



Fig. 3. Contents of one unit cell. The sulfur atoms are shown as \bullet and the nitrogen atoms as \odot (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). B28, 2754

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

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N-p-Bromobenzoyl-*exo*-2,3-aziridinobicyclo[2,2,1]heptane, BrC₆H₄CONC₇H₁₀, crystallizes in the monoclinic space group $P2_1/a$ with $a=12\cdot43\pm0\cdot01$, $b=17\cdot13\pm0\cdot02$, $c=6\cdot08\pm0\cdot01$ Å, $\beta=104\cdot2\pm0\cdot1^{\circ}$ 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 $2\theta \le 130^{\circ}$ with Cu K α 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-

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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 = 12.43 + $0.01, b = 17.13 \pm 0.02, c = 6.08 \pm 0.01$ Å and $\beta = 104.2 \pm 0.01$ 0.1°. 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 α 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 $0.1 \times 0.15 \times 0.25$ mm in size. No absorption corrections were applied to the measured intensities [μ (Cu K α) = 48.0 cm⁻¹; μ (r_{max}) = 0.7; maximum effect on intensities is 18%]. All the 2114 independent reflexions within the copper sphere of limits $2\theta \le 130^\circ$ 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 Crys-tallography* (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

weight = 1 if $F(obs) \le 55$ and weight = 55/F(obs) 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 leastsquares 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 posi-

tions 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 ($\times 10$)

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

L [FO] . K	1 10 10	1 1 FO FC	1 10 10	1 10 m	1 10 10	1 1 m 1 m	L 10 FC	1 10 10	1 10 10	L [F] FC	L 10 10	1 [*n] *C	1 10 10	1 10 10	. [m] .c.]
1 105 -104		2 1006 1052	-1 2516 -2532	-1 13, 5 - 3		2 227 -176 1 320 - 22 -1 133 124	0 179 152 1 73 -63 2 195 199	-1 227 -207	-1 11 -10	-2 180 374 -3 430 12 -4 330 -22	H- 10, #+ 10 0 165 -155	10* 13 5 46 -30	-3 -3 -32	0 00 01 1 210 227 2 120 100	-1 112 -118
4 6CA -672 5 42C -4C4 6 211 201	0 113 193	4 46 61 6 213 -215 -1 1925 -1943	- 33 - 33		0 47 7L 1 120 17	-3 726 -176 -4 136 -150	-1 302 -273	· · · · · · · · · · · · · · · · · · ·	-1 204 -271 -4 176 -150 -5 38 C	-5 211 -143	1 241 225 2 141 151 -1 331 -297	He 1, E 17 0 446 429 1 747 778	0 A23 AN4 1 216 -210	-1 42 11 -2 124 -124 -1 201 -146	10 0 90 107
÷	2 571 570 1 551 571 5 10	-2 640 -694 -3 292 300 -4 413 746	0 10% 10% 1 1402 -1407	0 864 -817 1 779 -771 2 26 71	-1 15 51	He 11. 1. 5	-6 78 -61 -5 166 136 -6 36 15	1 155 -151		1 226 207		2 121 316 1 48 -76 4 212 -253	1 108 -111		-1 34 -180 -1 34 -26
2 2419 -2427	-1 669 -673	-5 544 495 -8 85 -43 -7 378 -42	2 247 267	3 824 860 4 831 846 5 131 119	3 32 47	1 154 -152 2 119 115	H- 10. K- 6	-2 15 44	1 186 -141	-1 106 -104	H- 11. K- 10 0 72 -61	-1 116 99 -2 456 -487		1 151 -144	-7 7 81
5 160 35C 6 66 60	-1 -6 -11	··· ·· ·· ·· ·· ·· ·· ·· ·· ·· ·· ·· ··	5 292 -296 6 67 68 -1 1129 -1136	• • • · · · •	H 11. 4. 4 0 77 -46 1 33 -11	-2 56 -11	2 170 -150	-5 165 -153	-1 234 224 -2 61 94		-1 61 -49 -2 115 66 -1 66 52		-3 10 -115	-1 106 - 01	1 102 110
-2 2130 2135	., 361	2 340 -370	-3 -32 -317	1 2132 2354	-1 53 55 -2 170 21		-1 191 186 -2 420 348 -3 104 117	0 115 -276 1 141 116 2 60 36	-1 14 1	0 01 -49 1 121 -106	-4 116 100 Ha 17, K+ 10	H+ 2, 8+ 12 C 248 2+3 1 352 -3+2	0 248 -244 1 208 -215 2 172 374	C 42 46 -1 149 149 -2 137 131	-1 5 11
-5 292 -269	1 571 536	3 44 30 0 74 11		5 240 -241				-1 120 -112 -2 166 -150	7 30 -19	2 154 -276	0 123 111 -1 100 #9 -2 37 -32	3 03 -274	3 371 166 4 106 116 -1 626 -651	1 420 -617	n 215 -216 -1 101 -101
T	1 55 -48 • 210 -250	-2 -7 -53 -3 715 -676 -6 203 -191	7 1490 1015 1 647 740 2 858 862	-1 454 -441	3 11 11	2 262 251	0 111 126	-4 50 35		-5 44 -21	-3 99 -91 4. 0. K. 11	5 106 97 -1 63 27 -7 163 319	-1 102 -01	2 116 -331 3 147 -133 4 124 116	-2 348 26
1 220 -216 2 155 154 3 175 166	-1 503 644 -7 774 -245 -1 441 -440	-5 63 -67 -6 146 129 -7 338 -15	5 10 15 6 260 -106 5 161 -162	-4 25) -171 -4 192 155 -5 224 265	1 1413 1144	······································	-1 05 04 -2 43 34 -3 104 -#4		-4 18C -145 -4 35+ 19	· · · · · · · · · · · · · · · · · · ·	3 246 275				1 11 114
6 165 -191			6 145 -144 -1 447 -584 -2 682 -722	· · · · ·	6 250 -227	-1 -1 -14	3 3 3	-1 104 114	0 14.0 - 15.7 1 56 - 71	-1 134 138 -2 82 -22 -3 185 -144	5 129 -116	He 1. L. 1. 0 691 644 1 7. 72	2 244 - 251	3 100 11	1 107 -107
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-6 50 50	2 121 142	-2 1411 - 1419	-7 770 153	A 140 -157 A 140 -157 -1 101 -770	2 160 -115	3 5 3	-2 125 119 -3 10 11 -5 59 65	H 12, K 1, C 44 1, L 11 15		-1 151 -167	• 247 251 • 71 • 67	-7 751 747		M. J. M. 14	-3 -5 -61
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3 470 114	-6 161 -153 -5 699 -163 -6 169 206	-7 77- 122	6 - 1 106 3 - 46 - 73 6 - 116 - 176	-6 52 24 -6 5, 8- 6	-1 146 241 -4 121 -45 -5 237 -155	1 414 -471 - 427 -477	2 15 12	· · · · · · ·	3 5 2	2 146 -167	· · · · ·	1 181 141	-1 207 -216	- 140 141 -1 477 -479 -7 47 -71	-1 44 45 -7 64 56
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1 566 547	-6 -70 -105	-6 108 -12* -6 108 -110	1 122 104	-6 -5 -574	-1 1157 1173 -7 650 -167 -1 757 -166	-1 113 -009	2 919 -952	5 117 -117 6 37 -66	4 114 124 6 11 61	-1 142 -147		3 156 -153		12 19 19 19	H 4, E 17 0 160 -158 1 90 -73
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-1 44* 28 -2 147 767 -3 200 -281	1 115 -11C	0 49 -12 1 12 -43	6 777 -733 5 76 13 -1 536 -517	-6 114 117 -6 5.45 6	-1 176 -161 -6 42 -61 -5 161 -114	- 1 111 - 136 - 0 761 - 766 - 6 167 - 166	1 111 137 6 106 10 6 136 -137	·	·· · · · · ·	-6 112 121	2 600 -381 3 331 -317	1. 1. 1			0 120 -122 1 41 47
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	2 34 20	3 160 163 -1 213 -262	-1 -2 -237	2 42 - W	-) 510 491 -1 141 344 -4 705 454	-1 12 -47 -7 473 433 -1 466 476	2 374 399	-6 62 67	-6 76 44 He 4, 64 6	-6 109 117	3 8 3	** 11: ** 12	-1 192 -119 -2 293 -294 -3 51 49	4 143 144 44 1. 44 14	1 147 19C
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2756

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Table 2. Atomic parameters

(a) Fractional atomic coordinates and anisotropic temperature factors for non-hydrogen atoms The temperature factor is of the form

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

	x/a	y/b	z/c	<i>B</i> (11)	<i>B</i> (22)	B(33)	<i>B</i> (23)	<i>B</i> (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
0	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 anal-

ysis 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) C(1)-C(2)-N NC(3)-C(4) C(3)-C(4)-C(5) C(7)-C(1)-H(1) C(3)-C(2)-H(2) C(2)-C(2)-H(2) C(3)-C(4)-C(3)-C(4) C(3)-C(4)-C(5) C(3)-C(2)-H(2) C(3)-C(2)-H(2) C(3)-C(2)-H(2) C(3)-C(2)-H(2) C(3)-C(2)-H(2) C(3)-C(2)-H(2) C(3)-C(3)-C(3)-C(3)-C(3)-C(3)-C(3)-C(3)-	$103.5 (3)^{\circ}$ $115.2 (3)$ $114.8 (3)$ $104.6 (4)$ $118 (3)$ $126 (2)$ (2)	C(7)-C(4)-H(4) C(4)-C(5)-H(205) C(6)-C(5)-H(105) C(1)-C(6)-H(106) C(5)-C(6)-H(206) C(1)-C(7)-H(107)	116 (3) 108 (3) 113 (3) 111 (2) 115 (3) 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	Р
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,	-0.5390	0.6616	-0.5214	-2.6369
	H(10), H(11), H(13), H(14)				
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-squar	es 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*
0	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 2	Angle (°)
4	4.3
4	4.2
4	3.7
5	124.7
6	110.7
7	108.6
8	128.7
8	122.7
	Plane 2 4 4 5 6 7 8 8 8

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.

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Table 7. Intermolecular contacts

Atom 1	Atom 2	N_{eqv}^*	Cell	*	Distance (Å)
Br	Ν	2	0 0	1	3.408
C(5)	0	1	0 0	1	3.249
C(6)	0	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
0	H(8)	1	0 0	1	2.52
0	H(5)	1	0 0	1	2.82
0	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. (1965a). Acta Cryst. 18, 243.
- MACDONALD, A. C. & TROTTER, J. (1965b). 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. B24, 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.