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The Crystal and Molecular Structure of 6,6-Diphenyl-3,3-diethyl-3-azabicyclo[3.1.0]hexane Bromide Monohydrate

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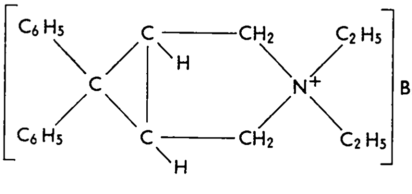
Crystals of 6,6-diphenyl-3,3-diethyl-3-azabicyclo[3.1.0]hexane bromide monohydrate are monoclinic, space group $P2_1/n$ with $a = 12\cdot044$, $b = 17\cdot598$, $c = 9\cdot137$ Å; $\beta = 95° 44'$. The structure has been determined from Patterson and Fourier syntheses employing 3611 observed reflexions measured on a counter diffractometer. The final atomic parameters have been obtained by obs. and calc. differential syntheses, and the hydrogen atoms have been located from a 3-D difference map. In this structure, the five-membered ring has its four carbon atoms nearly, but not exactly, in one plane with the nitrogen atom at 0·534 Å from the plane. The three-membered ring forms a nearly equilateral triangle of side 1·520 Å and is fused to the five-membered ring through the C(1)–C(5) bond at an angle of 65·0° from the mean plane of C(1), C(2), C(4), and C(5). One of the ethyl groups appears to be disordered, occupying one orientation more frequently than the other. Hydrogen bonding is indicated between the unattached bromine and the oxygen atoms of the water molecules.

Introduction

A series of the 3-azabicyclo[3.1.0]hexanes (cyclopropanes derived from diaryldiazomethanes) and their azaspiroquaternary salts have been synthesized by Baltzly, Mehta, Russell, Brooks, Grivsky & Steinberg (1962). In view of the excellent ease of formation, stereospecifity and stability of this class of compounds beyond what would be expected for a six-membered bridged system, a study of some of them by X-ray diffraction methods was undertaken, the main purpose being to examine the manner and extent of distortion of the bond angles in the azabicyclohexane ring system. The monohydrated form of the 6,6-diphenyl-3,3-diethyl-3-azabicyclo[3.1.0]hexane bromide



($C_{21}H_{26}N.Br$) was selected for this first X-ray analysis. The crystals were prepared by N. B. Mehta by adding dry ether to a methanolic solution to incipient turbidity and then chilling. By dissolving some of these crystals in an acetone–methanol solution and slowly evaporating, larger single crystals suitable for the X-ray analysis were obtained.

Experimental

Crystal data

Preliminary examination of the space group and cell dimensions were carried out with precession and Weissenberg photographs. The cell dimensions were remeasured more accurately on a counter diffractometer using copper radiation and a small crystal of dimensions 0·15 × 0·20 × 0·30 mm mounted with the b axis parallel to the φ axis of the goniostat. At a take-off angle of 1° and with a 0·02° slit, the 2θ values were recorded for the peak positions of the $K\alpha_1$ ($\lambda = 1\cdot54051$ Å) and $K\alpha_2$ ($\lambda = 1\cdot54433$ Å) for some of the medium and high order axial reflexions.

Crystals of the monohydrated 6,6-diphenyl-3,3-diethyl-3-azabicyclo[3.1.0]hexane bromide,

$$C_{21}H_{26}N.Br.H_2O,$$

are monoclinic, space group $P2_1/n$ (C_{2h}^5), $Z = 4$; $M = 390\cdot38$; $m.p.$ 178 to 179 °C.

$$a = 12\cdot044 \pm 0\cdot003,\ b = 17\cdot598 \pm 0{:}003,\ c = 9\cdot137 \pm 0.003\ \text{Å},$$
$$\beta = 95°\ 44' \pm 2'.$$

Volume per unit cell, 1926·88 Å³.

$$D_c\ (\text{with } Z = 4) = 1\cdot345\ \text{g.cm}^{-3}\ ,$$
$$D_m \text{ by flotation} = 1\cdot347\ \text{g.cm}^{-3}\ .$$

Absorption coefficient for X-rays,

$$\lambda = 1\cdot5418\ \text{Å},\ \mu = 31\cdot4\ \text{cm}^{-1}\ .$$

$F(000) = 816$

Intensity data

For collection of the intensity data, a relatively

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large crystal ground to a nearly spherical shape of dimensions $0{\cdot}48 \times 0{\cdot}48 \times 0{\cdot}53$ mm was chosen. With copper radiation, a nickel filter, and a scintillation counter, all the reciprocal lattice sites within the range of the single-crystal orienter ($2\theta = 0°$ to $160°$), excluding those prohibited by the space group symmetry, were scanned by the moving-crystal moving-counter method (Furnas, 1957). The integrated intensities, covering 2° to 3.5° in 2θ, were measured at a take-off angle of 2·5° and with an open counter window. The background was evaluated separately for each reflexion on the streak through it (Bachmann, Ahmed & Barnes, 1961) and was subtracted from the integrated intensity. For reduction of the data onto the same relative scale, the 004 reflexion was scanned every 20 to 40 minutes throughout the duration of data collection. Of a possible 4223 reflexions, 3611 (or 85%) of them were observed. The measured intensities were corrected by the $1/Lp$ factors for zero layer, and for absorption assuming a spherical crystal of radius 0·24 mm. In addition, an empirical absorption correction varying between 1·0 and 1·1 and taken as a function of the φ setting was applied to the intensities in order to compensate for the difference in the radii of the crystal.

Structure analysis

The coordinates of the bromine atom were derived from the Br–Br vectors in a three-dimensional Patterson synthesis for which the $1/Lp$ function for zero layer was employed as a sharpening function. Locations of the other atoms, except atom C(20), which is the carbon atom of one of the methyl groups, and the hydrogen atoms, were determined unambiguously from a vector-convergence map derived by placing the origin of the Patterson synthesis at the four bromide positions in the unit cell and summing the contour lines of the four superpositions. In the next Fourier synthesis, which was evaluated with 95% of the observed data, the electron-density distribution corresponded very nearly to the assumed structure showing $\varrho_o = 70\text{e.Å}^{-3}$ for Br, about 10 e.Å^{-3} for O and N, and between 6 and 9 e.Å^{-3} for the assumed carbon atoms. The remainder of the map was flat with the exception of two locations at distances 1·39 and 1·31 Å from C(19) and about 1·8 Å apart, with positive electron-density distributions of 2·9 and 2·2 e.Å^{-3} maxima, respectively. For simplicity of the discussion these two locations are identified as C(20′) and C(20″), respectively. Assuming a perfectly ordered structure, the remaining atom was placed at location C(20′) since the other location was only 1·2 Å away from a centre of symmetry, had lower electron-density distribution, and was too close to C(19). Two cycles of refinement of this model by Fourier synthesis and by obs. and calc. differential syntheses resulted in increasing the electron density at C(20′) to 4 e.Å^{-3} but failed to reduce that at C(20″) below 2 e.Å^{-3}. At this stage, assuming anisotropic temperature parameters for Br and different isotropic B-values for the other atoms, and excluding the hydrogen atoms, the discrepancy factor for the observed data was as follows:

(*a*) $R = 0{\cdot}13_0$ if no atom was placed at location C(20′) or C(20″),

(*b*) $R = 0{\cdot}12_5$ if a whole carbon atom was placed at C(20′),

(*c*) $R = 0{\cdot}12_7$ if a whole carbon atom was placed at C(20″), or

(*d*) $R = 0{\cdot}11_4$ if C(20) was shared equally between C(20′) and C(20″).

Combination (*d*) which gave the lowest R index was that of a disordered orientation for atom C(20). However, taking the F_c amplitudes and phases of combination (*a*), a 3-D difference map was evaluated. In this map, there were positive electron-density distributions of maxima between 0·4 and 0.8 e.Å^{-3} corresponding to the hydrogen atoms in the structure and a few positive and negative areas indicative of thermal anisotropy for some of the atoms and especially for C(19). At locations C(20′) and C(20″) the electron densities were 2·8 and 2·1 e.Å^{-3}, respectively, and about 1·1 Å away from each of them there were three low satellite peaks corresponding to the three hydrogens of that methyl group.

For a check on these results, all the very strong reflexions were remeasured with a much smaller crystal in order to reduce extinction errors. The overall scale factor was redetermined from a Wilson plot and was found to agree within 4% with that estimated by comparison of $\Sigma|F_o|$ and $\Sigma|F_c|$. The first Fourier synthesis was re-evaluated with about 85% of the observed data, taking the phases directly from the contributions of the bromine atom alone, and still gave the same features as in the previous maps.

The third cycle of refinement was computed assuming locations C(20′) and C(20″) to be occupied equally, and allowing for the thermal anisotropy of Br and C(19). A second difference map was evaluated, and the coordinates of the hydrogen atoms were deduced from it. Adding the contribution of the hydrogen atoms to the previous structure factor calculation the R index was $0{\cdot}08_9$. The final parameters for the C, N, O, Br atoms were obtained after one more cycle of refinement. Assuming thermal anisotropy for some of the atoms and disorder for all the atoms of the ethyl group containing C(19) and C(20), and including the contribution of the hydrogen atoms, the R index for the observed data at the final structure factor calculation was $0{\cdot}07_9$.

Results and discussion

Throughout this structure analysis, the electron-density maps and consequently the agreement between the obs. and calc. data have shown consistently that the carbon and three hydrogen atoms of one of the

Table 1. *Fractional atomic coordinates, and their e.s.d.'s*

Each anisotropic atom was represented in the structure factor calculation by two isotropic half atoms separated from the mean position by the fractional shifts given in parentheses $\times 10^{-4}$ (Kartha & Ahmed, 1960)

Atom	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
C(1)	0·3551	0·3249	0·4146	0·004 Å	0·004 Å	0·004 Å
C(2)	0·3972 (±28)	0·3780 (±0)	0·3043 (∓70)	0·004	0·004	0·005
N(3)	0·3080 (±55)	0·3761 (∓23)	0·1727 (∓60)	0·004	0·003	0·004
C(4)	0·2646 (±40)	0·2948 (±0)	0·1721 (∓46)	0·004	0·004	0·004
C(5)	0·2690 (±0)	0·2729 (±0)	0·3320 (±59)	0·004	0·004	0·004
C(6)	0·3769	0·2403	0·4073	0·004	0·003	0·004
C(7)	0·3647	0·1982	0·5484	0·004	0·004	0·004
C(8)	0·2874	0·1400	0·5538	0·005	0·004	0·005
C(9)	0·2782 (±49)	0·1013 (±0)	0·6851 (±0)	0·006	0·006	0·006
C(10)	0·3474 (±63)	0·1199 (±0)	0·8093 (±0)	0·007	0·006	0·005
C(11)	0·4255 (±0)	0·1768 (±43)	0·8047 (±0)	0·005	0·006	0·005
C(12)	0·4344	0·2164	0·6746	0·004	0·004	0·004
C(13)	0·4634	0·2062	0·3201	0·004	0·004	0·004
C(14)	0·5715 (±0)	0·2348 (±47)	0·3287 (±75)	0·004	0·004	0·004
C(15)	0·6533 (±40)	0·1982 (±64)	0·2575 (±91)	0·004	0·006	0·005
C(16)	0·6275 (±28)	0·1314 (±61)	0·1792 (±65)	0·005	0·006	0·005
C(17)	0·5199 (±45)	0·1027 (±36)	0·1699 (±0)	0·006	0·005	0·005
C(18)	0·4377	0·1403	0·2387	0·004	0·004	0·004
C(19′)	0·3441	0·4079	0·0320	0·007	0·007	0·006
C(19″)	0·3633	0·3905	0·0320	0·007	0·007	0·006
C(20′)	0·4470	0·3637	−0·0067	0·013	0·013	0·010
C(20″)	0·4264	0·4615	0·0251	0·022	0·018	0·015
C(21)	0·2151 (±66)	0·4304 (±0)	0·2074 (∓118)	0·006	0·005	0·006
C(22)	0·1208 (±60)	0·4408 (±0)	0·0862 (∓118)	0·007	0·006	0·008
O	−0·1254 (±41)	0·0212 (±27)	0·1470 (±87)	0·005	0·005	0·005
Br	0·1231 (±50)	0·1037 (±0)	0·1362 (∓172)	0·001	0·001	0·001

methyl groups have two different orientations, one of which is occupied more frequently than the other. The extremely short distances C(19)–C(20′) and C(19)–C(20″) of about 1·39 and 1·31 Å, respectively, are improved considerably if the elongated electron-density distribution around atom C(19) is taken to represent a disordered orientation for that atom instead of an unusually high thermal anisotropy. Thus in order to satisfy the observed anomalies in the bond lengths and in the Fourier maps, the whole ethyl group must be disordered, taking the orientation of C(19′) and C(20′) in some unit cells, and that of C(19″) and C(20″) in the others. On this basis, C(19′)–C(20′) = 1·534 Å and C(19″)–C(20″) = 1·467 Å. The fact that C(20″) is only 1·2 Å from the centre of symmetry at ($\frac{1}{2}$, $\frac{1}{2}$, 0) implies that the site of C(20″) cannot be occupied in any two adjacent cells in order to maintain the conditions of van der Waals interactions, while no such restrictions need be imposed on location C(20′). This qualification for the disordered structure favours more frequent occurrence of the orientation involving the site of C(20′) than that of C(20″) as indicated by their relative electron densities. The ratio of the two orientations has been estimated approximately as 0·6:0·4. The proposed disorder for one of the ethyl groups while the rest of the molecule is perfectly ordered resembles in some ways the disorder reported for one of the carbon atoms of L-leucyl-L-prolyl-glycine reported by Leung & Marsh (1958). Coordinates of the C, N, O and Br atoms of the proposed structure, and their standard deviations as estimated by Cruickshank's expressions (1949, 1954), are given in Table 1. The obs. and calc. electron densities and mean curvatures, and the temperature parameters assumed for the final cycle are listed in Table 2. In Table 3 are the coordinates of the hydrogen atoms as determined from the second difference map and without any

Table 2. *Electron densities* (e.Å^{-3}), *mean curvatures* (e.Å^{-5}), *and isotropic temperature parameters* (Å^2), *with the additional anisotropic componets* (Å^2) *in parentheses*

Atom	ϱ_o	ϱ_c	ϱ_o''	ϱ_c''	B_{iso} (ΔB)
C(1)	9·6	9·6	85	86	2·60
C(2)	9·0	9·0	76	79	2·75 (0·48)
N(3)	10·8	10·7	90	91	2·70 (0·84)
C(4)	9·1	9·1	79	80	2·75 (0·38)
C(5)	9·6	9·7	85	87	2·45 (0·25)
C(6)	10·2	10·2	93	95	2·40
C(7)	9·5	9·5	84	86	2·70
C(8)	8·3	8·4	70	71	3·50
C(9)	7·1	7·2	55	57	4·45 (0·30)
C(10)	7·0	7·1	54	55	4·40 (0·50)
C(11)	7·6	7·7	61	62	3·90 (0·49)
C(12)	8·8	8·9	76	78	3·20
C(13)	10·0	9·9	89	90	2·50
C(14)	8·9	9·0	78	80	2·80 (0·99)
C(15)	7·9	8·0	66	68	3·30 (1·81)
C(16)	7·3	7·5	59	61	3·90 (1·35)
C(17)	7·7	7·7	62	64	3·80 (0·60)
C(18)	8·9	9·0	77	79	3·10
C(19)*	6·6	6·7	50	52	3·90 (3·16)
C(20′)	4·0	4·2	28	30	5·00
C(20″)	2·7	2·9	19	20	5·00
C(21)	7·5	7·5	58	59	3·50 (1·68)
C(22)	6·6	6·6	50	50	4·50 (1·57)
O	9·2	9·4	68	70	5·15 (0·87)
Br	68·0	69·4	616	624	3·55 (2·60)

* C(19′) and C(19″) are not resolved; the values given are for the combined distribution.

further refinement. A list of the observed amplitudes and calculated structure factors for the parameters in Tables 1, 2, and 3 may be obtained from the authors on request. The C, O, Br and H scattering factor curves employed in the calculations were taken from *International Tables for X-ray Crystallography* (1962), and that for N^+ was derived approximately from the curve given for N. A summary of the agreement between the obs. and calc. data in terms of their amplitudes and the corresponding threshold values (Ahmed & Barnes, 1963) and based on an overall R index of 0·08 is given in Table 4. For the observed reflexions in categories 3 and 4, $|\Delta F| \leq 7{\cdot}4$, and for all the unobserved reflexions $|F_c| \leq 6{\cdot}6$.

Table 3. *Fractional coordinates of the hydrogen atoms*

Atom	x	y	z	Bonded to
H(1)	0·347	0·342	0·528	C(1)
H(2)	0·403	0·437	0·340	C(2)
H(3)	0·470	0·360	0·270	C(2)
H(4)	0·318	0·258	0·107	C(4)
H(5)	0·185	0·306	0·118	C(4)
H(6)	0·195	0·260	0·377	C(5)
H(7)	0·232	0·126	0·458	C(8)
H(8)	0·220	0·053	0·677	C(9)
H(9)	0·325	0·090	0·903	C(10)
H(10)	0·473	0·198	0·897	C(11)
H(11)	0·498	0·260	0·685	C(12)
H(12)	0·590	0·283	0·402	C(14)
H(13)	0·732	0·225	0·260	C(15)
H(14)	0·697	0·102	0·135	C(16)
H(15)	0·505	0·050	0·108	C(17)
H(16)	0·357	0·123	0·238	C(18)
H(17′)	0·270	0·407	−0·040	C(19′)
H(18′)	0·403	0·450	0·023	C(19′)
H(17″)	0·293	0·400	−0·060	C(19″)
H(18″)	0·427	0·358	0·000	C(19″)
H(19′)	0·501	0·357	0·063	C(20′)
H(20′)	0·445	0·390	−0·117	C(20′)
H(21′)	0·435	0·307	0·000	C(20′)
H(19″)	0·447	0·475	−0·089	C(20″)
H(20″)	0·520	0·457	0·070	C(20″)
H(21″)	0·448	0·525	0·055	C(20″)
H(22)	0·258	0·483	0·238	C(21)
H(23)	0·174	0·408	0·297	C(21)
H(24)	0·062	0·473	0·142	C(22)
H(25)	0·147	0·467	−0·013	C(22)
H(26)	0·075	0·392	0·053	C(22)
H(27)	0·952	0·050	0·142	O
H(28)	0·877	−0·022	0·070	O

Table 4. *Agreement summary*

3611 observed reflexions ($1{\cdot}4 \leq |F_o| \leq 214{\cdot}3$)

Category	Limits	Number
1.	$|\Delta F| \leq 1{\cdot}0|F_{th}|$, or $|\Delta F|/|F_o| \leq 0{\cdot}16$	3446
2.	$1{\cdot}0|F_{th}| < |\Delta F| \leq 2{\cdot}0|F_{th}|$, or $0{\cdot}16 < |\Delta F|/|F_o| \leq 0{\cdot}24$	142
3.	$2{\cdot}0|F_{th}| < |\Delta F| \leq 3{\cdot}0|F_{th}|$, or $0{\cdot}24 < |\Delta F|/|F_o| \leq 0{\cdot}32$	19
4.	$3{\cdot}0|F_{th}| < |\Delta F| \leq 4{\cdot}0|F_{th}|$, or $0{\cdot}32 < |\Delta F|/|F_o| \leq 0{\cdot}40$	4

612 unobserved reflexions ($|F_c|_{\max} = 6{\cdot}6$)

1.	$|F_c| \leq 1{\cdot}0|F_{th}|$	511
2.	$1{\cdot}0|F_{th}| < |F_c| \leq 1{\cdot}5|F_{th}|$	83
3.	$1{\cdot}5|F_{th}| \leq |F_c| \leq 2{\cdot}0|F_{th}|$	16
4.	$2{\cdot}0|F_{th}| < |F_c| \leq 2{\cdot}5|F_{th}|$	2

$|F_{th}|$ = threshold amplitude = 1·2 to 3·7.

A perspective view of the 6,6-diphenyl-3,3-diethyl-3-azabicyclo[3.1.0]hexane molecule is shown in Fig. 1. The bond lengths with their e.s.d.'s (Ahmed & Cruickshank, 1953), and the bond angles are presented in Fig. 2. Estimated standard deviations for the angles as computed by the expression given in *International Tables for X-ray Crystallography* (1959) are 0·26° in the three-membered ring, 0·32° in the five-membered ring, 0·34° for C(6)–C(1)–C(2) and C(6)–C(5)–C(4), and 0·46° in the two phenyl rings. In the azabicyclohexane ring, chemically equivalent bonds differ in length by ±0·004 Å from their respective mean values, or by less than their e.s.d.'s. The bond angles N(3)–C(2)–C(1) and N(3)–C(4)–C(5) are nearly equal and so are the angles C(6)–C(1)–C(5) and C(6)–C(5)–C(1). The difference of 0·9° between the angles C(2)–C(1)–C(5) and C(4)–C(5)–C(1) is not significant ($t = 1{\cdot}99$, $P > 1\%$), while the difference of 2·1° between the angles C(2)–C(1)–C(6) and C(4)–C(5)–C(6) is significant ($t = 4{\cdot}37$, $P < 0{\cdot}01\%$). The three-membered ring forms a nearly equilateral triangle of side 1·520 Å. In the two phenyl rings, the aromatic C–C bonds have a mean length of 1·390 Å, $\sigma = 0{\cdot}006$ Å, and the angles between them have a mean value of 120·0°, $\sigma = 0{\cdot}4°$. With the unrefined hydrogen positions, the mean length for the C–H bonds is 1·07 Å, $\sigma = 0{\cdot}05$ Å, and the O–H distances are 1·07 and 1·04 Å. In view of the overlap in the electron-density maps as a result

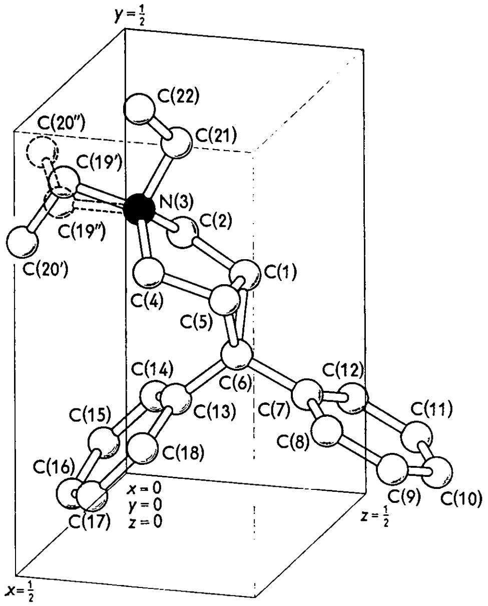

Fig. 1. Perspective view of the molecule.

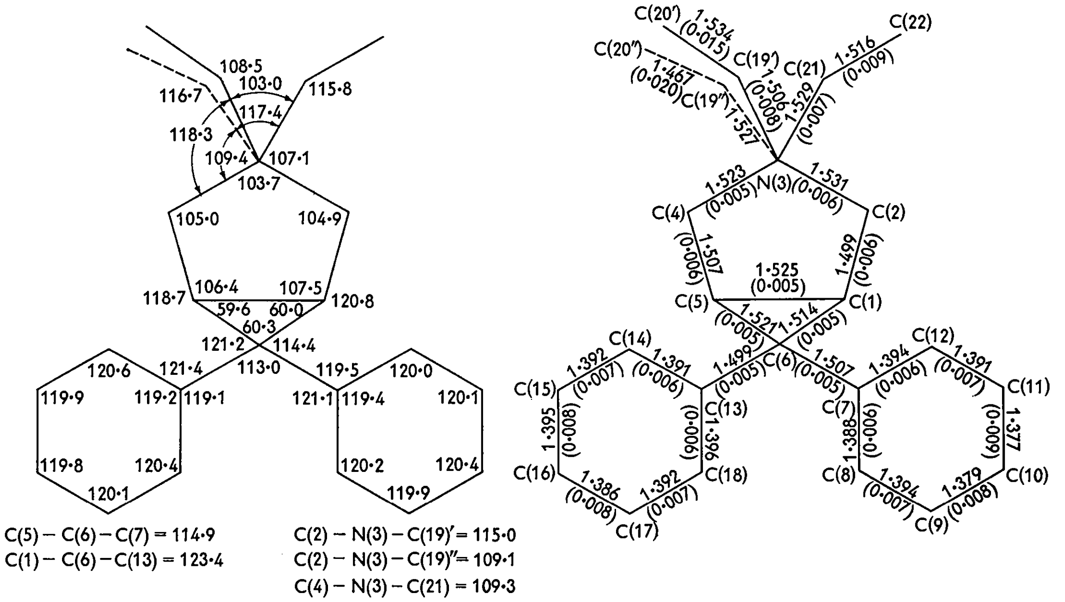

Fig. 2. Bond lengths (Å; e.s.d.'s in parentheses) and bond angles (°).

of the disorder of atoms C(19), C(20), and their hydrogen atoms, the e.s.d.'s for C(19) and C(20) as calculated by Cruickshank's expression may be underestimated. For this reason, the difference of 0·067 Å between the two observed values for the C(19)–C(20) bond probably should not be considered as significant.

Planarity of the rings

The five-membered ring in the molecule has its four carbon atoms C(1), C(2), C(4), and C(5) nearly in the plane

$$0{\cdot}7469x' - 0{\cdot}6508y' - 0{\cdot}1364z' + 1{\cdot}3342 = 0 \qquad (1)$$

referred to the orthogonal axes $x' = x + z\cos\beta$, $y' = y$, $z' = z\sin\beta$, and the nitrogen atom is 0·534 Å from the plane. Projection of the atoms of the azabicyclohexane ring and of their substituents onto this plane and their distances from it as shown in Fig. 3 demonstrate the chair of the ring, with atoms N(3) and C(6) lying on opposite sides of the plane. The χ^2 test for atoms C(1), C(2), C(4), and C(5) indicates that they deviate significantly from exact planarity: $\chi^2 = 20$, $n = 1$, $P < 0{\cdot}1\%$ (*International Tables*, 1959). The three-membered ring formed by C(1), C(5), and C(6) is tilted by 65·0° from plane (1), while the other side of the chair containing C(2), N(3). and C(4) is at an angle of only 34·5° from this plane.

Each of the two phenyl rings is exactly planar. The mean plane through atoms C(7) to C(12) is given by the equation

$$0{\cdot}7016x' - 0{\cdot}6658y' - 0{\cdot}2537z' + 0{\cdot}8518 = 0\,, \qquad (2)$$

$\chi^2 = 5{\cdot}3$, $P > 5\%$, and that through atoms C(13) to C(18) by

$$0{\cdot}1608x' - 0{\cdot}5442y' + 0{\cdot}8234z' - 1{\cdot}2662 = 0\,, \qquad (3)$$

$\chi^2 = 14{\cdot}6$, $P > 0{\cdot}1\%$.

Intermolecular distances

The shortest distances between carbon or nitrogen atoms of different molecules are C(20′)–C(20″) = 3·445 Å, C(11)–C(17) = 3·656 Å, and C(19′)–C(20″) = 3·672 Å, assuming the aforementioned restriction on location C(20″). The nearest contacts between the molecule and the unattached Br, and O of the water molecule are Br–C(4) = 3·770 Å, and O–C(9) = 3·309 Å, respectively. Each oxygen atom is at distances 3·337 and 3·397 Å from two centrosymmetrically related bromine atoms, and *vice versa*, with the angles Br–O–Br = 100·6° and O–Br–O = 79·4°. Hydrogen atoms of the water molecule lie very close to the lines joining the O and Br atoms, at distances 2·27 and 2·37 Å from Br, and form an angle H–O–H = 103·6°. This arrangement suggests the existence of hydrogen bonds linking each pair of O and Br atoms and those centrosymmetrically related to them to form a closed parallellogram $\mathrm{Br^-}\ldots\mathrm{H{-}O{-}H}\ldots\mathrm{Br^-}\ldots\mathrm{H{-}O{-}H}\ldots\mathrm{Br^-}$. In the structure of codeine hydrobromide dihydrate, similar distances of 3·262, 3·395 and 3·397 Å have been reported for possible hydrogen bonds between H_2O and Br atoms (Kartha, Ahmed & Barnes, 1962).

Conclusions

The azabicyclo[3·1·0]hexane ring has the chair form with the bonds C(1)–C(2) and C(14)–C(5) (Figs. 1 and 3) nearly but not exactly in one plane; the propane ring is at an angle of 65·0° from the mean plane of these two bonds, while the opposite side of the chair (through atoms C(2), N(3), and C(4)) is only 34·5° from this plane. Both the hydrogen atoms H(1) and H(6), which are bonded to C(1) and C(5) respectively, are equatorial but have been rotated by the formation of the C(1)–C(5) bond until they are *cis* to the neighbouring equatorial atoms H(2) and H(5), respectively, instead of *trans* as in an undistorted piperidine ring (Fig. 3). All the bond angles at C(6) deviate from the value of 109·5° for an unstrained tetrahedral arrangement, with the angle C(1)–C(6)–C(5) = 60·3° and the other five angles having values between 113·0° and 123·4°. It is particularly interesting to note that the phenyl ring defined by atoms C(13) to C(18) is joined to the propane ring at angles C(13)–C(6)–C(1) = 123·4° and C(13)–C(6)–C(5) = 121·2°, while the other phenyl ring, defined by atoms C(7) to C(12), is joined to the same propane ring at angles C(7)–C(6)–C(1) = 114·4° and C(7)–C(6)–C(5) = 114·9°. The difference between these two pairs of angles may be attributed, presumably, to larger interaction between the mass of the central system and the phenyl ring defined by atoms C(13) to C(18) (see Fig. 2).

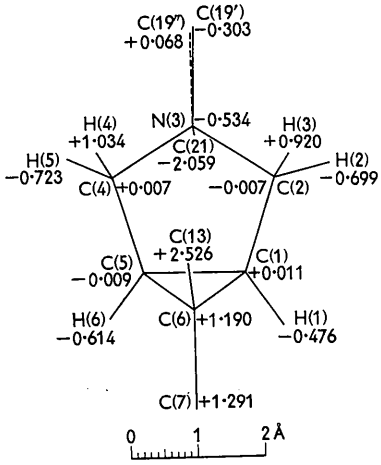

Fig. 3. Projection of the azabicyclohexane ring and its substituents onto the mean plane through atoms C(1), C(2), C(4), and C(5) and their distances (Å) from it.

The computations involved in this analysis were carried out on IBM 1620 and 650 computers with programs written by Ahmed (1962), a centres' location program by Gabe, and a bond angles program by Mrs M. E. Pippy.

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