, 1976), and 1-cyclohexyl-3-(*p*-bromophenyl)diaziridine (4) (Nabeya *et al.*, 1973) respectively. The N–N value of 1·510 Å is slightly larger than the 1·479, 1·453, and 1·506 Å found in the other three compounds and may reflect additional strain placed on the bond by its being common to two small rings. In all four diaziridine structures these bond lengths result in the angle at the diaziridine ring C being slightly larger than those at N. Needless to say, the angles of 62·6, 59·3, and 58·1°

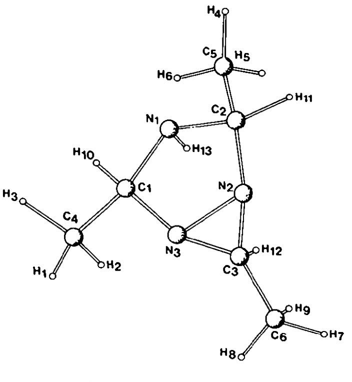

Fig. 1. Atomic labelling.

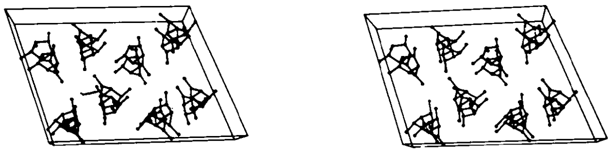

Fig. 2. Molecular packing and proposed hydrogen bonding as seen down the *b* axis.

are all at least 45° less than sp^3 and 60° less than sp^2 hybrid C—N bonds. The C(6)—C(3) distance of 1·495 Å is typical for a C—C bond shortened by two adjacent partial double bonds with the two C(6)—C(3)—N angles of 117·5 and 118·3° being considerably larger than those found at normal sp^3 carbon. This again reflects the bonding distortion at C(3) created by its being a member of a diaziridine ring. The enlargement of the exocyclic diaziridine ring angle is also shown in compounds (3) and (4).

There is a short distance of 3·17 Å between N(1)(x,y,z) and N(3)′(x, y − 1, z) which may be attributed to intermolecular hydrogen bonding involving H(13). Strong evidence for this is given by the angles C(2)—N(1)···N(13)′ = 111·1°, C(1)—N(1)···N(3)′ = 112·7°, and N(1)—H(13)···N(3)′ = 172·5°. The hydrogen-bonded strings of molecules stacked along the b axis are shown in Fig. 2.

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Acta Cryst. (1979). B**35**, 1507–1509

2-[1-(4-Quinazolinyl)hydrazino]ethanol Hydrochloride

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(*Received* 18 *January* 1979; *accepted* 12 *February* 1979)

Abstract. $C_{10}H_{13}N_4O^+.Cl^-$, $M_r = 240\cdot7$, monoclinic, $a = 14\cdot083$ (2), $b = 5\cdot019$ (1), $c = 16\cdot182$ (2) Å, $\beta = 103\cdot8$ (2)°, $U = 1111\cdot00$ Å^3, $D_m = 1\cdot46$, $Z = 4$, $D_c = 1\cdot44$ Mg m^{-3}, $F(000) = 504$, space group $P2_1/c$. Mo $K\alpha$ radiation, $\lambda = 0\cdot7107$ Å, μ(Mo $K\alpha$) = 0·087 mm^{-1}. The reaction of hydroxyethylhydrazine with 4-chloroquinazoline in isopropanol yielded a product for which several plausible structures could be postulated, but for which no one structure could be chosen unambiguously. An X-ray analysis has confirmed that the product is the title compound, N-protonation taking place at N(1) of the quinazoline ring.

Introduction. Exposure of a small crystal to Zr-filtered Mo $K\alpha$ radiation on a Hilger & Watts Y290 diffractometer yielded 1696 independent reflexions [$I \geq 3\sigma_I$, $\sigma_I = (I + B_1 + B_2)^{1/2}$], measured by the θ,ω-scan technique in the 2θ range 0–54°. The intensities were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved by the heavy-atom technique with XRAY (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Refinement of positional and thermal parameters by full-matrix least-squares calculations converged when R was 0·050. Difference syntheses, evaluated after the preliminary cycles of refinement, revealed all the H atoms, and positional parameters were refined for these atoms in later cycles. Throughout the refinement it was not found necessary to apply weights other than unity.

Final fractional coordinates are presented in Table 1.* Table 2 contains details of the molecular geometry and interionic associations. The e.s.d.'s are derived from the least-squares calculations and should be regarded as minimum values. A view of one molecule, defining the atomic numbering, is shown in Fig. 1.

Discussion. The organic moiety of the title compound (I) may be regarded as a protonated and amine-substituted pyrimidine system which is fused *via* C(9) and C(10) to a benzene ring. Comparisons may thus be made with pyrimidine itself (Wheatley, 1960), and with other pyrimidine-containing systems, including bis(2-pyrimidyl) disulphide (Furberg & Solbakk, 1973) and numerous purine and adenine derivatives and analogues (*e.g.* Stewart & Jensen, 1964; Watson, Sweet & Marsh, 1965; McMullan & Sundaralingam,

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34271 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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