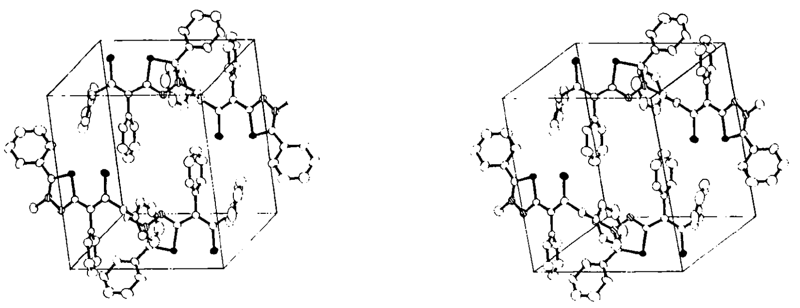

Fig. 3. Contents of one unit cell. The sulfur atoms are shown as ● and the nitrogen atoms as ◎ (a is into the paper).

Karle, J. & Karle, I. L. (1966). *Acta Cryst.* **21**, 849.

Moriarty, R. M., Mukherjee, R., Flippen, J. L. & Karle, J. (1971). *Chem. Commun.* p. 1436.

Pauling, L. (1960). *The Nature of the Chemical Bond.* Cornell Univ. Press: Ithaca.

Sletten, J. (1969). *Chem. Commun.* p. 688.

Acta Cryst. (1972). B**28**, 2754

Crystal and Molecular Structure of *N*-*p*-Bromobenzoyl-*exo*-2,3-aziridinobicyclo[2,2,1]heptane*

By E. M. Gopalakrishna†

Biochemistry Laboratory, National Research Council of Canada, Ottawa, Canada K1A 0R6

(*Received* 21 *May* 1971)

N-*p*-Bromobenzoyl-*exo*-2,3-aziridinobicyclo[2,2,1]heptane, $BrC_6H_4CONC_7H_{10}$, crystallizes in the monoclinic space group $P2_1/a$ with $a=12{\cdot}43\pm0{\cdot}01$, $b=17{\cdot}13\pm0{\cdot}02$, $c=6{\cdot}08\pm0{\cdot}01$ Å, $\beta=104{\cdot}2\pm0{\cdot}1°$ and $Z=4$ (at 22°C). The structure was determined by the heavy-atom method using three-dimensional diffractometer data. The final R value for 1924 observed reflexions within the limits $2\theta\le130°$ with Cu $K\alpha$ radiation is 5·2%. The three bond distances in the bicyclo[2,2,1]heptane system, C(1)–C(2), C(2)–C(3) and C(3)–C(4) with values of 1·497, 1·491 and 1·512 Å respectively, are shorter than the unstrained C–C single-bond distance. The bond angle C(1)–C(7)–C(4) in the same heptane system with a value of 95·4° is highly strained.

Introduction

The addition of alkoxycarbonyl nitrenes to norbornylene has been assumed to give the corresponding alkoxycarbonylaziridine (Scheiner, 1967; Ochlsehlager, McDaniel, Thakore, Tillman & Zalkow, 1969), as shown in Fig. 1(*a*). This conclusion was supported by the n.m.r. spectra of the products, which indicated apparent equivalence of the two hydrogens on the carbons attached to nitrogen (Tori, Kitahnoki, Takono, Tanida & Tsuji, 1965). However ring-opening reactions of the corresponding base gave 2,7-disubstituted norbornane derivatives (Edwards, Elder & Lesage, 1971; Tanida, Tsuji & Irie, 1966). Similarly the product of addition of *N*-benzenesulphoxylnitrene to norbornylene gave 2,7-disubstituted derivatives on ring-opening on the base (Ochlsehlager & Zalkow, 1963). These results suggested that the addition products were actually the azetidine derivatives [Fig. 1(*b*)]. Hence it seemed desirable to provide more conclusive proof of the structure of one of these adducts by X-ray analysis.

The adduct from light-induced addition of ethyl azidoformate to norbornylene was hydrolysed gently to the free base and this acylated with *p*-bromobenzoyl chloride yielded the compound of the present study.

Experimental

Slow evaporation of a solution of the substance in benzene yielded small needle-like crystals elongated along the *c* axis. The crystals were colourless before exposure to the atmosphere, but developed a strong purple colour when exposed. The space-group symmetry and the initial lattice parameters were determined from precession photographs taken with the X-ray beam parallel to the a^* and b^* axes. The crystals be-

---

* Issued as N.R.C.C. No. 12755.

† National Research Council postdoctoral fellow, 1969–1971. Present address: Department of Physics, University of Mysore, Mysore-6, India.

long to the monoclinic space group $P2_1/a$. The lattice parameters were later refined using the diffractometer data from high-angle reflexions. They are $a=12{\cdot}43\pm0{\cdot}01$, $b=17{\cdot}13\pm0{\cdot}02$, $c=6{\cdot}08\pm0{\cdot}01$ Å and $\beta=104{\cdot}2\pm0{\cdot}1°$. The density calculated on the basis of four molecules per unit cell is 1·557 g.cm^{-3}, as compared to the measured value of 1·552 g.cm^{-3} determined by the flotation method. All the intensity measurements were made on a Picker punched-card operated automatic single-crystal diffractometer using a scintillation counter. Cu $K\alpha$ radiation was used in both the precession method and the diffractometer. Intensities were collected by the 2θ scan method. A set of four standard reflexions was chosen and their intensities were measured at regular intervals as a check for possible crystal decay. However, the crystal did not show any such decay, even though it grew darker in colour with time. The crystal used was $0{\cdot}1\times0{\cdot}15\times0{\cdot}25$ mm in size. No absorption corrections were applied to the measured intensities [μ(Cu $K\alpha$)$=48{\cdot}0$ cm^{-1}; $\mu(r_{\max})=0{\cdot}7$; maximum effect on intensities is 18%]. All the 2114 independent reflexions within the copper sphere of limits $2\theta\leq130°$ were measured, out of which 1924 had observable intensities. All the calculations in this work were done on the IBM 360/50 computer system at the N.R.C. Computation Centre.

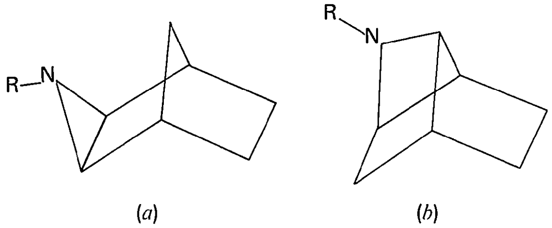

Fig. 1. (a) Aziridine. (b) Azetidine.

Structure analysis

The position of the Br atom was determined from a sharpened Patterson map. Structure factors calculated with the contribution from the Br atom alone gave an R value of 32%. The electron density map phased on the Br atom yielded the positions of all the non-hydrogen atoms. The block-diagonal least-squares method was used for refining the structure, using a 9×9 matrix block for each atom with an anisotropic temperature factor and a 4×4 block for each with an isotropic temperature factor. Four cycles of least-squares refinement using all the non-hydrogen atoms with isotropic temperature factors reduced the R value from 26 to 18%. On introducing anisotropic temperature factors, the R value came down to 6·5% after six cycles of refinement. A difference map computed at this stage revealed the positions of all the hydrogen atoms except H(206) whose position was calculated from the usual bond distances and bond angles. On including all the hydrogen atoms with isotropic temperature factors and further refining, the R value finally came down to 5·2%. At this stage, all the shifts were less than one third their corresponding estimated standard deviations.

The scattering factors used in these calculations were taken from *International Tables for X-ray Crystallography* (1962) for Br, C, N and O atoms an from Stewart, Davidson & Simpson (1965) for H atoms. The scattering factors for Br atoms were corrected for the anomalous dispersion factors $\Delta f'$. A weighting scheme with

$$\text{weight}=1 \qquad \text{if } F(\text{obs})\leq55$$

and

$$\text{weight}=55/F(\text{obs}) \qquad \text{for others}$$

was used in the final stages of least-squares refinement.

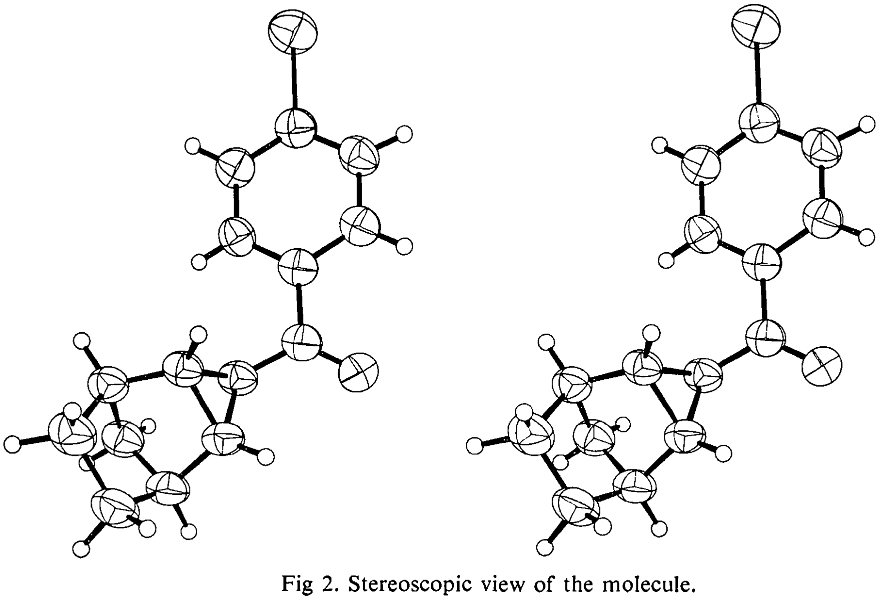

Fig 2. Stereoscopic view of the molecule.

The unobserved reflexions were included in the least-squares sums and R value only when their F(calc) were greater than their threshold values.

The observed and calculated structure factors are listed in Table 1. Table 2 gives the final atomic positions and temperature factors. The estimated standard deviations obtained from the inverse of the block diagonal matrices are given in parentheses in Table 2. These numbers refer to the least significant digit in the values given.

Table 1. *Observed and calculated structure factors* (× 10)

An asterisk indicates an unobserved reflexion, with $F_{\min}$ given in place of $|F_o|$.

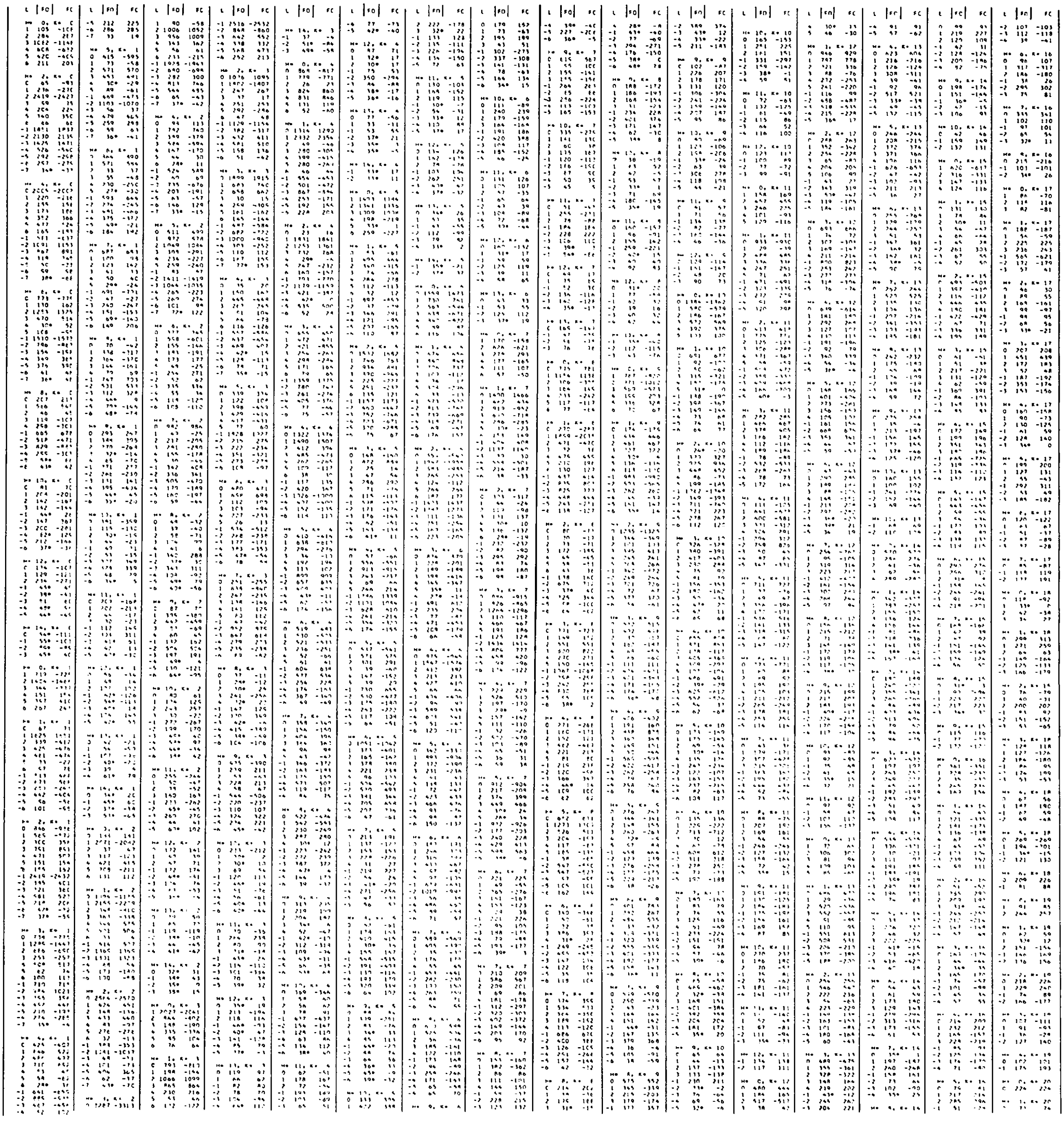

Table 2. *Atomic parameters*

(*a*) Fractional atomic coordinates and anisotropic temperature factors for non-hydrogen atoms

The temperature factor is of the form

$$T = \exp -[h^2B(11)+k^2B(22)+l^2B(33)+hkB(12)+hlB(13)+klB(23)]\,.$$

	x/a	y/b	z/c	$B(11)$	$B(22)$	$B(33)$	$B(23)$	$B(13)$	$B(12)$
Br	0·61811 (6)	0·35076 (4)	1·13248 (11)	0·01470	0·00434	0·05033	−0·00720	0·01110	−0·00645
C(1)	0·1709 (7)	−0·0589 (4)	0·4784 (12)	0·0078	0·0041	0·0350	−0·0023	0·0001	−0·0022
C(2)	0·2871 (7)	−0·0306 (5)	0·4841 (12)	0·0083	0·0030	0·0297	−0·0021	0·0024	−0·0009
C(3)	0·3336 (8)	−0·0075 (5)	0·7263 (13)	0·0069	0·0027	0·0313	0·0011	0·0020	−0·0003
C(4)	0·2425 (6)	−0·0236 (4)	0·8429 (11)	0·0084	0·0031	0·0315	−0·0002	0·0040	−0·0007
C(5)	0·2401 (7)	−0·1143 (4)	0·8564 (12)	0·0116	0·0035	0·0433	0·0033	0·0040	−0·0017
C(6)	0·1884 (7)	−0·1378 (4)	0·6055 (10)	0·0107	0·0036	0·0495	−0·0039	0·0104	−0·0034
C(7)	0·1377 (8)	−0·0076 (5)	0·6566 (11)	0·0071	0·0039	0·0383	0·0007	0·0025	−0·0001
C(8)	0·3917 (8)	0·0924 (5)	0·4809 (11)	0·0079	0·0032	0·0312	0·0023	0·0027	−0·0002
C(9)	0·4433 (8)	0·1557 (5)	0·6398 (11)	0·0075	0·0026	0·0318	0·0028	0·0029	0·0006
C(10)	0·4075 (7)	0·1746 (4)	0·8302 (11)	0·0080	0·0029	0·0350	0·0009	0·0092	−0·0006
C(11)	0·4569 (7)	0·2332 (4)	0·9750 (11)	0·0093	0·0031	0·0346	−0·0008	0·0094	−0·0000
C(12)	0·5445 (7)	0·2737 (4)	0·9266 (10)	0·0091	0·0028	0·0355	0·0022	0·0042	−0·0007
C(13)	0·5818 (8)	0·2568 (5)	0·7349 (12)	0·0077	0·0033	0·0381	0·0036	0·0055	−0·0014
C(14)	0·5316 (7)	0·1979 (4)	0·5932 (10)	0·0076	0·0033	0·0347	0·0039	0·0041	−0·0000
O	0·4169 (6)	0·0809 (4)	0·3009 (10)	0·0104	0·0052	0·0321	−0·0026	0·0099	−0·0034
N	0·3072 (7)	0·0518 (4)	0·5436 (11)	0·0075	0·0029	0·0302	0·0008	0·0020	−0·0005

Table 2 (*cont.*)

(*b*) Fractional atomic coordinates and isotropic temperature factors for hydrogen atoms

	x/a	y/b	z/c	B(Å^2)
H(1)	0·113 (6)	−0·060 (4)	0·312 (9)	6·3
H(2)	0·337 (6)	−0·055 (5)	0·383 (9)	5·8
H(3)	0·417 (6)	−0·017 (5)	0·792 (10)	4·3
H(4)	0·253 (7)	0·006 (4)	0·988 (10)	5·6
H(105)	0·182 (6)	−0·134 (4)	0·958 (11)	6·3
H(205)	0·318 (6)	−0·139 (4)	0·930 (10)	8·3
H(106)	0·116 (7)	−0·168 (4)	0·585 (9)	7·9
H(206)	0·241 (7)	−0·174 (5)	0·529 (9)	8·6
H(107)	0·077 (6)	−0·030 (4)	0·680 (9)	7·4
H(207)	0·125 (6)	0·043 (5)	0·595 (11)	4·6
H(10)	0·352 (7)	0·147 (5)	0·861 (10)	6·6
H(11)	0·433 (7)	0·246 (5)	1·117 (10)	5·1
H(13)	0·636 (6)	0·286 (6)	0·680 (9)	6·4
H(14)	0·559 (6)	0·184 (6)	0·462 (9)	6·7

Discussion

A stereoscopic plot of the molecule is shown in Fig. 2. This and the packing diagram in Fig. 3 were drawn by a computer using the *ORTEP* program by Johnson (1965). The thermal ellipsoids in these diagrams correspond to the 50% probability level. The present analysis confirms the n.m.r. evidence that this product is an aziridine. Chemical proof of the validity of this assignment has in the meantime also been obtained (Edwards *et al.*, 1971).

Bond lengths and bond angles are given in Fig. 4. The estimated standard deviations are given in parentheses and the numbers refer to the least significant digit in the values given. Table 3 gives bond angles not marked on Fig. 4. The C–C bond distances in the benzene ring vary from 1·372 to 1·396 Å, averaging 1·380 Å, as compared to the normal C–C resonance bond distance of 1·395 ± 3 Å expected in aromatic rings (*International Tables for X-ray Crystallography*, 1962). The C–C single-bond distances in the bicyclo-[2,2,1]heptane ring system vary from 1·491 to 1·551 Å, as compared to the ideal C–C single bond distance of 1·541 Å (*International Tables for X-ray Crystallography*, 1962). The C–C bonds which are away from the aziridine ring have values close to the theoretical value, whereas the ones which are close to the aziridine ring are slightly shortened. The two C–N bonds in the aziridine ring with lengths 1·462 and 1·478 Å are in good agreement with the value 1·472 Å given in *International Tables for X-ray Crystallography* (1962) for similar bonds with a 3-covalent nitrogen. The C–N

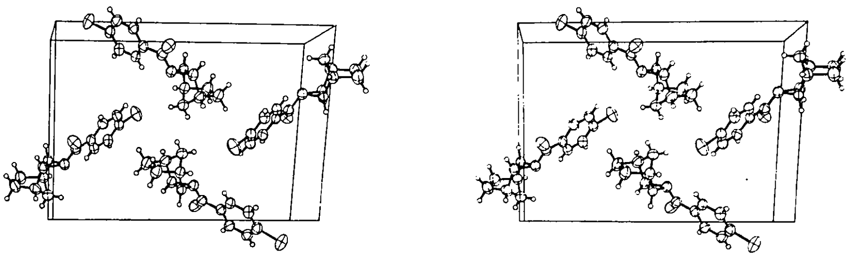

Fig. 3. Stereoscopic packing diagram, as seen down the *c* axis. The *b* axis is parallel to the inter-ocular direction.

bond length 1·386 Å between C(8) and N is slightly larger than the expected value of 1·322 A (*International Tables for X-ray Crystallography*, 1962). All the other bond lengths are close to their expected values.

Table 3. *Bond angles which are not marked in Fig.* 4

C(6)–C(1)–C(2)	103·5 (3)°	C(7)–C(4)–H(4)	116 (3)°
C(1)–C(2)–N	115·2 (3)	C(4)–C(5)–H(205)	108 (3)
N——C(3)–C(4)	114·8 (3)	C(6)–C(5)–H(105)	113 (3)
C(3)–C(4)–C(5)	104·6 (4)	C(1)–C(6)–H(106)	111 (2)
C(7)–C(1)–H(1)	118 (3)	C(5)–C(6)–H(206)	115 (3)
C(3)–C(2)–H(2)	126 (2)	C(1)–C(7)–H(107)	114 (3)
C(2)–C(3)–H(3)	122 (3)	C(4)–C(7)–H(207)	107 (2)

The amount of strain in the bicyclo[2,2,1]heptane system is revealed in the bond angles. The bond angle C(1)–C(7)–C(4) with a value of 95·4° is the most affected. The distance between C(1) and C(2) is 2·156 Å. All the other bond angles in this system are also smaller than the unstrained tetrahedral bond angle of 109·5°. All the structural features of the bicycloheptane system observed in the present molecule are in conformity with the ones observed in similar compounds (Macdonald & Trotter, 1965*a*, *b*) except the shortening of the C–C bond distances which are close to the aziridine ring. The bond angles surrounding the atoms C(8), C(9) and C(12) deviate slightly from the ideal 120°.

The benzene ring is planar within experimental error. Atom C(8) lies practically in this plane, the perpendicular distance being 0·008 Å, which is twice the corresponding e.s.d. O and N atoms are 0·116 (3) and −0·043 (3) Å, respectively, away from the benzene ring. The Br atom is 0·099 Å away from the plane of the benzene ring, possibly owing to packing. These and other perpendicular distances of atoms from mean planes (Table 4) are given in Table 5. The dihedral angles of interest are given in Table 6. The aziridine ring and the benzene ring are inclined to each other at an angle of 120·8°. The dihedral angle of 124·7° between the aziridine ring and the mean plane of the atoms C(9), C(8), N and O shows that the amide resonance exists only slightly, if at all. The mean plane of the three atoms C(1), C(4) and C(7) in the bicycloheptane system is almost equally inclined to the two mean planes containing atoms C(1), C(2), C(3) and C(4) and C(1), C(4), C(5) and C(6), with angles 128·7 and 122·7° respectively. The latter two planes are inclined to each other at an angle of 108·6°.

The bicycloheptane system has mirror symmetry about a plane perpendicular to the direction C(1)–C(4). The bond lengths and bond angles are all symmetrical about this plane within experimental error.

There are very few short intermolecular distances (Table 7). The shortest intermolecular distance involving the Br atom is with a neighbouring N atom at 3·408 Å. There are three other distances less than 3·5 Å between non-hydrogen atoms, seven distances less than 3·0 Å between hydrogen and heavier atoms, and two distances less than 2·5 Å between hydrogen atoms themselves. None of these distances are shorter than the usual van der Waals distances.

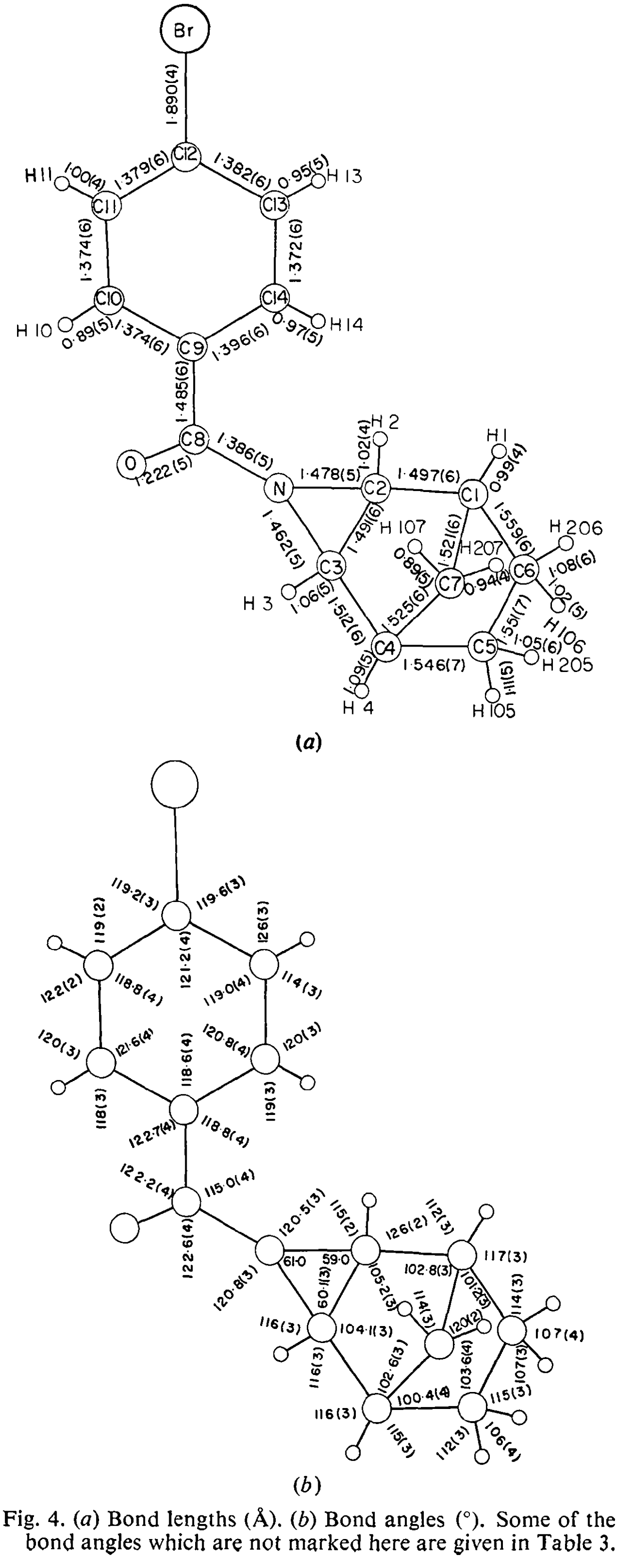

Fig. 4. (*a*) Bond lengths (Å). (*b*) Bond angles (°). Some of the bond angles which are not marked here are given in Table 3.

Table 4. *Least-squares planes*

The equations to the least-squares planes are of the form $lX+mY+nZ=P$, where X, Y, Z and P are in Å units relative to the crystal axes.

Plane	Atoms included	*l*	*m*	*n*	*P*
1	C(9), C(10), C(11), C(12), C(13), C(14)	−0·5322	0·6594	−0·5310	−2·6487
2	C(9), C(10), C(11), C(12), C(13), C(14), C(8), Br	−0·5285	0·6682	−0·5237	−2·5776
3	C(9), C(10), C(11), C(12), C(13), C(14), C(8), Br, H(10), H(11), H(13), H(14)	−0·5390	0·6616	−0·5214	−2·6369
4	C(8), C(9), N, O	−0·5840	0·6574	−0·4762	−2·6950
5	N, C(2), C(3)	0·9884	−0·0808	−0·1283	2·4808
6	C(1), C(2), C(3), C(4)	−0·3085	0·9273	−0·2119	−1·9638
7	C(1), C(4), C(5), C(6)	0·9872	−0·0497	−0·1518	1·0034
8	C(1), C(4), C(7)	0·5398	0·7832	−0·3086	−0·8986

Table 5. *Perpendicular distances of atoms* (in Å) *from the least-squares planes*

	Least-squares plane No.			
	1	2	3	4
Br	−0·099	−0·047*	−0·074*	
C(12)	−0·006*	0·023*	0·009*	
C(13)	0·005*	0·026*	0·002*	
C(14)	0·000*	0·005*	−0·010*	
C(9)	−0·004*	−0·008*	−0·004*	0·007*
C(10)	0·003*	0·007*	0·019*	
C(11)	0·002*	0·023*	0·025*	
H(13)	0·100	0·048	0·091*	
H(14)	−0·030	0·049	−0·051*	
H(10)	−0·017	0·049	0·005*	
H(11)	−0·029	0·043	0·007*	
C(8)	−0·008	−0·030*	−0·017*	−0·025*
O	0·116	0·084	0·098	0·010*
N	−0·043	−0·076	−0·006	0·008*

* Atoms included in the calculation of the corresponding least-squares plane.

Table 6. *Dihedral angles*

The reference numbers for the least-squares planes are the ones given in Table 4.

Plane 1	Plane 2	Angle (°)
1	4	4·3
2	4	4·2
3	4	3·7
4	5	124·7
5	6	110·7
6	7	108·6
6	8	128·7
7	8	122·7

Since the crystal did not exhibit any decay as judged from the intensities of the standard reflexions, the cause of the colouration of the crystals on exposure to the atmospheric air is not known.

The author is grateful to Dr M. Przybylska for her keen interest in this work and to Dr C. P. Huber for her unfailing help during the course of this work. He is also highly thankful to Drs E. Edwards and M. Lesage for providing the material for this study.

Table 7. *Intermolecular contacts*

Atom 1	Atom 2	N_{eqv}*	Cell*			Distance (Å)
Br	N	2	0	0	1	3·408
C(5)	O	1	0	0	1	3·249
C(6)	O	1	0	0	1	3·381
C(9)	C(9)	−1	0	0	1	3·483
C(1)	H(23)	−1	1	0	2	2·87
C(2)	H(23)	−1	1	0	2	2·91
C(3)	H(11)	−1	1	0	1	2·92
C(3)	H(14)	−2	0	−1	1	2·97
O	H(8)	1	0	0	1	2·52
O	H(5)	1	0	0	1	2·82
O	H(10)	1	0	0	1	2·74
H(3)	H(24)	−1	1	0	1	2·47
H(6)	H(13)	−2	0	−1	2	2·48

* $N_{eqv.}$ and Cell specify the Atom-2 with respect to Atom-1. $N_{eqv.}=1$, -1, 2 and -2 refer to the equivalent positions x, y, z; $-x, -y, -z$; $\frac{1}{2}+x, \frac{1}{2}-y, z$; $\frac{1}{2}-x, \frac{1}{2}+y, -z$, respectively. Cell refers to unit translations along the three crystallographic axes.

References

Edwards, E., Elder, J. & Lesage, M. (1971). Unpublished work.

International Tables for X-ray Crystallography (1962). Vol. III, Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP*. ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Macdonald, A. C. & Trotter, J. (1965*a*). *Acta Cryst.* **18**, 243.

Macdonald, A. C. & Trotter, J. (1965*b*). *Acta Cryst.* **19**, 456.

Ochlsehlager, A. C., McDaniel, R. S., Thakore, A., Tillman, P. & Zalkow, L. H. (1969). *Canad. J. Chem.* **47**, 4367.

Ochlsehlager, A. C. & Zalkow, L. H. (1963). *J. Org. Chem.* **28**, 3303.

Scheiner, P. (1967). *J. Amer. Chem. Soc.* **90**, 988.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* B**24**, 63.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175.

Tanida, H., Tsuji, T. & Irie, T. (1966). *J. Org. Chem.* **31**, 3941.

Tori, K., Kitahnoki, K., Takano, Y., Tanida, H. & Tsuji, T. (1965). *Tetrahedron Letters*, No. 14, 869.