152. *The Crystal and Molecular Structure of (−)-2-Bromo-2-nitrocamphane.*

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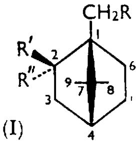
Crystals of (−)-2-bromo-2-nitrocamphane have been subjected to quantitative *X*-ray analysis. They are orthorhombic, of space group $P2_12_12_1$-$D_2{}^4$, with four molecules of $C_{10}H_{16}BrNO_2$ in the unit cell. The atoms (other than hydrogen) were located by computing successive three-dimensional Fourier syntheses. The bromine atom is *cis* to the CMe_2 bridge.

Studies of the optical rotatory dispersion of 2,2-disubstituted camphanes and related compounds have been reported by Mitchell and his co-workers.[1] In view of the current interest in the correlation of optical rotatory dispersion and stereochemistry we are determining by *X*-ray analysis the crystal, and hence molecular, structures of a number of these substances. For (+)-10-bromo-2-chloro-2-nitrosocamphane [2] we have shown [3] that the stereochemistry is as in (I; R = Br, R′ = Cl, R″ = NO), with the halogen atom at position 2 *cis* to the CMe_2 bridge. We now report that in (—)-2-bromo-2-nitrocamphane [2,4] also the halogen atom is *cis* to the CMe_2 bridge, the stereochemistry being as in (I; R = H, R′ = Br, R″ = NO_2).



(I)

Several cycles of three-dimensional Fourier and least-squares refinement of positional and thermal atomic parameters were carried out and the final value of *R*, the average discrepancy between measured and calculated structure amplitudes, is 12·5%.

The final electron-density distribution for (—)-2-bromo-2-nitrocamphane is shown in Fig. 1 as superimposed contour sections drawn parallel to (010) and covering the region of one molecule; the corresponding atomic arrangement is explained in Fig. 2. The interatomic distances and valency angles calculated from the final atomic co-ordinates (see Table 1) are listed in Table 2. The standard deviations of the final atomic co-ordinates

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[1] Mitchell, Watson, and Dunlop, *J.*, 1950, 3440; Hope and Mitchell, *J.*, 1953, 3483; see also ref. 2.

[2] Davidson, Ph.D. Thesis, Univ. Glasgow, 1958.

[3] Ferguson, Fritchie, Robertson, and Sim, *J.*, 1961, 1976.

[4] Ginnings and Noyes, *J. Amer. Chem. Soc.*, 1922, **44**, 2567.

were estimated in the usual manner from the least-squares residuals (see Experimental section) and are shown in Table 3; from the results the average e.s.d. of a carbon–carbon bond is about 0·03 Å and the average e.s.d. of a valency angle about 2°.

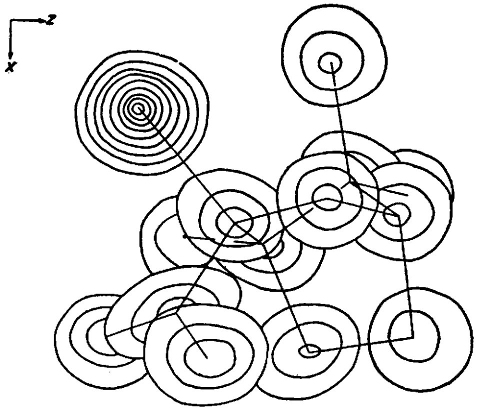

FIG. 1.

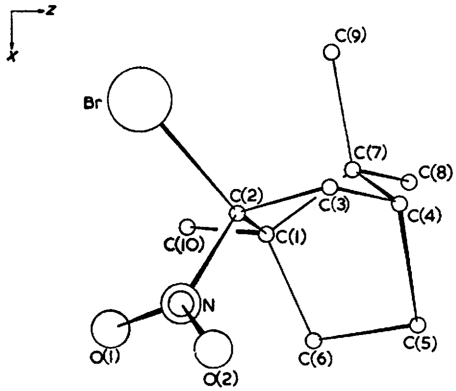

FIG. 2.

FIG. 1. Final three-dimensional electron-density distribution for (—)-2-bromo-2-nitrocamphane shown by means of superimposed contour sections drawn parallel to (010). Contour interval 2 e/Å^3, except around the bromine atom where it is 5 e/Å^3.

FIG. 2. Atomic arrangement corresponding to Fig. 1.

The average carbon–carbon bond length of 1·547 Å compares favourably with the value of 1·545 Å in diamond. The carbon–bromine bond length of 1·96 Å is in good agreement with the average value of 1·94 Å reported for various alkyl bromides.[5] The dimensions of the nitro-group do not differ significantly from the accepted values; that the angle ONO (124°) is as usual greater than the angles CNO (118°) can be attributed to the repulsion between non-bonding pairs of electrons on the oxygen atoms.[6]

TABLE 1.

Atomic co-ordinates.

(Origin of co-ordinates as in " International Tables for X-Ray Crystallography," Kynoch Press, Birmingham, 1952, Vol. I.)

Atom	x/a	y/b	z/c	B	Atom	x/a	y/b	z/c	B
C(1)	0·0411	0·5594	−0·1481	4·3	C(8)	−0·0167	0·4487	0·1296	6·4
C(2)	0·0156	0·6682	−0·1976	4·1	C(9)	−0·1788	0·5453	−0·0156	5·4
C(3)	−0·0149	0·7209	−0·0194	4·1	C(10)	0·0362	0·4849	−0·2916	4·9
C(4)	0·0095	0·6433	0·1144	4·6	O(1)	0·1577	0·6728	−0·4323	6·1
C(5)	0·1466	0·6170	0·1348	6·4	O(2)	0·1756	0·7834	−0·2308	8·2
C(6)	0·1689	0·5608	−0·0501	4·8	N	0·1240	0·7135	−0·2979	4·5
C(7)	−0·0403	0·5464	0·0235	5·0	Br	−0·1116	0·6893	−0·3763	4·4

While a number of the exocyclic valency angles, *e.g.*, C(6)C(1)C(10), C(2)C(1)C(10), C(1)C(7)C(8), C(1)C(7)C(9), C(4)C(7)C(8), C(4)C(7)C(9), C(1)C(2)Br, exceed the tetrahedral value of 109°28′ the valency angles in the cyclopentane rings C(1)C(2)C(3)C(4)C(7) and C(1)C(6)C(5)C(4)C(7) are consistently smaller than tetrahedral, the average value being

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[5] Sutton *et al.*, " Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Special Publ.* No. 11, 1958.

[6] Ferguson and Sim, *J.*, 1962, in the press.

TABLE 2.

Interatomic distances (Å) and angles.

Intramolecular bonded distances

C(1)–C(2)	1·54	C(5)–C(6)	1·59	C(7)–C(8)	1·56	C(2)–N	1·54
C(2)–C(3)	1·54	C(6)–C(1)	1·59	C(7)–C(9)	1·56	N–O(1)	1·20
C(3)–C(4)	1·47	C(1)–C(10)	1·47	C(7)–C(4)	1·57	N–O(2)	1·21
C(4)–C(5)	1·57	C(1)–C(7)	1·57	C(2)–Br	1·96		

Intramolecular non-bonded distances

C(1) ··· C(4)	2·28	C(2) ··· C(6)	2·49	C(4) ··· C(6)	2·42	C(6) ··· N	2·81
C(1) ··· C(8)	2·63	C(2) ··· C(7)	2·41	C(4) ··· C(8)	2·64	C(6) ··· O(1)	3·22
C(1) ··· C(9)	2·63	C(2) ··· C(9)	3·03	C(4) ··· C(9)	2·65	C(6) ··· O(2)	3·29
C(1) ··· C(3)	2·45	C(2) ··· C(10)	2·57	C(5) ··· C(7)	2·42	C(7) ··· N	3·75
C(1) ··· C(5)	2·53	C(3) ··· C(5)	2·54	C(5) ··· C(8)	2·90	C(8) ··· C(10)	3·23
C(1) ··· Br	2·97	C(3) ··· C(7)	2·39	C(5) ··· C(9)	3·89	C(9) ··· C(10)	3·25
C(1) ··· N	2·53	C(3) ··· C(9)	2·98	C(6) ··· C(7)	2·39	C(9) ··· Br	3·39
C(1) ··· O(1)	2·91	C(3) ··· Br	2·89	C(6) ··· C(8)	2·88	C(10) ··· Br	3·26
C(1) ··· O(2)	3·42	C(3) ··· O(1)	3·68	C(6) ··· C(10)	2·54	C(10) ··· O(1)	3·15
C(2) ··· C(4)	2·35	C(3) ··· O(2)	2·76				

Intermolecular distances ($\leqslant 4$ Å)

O(1) ··· C(5)$_{\mathrm{I}}$	3·31	O(1) ··· C(4)$_{\mathrm{I}}$	3·77	C(10) ··· C(3)$_{\mathrm{IV}}$	3·83	O(2) ··· C(4)$_{\mathrm{II}}$	3·92
O(2) ··· C(9)$_{\mathrm{II}}$	3·36	O(2) ··· Br$_{\mathrm{III}}$	3·77	C(10) ··· C(6)$_{\mathrm{V}}$	3·84	C(6) ··· C(5)$_{\mathrm{V}}$	3·92
O(1) ··· Br$_{\mathrm{III}}$	3·46	O(1) ··· C(6)$_{\mathrm{V}}$	3·79	O(2) ··· C(3)$_{\mathrm{II}}$	3·90	C(9) ··· O(2)$_{\mathrm{IV}}$	4·00
C(10) ··· O(2)$_{\mathrm{IV}}$	3·59	C(10) ··· C(5)$_{\mathrm{V}}$	3·81				

The subscripts refer to the positions

I $x, y, z - 1$
II $\frac{1}{2} + x, 1\frac{1}{2} - y, -z$
III $\frac{1}{2} + x, 1\frac{1}{2} - y, -1 - z$
IV $-x, y - \frac{1}{2}, -\frac{1}{2} - z$
V $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$

Interbond angles

C(1) C(2) C(3)	106°	C(6) C(1) C(2)	105°	C(1) C(2) N	111°	C(1) C(7) C(4)	93°
C(2) C(3) C(4)	103	C(6) C(1) C(7)	98	C(3) C(2) N	114	C(1) C(7) C(8)	114
C(3) C(4) C(5)	114	C(2) C(1) C(7)	101	C(3) C(2) Br	111	C(1) C(7) C(9)	114
C(3) C(4) C(7)	104	C(2) C(1) C(10)	118	Br C(2) N	100	C(4) C(7) C(8)	115
C(7) C(4) C(5)	101	C(6) C(1) C(10)	112	C(2) N O(1)	118	C(4) C(7) C(9)	116
C(4) C(5) C(6)	100	C(7) C(1) C(10)	120	C(2) N O(2)	118	C(8) C(7) C(9)	105
C(5) C(6) C(1)	105	C(1) C(2) Br	116	O(1) N O(2)	124		

TABLE 3.

Standard deviations of the final atomic co-ordinates (Å).

Atom	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	Atom	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	Atom	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
C(1)	0·016	0·020	0·025	C(6)	0·021	0·024	0·024	O(1)	0·015	0·016	0·016
C(2)	0·019	0·022	0·022	C(7)	0·022	0·022	0·030	O(2)	0·020	0·017	0·027
C(3)	0·020	0·022	0·027	C(8)	0·025	0·023	0·034	N	0·017	0·016	0·023
C(4)	0·021	0·020	0·027	C(9)	0·021	0·023	0·031	Br	0·002	0·003	0·003
C(5)	0·023	0·023	0·029	C(10)	0·026	0·023	0·030				

101°12′: particularly striking is the value of 93° for the angle C(1)C(7)C(4) at the CMe_2 bridge. A similar pattern of angles exists in (+)-10-bromo-2-chloro-2-nitrosocamphane[3] and it is likely that it is a consistent feature of the camphane molecular framework.

The molecule appears to be distorted slightly by the bulky halogen atom *cis* to the CMe_2 bridge. Thus the angle C(2)C(1)C(7) at 101° is rather greater than the angle C(6)C(1)C(7) which is only 98°. In addition, the distances from C(2) to C(7) and C(9) are 2·41 and 3·03 Å, respectively, rather greater than the distances from C(6) to C(7) and C(8) which are 2·39 and 2·88 Å, respectively. The effects, though small, are very similar to those noted in (+)-10-bromo-2-chloro-2-nitrosocamphane and are probably genuine.

The arrangement of the molecules in the crystal as viewed in projection along the *a* axis is shown in Fig. 3. The intermolecular separations (see Table 2) are all greater than 3 Å and correspond to normal van der Waals interactions; the shorter contacts involve the oxygen atoms of the nitro-group.

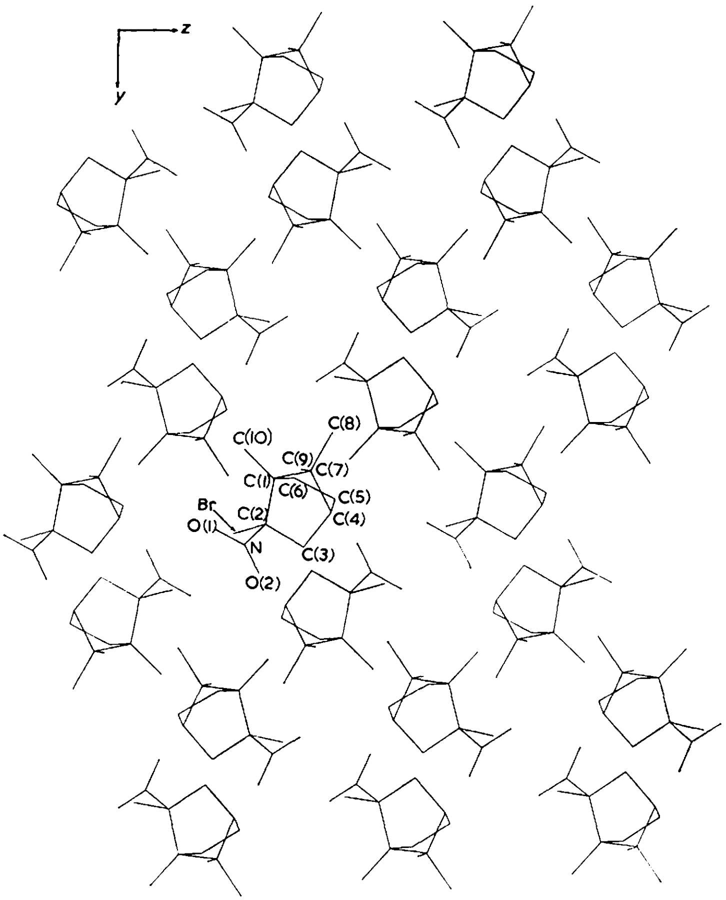

FIG. 3. The arrangement of molecules in the crystal as viewed in projection along the *a*-axis.

EXPERIMENTAL

Crystal Data.—(—)-2-Bromo-2-nitrocamphane, $C_{10}H_{16}BrNO_2$; $M = 262{\cdot}2$. Orthorhombic, $a = 11{\cdot}07$, $b = 13{\cdot}46$, $c = 7{\cdot}44$ Å, $U = 1108$ Å^3, $D_m = 1{\cdot}56$ (by flotation), $Z = 4$, $D_c = 1{\cdot}57$, $F(000) = 537$, space group $P2_12_12_1$ (D_2^4). Absorption coefficient for *X*-rays ($\lambda = 1{\cdot}542$ Å) $\mu = 50{\cdot}4$ cm.$^{-1}$.

Experimental Measurements.—Copper K_α radiation, $\lambda = 1{\cdot}542$ Å, was employed in all the *X*-ray measurements. Rotation, oscillation, and moving-film photographs were taken from crystals rotated about the principal zone axes, and these were analysed in the usual way to determine the cell dimensions and systematic halvings, from which the space group was determined uniquely. For the intensity measurements small crystals were employed, completely bathed in a uniform *X*-ray beam; no corrections for absorption of the beam in the crystal were applied. The multiple-film technique with visual estimation of intensities was applied to equatorial and equi-inclination upper-layer Weissenberg photographs taken from crystals rotated about the *b*- and *c*-crystal axes. The usual formulæ for mosaic-type crystals were used to derive values of $|F_o|$. The various layers were put on the same relative scale by comparison of common reflexions on different photographs. The absolute scale was obtained at a later stage by correlation with the final calculated structure amplitudes, $|F_c|$. In all 825 independent structure amplitudes were measured and are listed in Table 4.

Structure Analysis.—Because of the presence of the bromine atom there was no need to postulate trial structures with assumptions as to the stereochemistry of the molecule, the analysis proceeding directly on the basis of the usual phase-determining heavy-atom method.[7] The position of the bromine atom was determined from two-dimensional Patterson syntheses along the *b*-and *c*-crystal axes; these functions are shown in Fig. 4.

Consideration of the unit-cell dimensions indicated that further analysis of the structure by two-dimensional methods would be difficult and tedious because of overlap of the atoms; in consequence recourse was made to three-dimensional methods for the location of the remaining atoms in the asymmetric crystals unit. The first three-dimensional Fourier synthesis was calculated with phase angles appropriate to the bromine atom alone and served to locate the atoms of the nitro-group and carbon atoms 1, 2, 3, 7, and 9. Co-ordinates were assigned to these atoms and they were included in the calculation of a second set of structure amplitudes and phase angles. An overall isotropic temperature factor *B* of 3·6 Å^2 was assumed. The value of *R* was 25·6%.

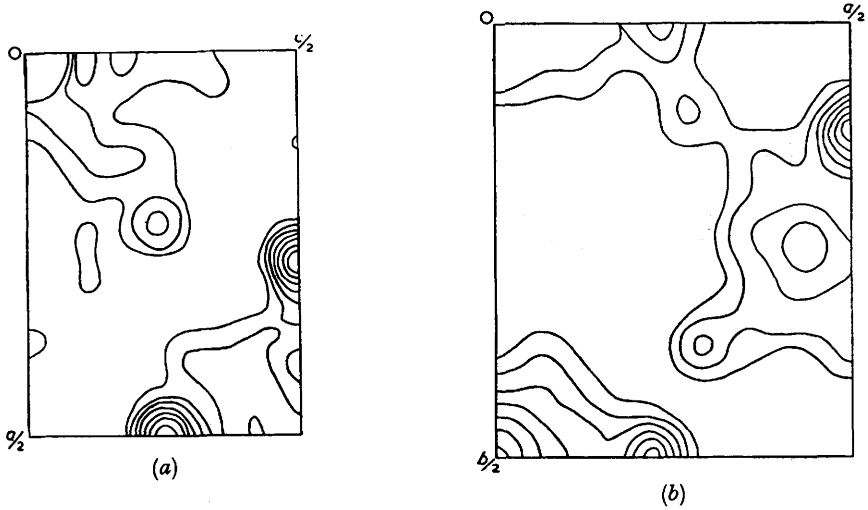

FIG. 4. Patterson projections along the *b*- and *c*-crystal axes. Contour scale arbitrary.

The improved phase angles were employed in the computation of a second three-dimensional Fourier synthesis in which it was possible to locate without ambiguity the remaining carbon atoms. When structure factors were recalculated with the inclusion of the additional atoms the value of *R* fell to 23·5%.

Four further rounds of structure-factor and Fourier calculations were carried out, back-shift corrections for termination of series being derived at each stage from a three-dimensional F_c synthesis. The value of *R* fell to 15·0%.

The refinement was concluded by performing five cycles of least-squares adjustment[8] of the positional and anisotropic thermal parameters of the atoms. The value of *R* fell to 11·1%. As some doubt was felt about the significance of the derived anisotropic temperature factors an isotropic value was deduced for each atom from the anisotropic parameters; these isotropic values are shown in Table 1. The final set of structure factors based on the isotropic *B* values was then calculated. The value of *R* was 12·5%. The final values of $|F_o|$, $|F_c|$ and α are shown in Table 4.

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[7] Robertson and Woodward, *J.*, 1937, 219; 1940, 36; Sim, "Computing Methods and the Phase Problem in X-Ray Crystal Analysis," ed. Pepinsky, Robertson, and Speakman, Pergamon Press, Oxford, 1961, p. 227.

[8] Rollett, "Computing Methods and the Phase Problem in X-Ray Crystal Analysis," edited by Pepinsky, Robertson, and Speakman, Pergamon Press, Oxford, 1961, p. 87.

TABLE 4.

Measured and calculated values of the structure factors.

h	*k*	*l*	$\|F_o\|$	$\|F_c\|$	α°
0	0	2	12	7	0
		4	60	56	180
		8	19	18	0
0	1	1	45	43	90
		3	60	55	270
		5	37	42	270
		6	32	16	90
0	2	0	67	88	180
		1	62	77	0
		2	28	32	0
		3	68	52	0
		4	42	37	0
		5	16	16	180
0	3	1	57	80	270
		3	33	28	90
		4	22	16	90
		5	12	11	90
0	4	0	38	32	0
		1	58	69	180
		4	27	24	0
		5	19	21	0
0	5	1	57	59	270
		3	22	20	270
		4	6	4	90
0	6	0	52	60	0
		1	60	65	0
		3	52	57	0
		4	35	33	180
		5	25	25	180
0	7	1	40	41	90
		2	15	16	90
		3	36	36	270
		4	10	11	270
		5	27	34	270
0	8	0	80	87	180
		2	10	12	180
		3	5	3	180
		4	30	34	0
0	9	1	46	44	270
		3	27	28	90
		4	15	15	90
		5	12	16	90
0	10	0	23	19	0
		1	33	33	180
		2	11	12	180
		3	16	18	180
		4	14	18	180
		5	7	9	0
0	11	1	13	13	90
		2	20	25	270
		3	12	13	270
		4	7	6	270
0	12	0	16	13	180
		1	12	15	0
		3	11	16	0
		5	6	10	180
0	13	1	12	12	90
		2	17	23	90
		3	5	3	90
		5	3	5	270
0	14	0	13	14	270
		1	13	13	180
		3	7	9	180
		4	5	8	0
		5	6	7	0
0	15	1	6	9	270
0	16	0	8	12	0
0	17	1	6	8	90
1	0	1	107	126	270
		2	54	49	0
		3	25	19	270
		5	13	13	90
		6	28	24	180
1	1	0	6	5	90
		1	50	45	169
		2	90	84	4
		3	49	48	108
		5	29	33	257
		6	37	30	175
1	2	0	162	159	90
		1	63	72	115
		2	32	36	152
		3	50	50	44
		4	49	38	280
		5	25	23	331
1	3	0	34	37	270
		1	55	66	170
		2	44	49	157
		3	34	37	307
		4	36	34	74
		5	27	28	15
1	4	0	90	101	270
		1	38	41	305
		2	23	19	49
		4	45	48	85
		5	17	19	176
1	5	0	57	61	90
		1	58	59	335
		2	54	52	182
		3	52	52	185
		4	33	32	257
		5	19	23	163
1	6	0	52	60	90
		1	37	39	252
		2	29	29	48
		3	24	22	318
		4	12	14	241
		5	16	22	28
1	7	0	27	26	270
		1	19	20	96
		2	26	30	4
		3	25	27	27
		4	16	16	38
		5	15	18	310
1	8	1	42	41	78
		2	33	38	176
		3	26	32	77
		5	14	18	255
1	9	0	6	6	270
		1	14	14	274
		2	27	30	176
		3	15	18	247
		4	6	7	66
		5	12	15	51
1	10	0	24	23	270
		1	28	25	298
		2	15	17	27
		3	15	17	238
		4	11	14	84
		5	5	8	110
1	11	0	14	15	90
		1	32	32	15
		2	15	16	349
		3	12	15	126
		4	14	16	258
		5	7	10	200
1	12	0	8	11	90
		1	12	11	187
		3	10	12	359
		4	12	16	262
1	13	0	15	16	270
		1	11	14	155
		3	7	10	1
		4	9	9	64
		5	5	7	352
1	14	1	6	10	30
		3	9	9	137
		4	7	8	77
		5	4	7	217
1	15	1	7	8	298
1	16	1	4	6	250
1	17	1	4	5	91
2	0	0	77	99	0
		1	53	60	90
		2	12	8	180
		3	79	73	270
		4	20	20	180
		5	41	45	270
		7	22	20	90
		9	9	7	90
2	1	0	27	28	100
		1	19	26	297
		2	45	34	218
		3	21	17	324
		4	64	58	352
		5	23	20	208
2	2	0	13	13	0
		1	51	53	300
		2	58	52	124
		3	37	34	108
		4	5	1	56
		5	23	24	119
2	3	0	32	32	0
		1	73	71	173
		2	16	17	345
		4	43	42	175
		5	30	31	5
2	4	0	11	8	0
		1	22	19	219
		2	44	57	280
		3	9	9	44
		4	7	6	18
		5	9	12	214
2	5	0	21	20	0
		1	43	40	11
		3	42	38	350
		4	22	19	166
		5	22	23	190
2	6	0	18	19	0
		2	54	54	107
		3	24	26	286
		4	6	7	110
		5	14	17	235
2	7	0	57	59	180
		1	15	15	171
		3	7	11	168
		4	32	33	6
		5	11	10	311
2	8	0	15	11	180
		1	34	33	258
		3	30	31	99
		4	9	14	319
		5	15	20	106
2	9	0	32	35	0
		1	11	9	254
		4	32	34	165
		5	5	7	26
2	10	0	8	4	180
		1	24	24	110
		2	23	27	276
		3	12	12	275
		4	5	5	51
		5	9	14	293
2	11	0	16	18	180
		1	17	19	9
		3	15	17	338
		4	11	11	11
		5	7	12	190
2	12	2	17	23	105
		3	6	6	32
2	13	0	10	10	180
		1	15	17	175
		3	10	13	173
		5	6	9	346
2	14	2	10	14	279
		3	6	9	99
2	15	0	11	13	0
		1	7	6	320
2	16	1	10	10	106
3	0	1	59	62	90
		2	70	75	0
		3	54	50	90
		4	10	7	0
		6	35	32	180
3	1	0	14	12	90
		1	48	53	119
		2	64	70	164
		4	17	15	281
		5	28	27	295
		7	21	17	252
3	2	0	58	48	270
		1	74	72	232
		2	48	45	207
		4	26	23	91
		5	30	25	32
3	3	0	69	62	270
		1	68	70	346
		2	12	13	358
		3	35	32	224
		4	50	45	70
		5	9	10	118
3	4	0	8	13	90
		1	45	46	17
		2	6	5	51
		3	34	29	200
		4	39	34	282
		5	23	26	185
3	5	0	57	53	90
		1	55	53	201
		2	15	17	53
		3	27	25	321
		4	45	44	283
		5	10	12	48
3	6	0	32	32	270
		1	25	27	162
		2	29	31	352
		3	40	40	47
		4	19	20	88
		5	17	21	333
3	7	0	23	24	270
		1	28	31	67
		2	31	33	192
		3	25	27	124
		4	15	14	68
		5	12	16	281
3	8	0	7	5	270
		1	23	25	271
		2	42	48	190
		3	19	22	279
		4	8	9	278
3	9	0	23	15	270
		1	19	22	291
		2	20	24	7
		3	26	27	234
		5	10	14	120
3	10	0	15	15	90
		1	19	18	29
		2	19	21	35
		3	11	12	184
		4	7	6	300
		5	7	10	232
3	11	0	20	23	90
		1	10	14	121
		2	8	9	196
		3	9	9	61
		4	15	18	265
		5	5	8	316
3	12	0	19	20	270
		1	15	17	204
		3	10	12	15
		4	7	10	102
3	13	0	19	20	270
		1	6	7	54
		4	10	12	99
3	14	0	7	10	90
		1	6	9	357
		3	7	9	212
4	0	0	64	73	180
		1	21	18	90
		3	19	16	270
		4	50	48	0
		5	18	16	270
		8	17	11	180
4	1	0	60	59	180
		1	82	88	259
		2	28	26	97
		3	51	46	74
		5	16	18	84
4	2	0	87	86	0
		1	42	42	214
		2	37	38	121
		3	38	41	166
		4	41	39	184
		5	15	13	41
4	3	0	29	26	0
		1	44	45	119
		3	36	31	213
		4	11	8	150
		5	7	9	310
4	4	1	58	61	353
		2	29	28	296
		3	54	48	2
		4	9	6	307
		5	27	30	188
4	5	0	6	6	0
		1	27	24	78
		2	57	62	87
		3	29	29	326
		4	14	14	174
		5	13	17	234
4	6	0	34	33	180
		1	37	40	148
		2	24	23	128
		3	18	19	186
		4	25	25	354
		5	12	13	330
4	7	0	16	17	180
		1	39	39	270
		2	27	27	260
		3	29	31	100
		4	9	8	30
		5	11	14	89
4	8	0	49	45	0
		1	16	15	289
		3	15	16	114
		4	22	25	175
		5	7	6	136
4	9	0	15	14	0
		1	27	25	103
		3	18	20	266
		4	8	9	165
		5	9	13	260
4	10	0	39	36	180
		1	7	10	30
		2	8	8	295
		3	17	18	358
		4	16	21	357
		5	5	7	225
4	11	0	12	10	180
		1	13	12	312
		2	21	26	77
		3	9	8	36
4	12	0	8	5	0
		1	16	16	173
		2	10	11	129
		3	10	12	178
		5	5	8	3
4	13	2	12	17	274
4	14	0	7	10	0
		1	8	8	334
		3	7	7	3
4	16	0	8	10	180
		1	6	5	152
5	0	1	42	43	90
		3	53	46	90
		5	27	32	270
		6	11	7	0
		7	23	19	270
5	1	1	52	45	184
		2	67	71	163
		3	16	19	316
		5	22	19	64
		6	19	15	352
5	2	0	26	30	270
		2	21	20	37
		3	29	28	270
		4	30	30	84
		5	15	19	113
5	3	1	48	44	347
		2	24	23	358
		3	37	43	170
		4	13	13	258
		5	15	17	185
5	4	0	83	64	90
		1	7	4	197
		2	9	8	174
		3	18	18	354
		4	32	31	274
		5	7	10	344
5	5	0	25	23	270
		1	49	43	165
		2	16	10	77
		3	28	28	349
		4	12	13	110
		5	13	14	353
5	6	0	51	43	270
		1	24	20	69
		2	20	22	123
		3	26	26	71
		4	30	31	77
		5	7	13	238
5	7	1	28	24	345
		2	34	41	183
		3	8	8	213
		4	10	10	287
		5	7	6	112
5	8	0	17	15	90
		1	25	26	254
		2	10	9	316
		3	18	19	274
		5	11	15	84
5	9	1	12	14	38
		2	28	33	352
		3	10	11	151
		4	8	6	277
		5	7	7	240
5	10	0	9	13	90
		1	15	15	92
		2	12	13	142
		3	11	12	69
		4	12	12	274
5	11	0	13	10	270
		1	5	7	172
		2	12	11	180
		3	12	16	330
		5	6	9	4
5	12	0	19	25	270
		1	8	7	307
		3	7	8	183
		4	11	14	84
5	13	1	10	11	354
		3	8	8	179
5	14	0	11	12	90
		3	3	5	292
5	15	1	9	7	128
6	0	0	38	36	0
		1	50	48	270
		3	19	15	90
		4	25	23	0
		5	19	19	90
		7	15	13	270
6	1	0	46	44	0
		1	51	44	226
		3	21	23	124
		4	44	38	177
		5	12	11	22
6	2	0	16	15	0
		1	22	22	127
		2	28	25	286
		3	24	18	246
		4	17	18	198
		5	22	25	301
6	3	0	20	16	180
		1	23	19	5
		2	13	16	249
		3	27	28	341
		4	10	12	46
		5	19	18	186
6	4	1	21	23	340
		2	43	45	88
		3	18	16	348
		4	10	11	20
		5	5	9	190
6	5	0	25	22	180
		1	22	24	188
		2	21	22	100
		3	27	29	222
		4	4	2	254
		5	14	16	334
6	6	0	10	10	180
		1	20	17	244
		2	21	23	261
		3	20	19	81
		4	6	8	324
		5	8	11	56
6	7	0	33	32	0
		1	12	12	298
		2	15	14	252
		3	17	19	26
		4	30	28	193
		5	9	9	166
6	8	0	8	10	0
		1	22	22	72
		3	9	10	263
		4	15	15	174
		5	8	14	272
6	9	0	25	29	180
		1	16	14	30
		3	8	9	298
		4	14	16	11
		5	4	6	232
6	10	0	17	17	180
		1	12	12	264
		2	13	13	105
		3	15	15	75
		4	8	8	348
		5	5	9	111
6	11	1	16	14	196
		2	9	11	68
		5	5	6	24
6	12	1	6	8	142
		2	13	15	261
		3	7	6	165
6	13	1	11	10	16
		3	8	10	24
6	14	0	3	5	0
		1	8	7	57
		3	5	6	295
6	15	0	8	10	180
7	0	1	13	11	270
		2	38	40	180
		4	9	7	180
		6	27	21	0
		7	8	3	270
7	1	0	26	26	270
		1	46	39	265
		2	20	19	29
		3	29	27	276
		4	20	18	86
		5	14	14	90
7	2	0	29	28	90
		1	38	29	33
		2	38	38	2
		3	8	8	150
		4	14	13	330
		5	12	12	191
7	3	0	50	47	90
		1	16	14	109
		2	13	13	102
		3	8	7	76
		4	33	31	271
		5	5	9	300
7	4	0	29	28	270
		1	42	37	189
		3	31	29	354
		4	8	7	78
		5	20	22	3
7	5	0	33	34	270
		1	14	14	49
		2	10	10	179
		3	12	9	152
		4	31	29	104
7	6	0	7	5	90
		1	32	26	344
		2	31	30	177
		4	6	4	119
		5	8	10	167
7	7	1	28	23	266
		3	26	23	293
		4	15	16	282
		5	7	10	82
7	8	1	11	8	97
		2	18	20	356
		3	7	8	47
7	9	0	18	15	90
		1	21	21	100
		3	12	16	102
		4	5	6	275
		5	8	9	281
7	10	1	9	9	211
		2	17	19	179
		3	7	10	344
		5	6	7	20
7	11	0	26	24	270
		1	8	6	344
		3	4	5	266
		4	6	8	106
7	12	1	11	13	354
		3	11	11	184
		4	3	3	274
7	13	0	11	11	90
		4	2	10	285
7	14	1	6	6	169
8	0	0	45	41	0
		1	28	25	270
		2	10	5	180
		4	28	27	180
		5	9	8	90
8	1	0	45	39	0
		1	32	26	130
		2	20	19	258
		3	23	21	247
		4	23	21	185
		5	7	10	281
8	2	0	46	39	180
		1	30	24	41
		2	18	20	256
		3	10	9	311
		4	14	12	340
		5	14	13	238
8	3	0	7	4	180
		1	11	11	351
		2	24	27	86
		3	15	20	48
		5	5	9	138
8	4	0	7	4	180
		1	37	30	194
		2	28	28	88
		3	15	14	169
		4	9	6	78
		5	9	9	345
8	5	0	16	15	180
		1	18	19	166
		2	20	21	259
		3	16	12	177
		5	7	9	31
8	6	0	25	21	0
		1	28	25	329
		2	13	9	265
		3	10	12	40
		4	11	12	186
		5	8	9	138
8	7	0	21	19	0
		1	23	20	74
		2	11	11	89
		3	15	13	318
		4	12	13	193
		5	5	9	235
8	8	0	17	16	180
		1	16	14	109
		4	12	13	350
		5	7	8	267
8	9	0	18	17	180
		1	16	15	305
		3	14	14	61
		4	6	8	25
		5	5	8	97
8	10	0	14	14	0
		1	10	9	232
		3	11	10	128
		4	6	6	172
		5	5	6	38
8	11	3	8	7	231
8	12	1	8	8	12
		3	6	8	5
8	13	3	5	5	2
9	0	1	24	19	270
		3	18	13	270
		5	11	13	90
9	1	1	18	13	354
		2	34	31	10
		5	4	3	109
9	2	0	27	21	90
		1	28	22	97
		2	11	8	301
		3	19	16	63
		4	17	16	279
		5	8	9	276
9	3	1	12	12	170
		2	10	10	188
		3	19	20	357
		5	11	12	353
9	4	0	51	47	270
		4	17	19	80
9	5	1	17	15	2
		3	17	16	188
		5	10	11	172
9	6	0	19	17	90
		1	15	13	281
		3	9	9	286
		4	13	11	265
		5	6	7	82
9	7	1	15	12	189
		2	17	19	352
		3	9	9	352
9	8	0	10	7	270
		1	14	14	102
		3	8	9	78
		4	5	3	314
		5	7	9	252
9	9	1	10	7	159
		2	15	16	172
9	10	1	10	11	275
		3	11	10	270
		4	6	8	79
9	11	1	6	7	18
		3	6	7	181
9	12	0	15	12	90
10	0	0	19	17	0
		1	13	11	90
		3	15	12	270
		4	14	14	180
		5	7	11	270
10	1	0	20	16	180
		1	11	10	91
		2	9	10	233
		3	14	14	300
		4	11	9	359
		5	10	8	261
10	2	0	26	22	180
		1	14	13	317
		2	14	11	90
		3	13	10	58
		4	9	8	351
		5	5	9	124
10	3	0	11	10	0
		1	12	10	180
		2	13	14	83
		3	14	14	163
		4	7	6	179

TABLE 4. (*Continued*).

h	*k*	*l*	$\lvert F_o\rvert$	$\lvert F_c\rvert$	α°
		5	9	7	36
10	4	1	16	14	197
		2	14	16	278
		3	11	9	165
		5	7	9	343
10	5	2	12	13	268
		3	10	12	2
		4	8	5	181
		5	6	6	161
10	6	0	12	12	0
		1	13	13	51
		2	9	10	97
		3	11	9	326
		4	12	9	179
10	7	0	13	10	180
		1	11	9	98
		2	7	8	99
		3	5	7	239
		4	9	8	347
10	8	0	8	11	180
		1	6	7	264
		3	11	8	111
		4	9	8	350
10	9	0	11	10	0
		1	6	8	253
		3	8	7	96
		4	7	7	184
10	10	0	9	8	0
10	11	0	7	5	180
		1	7	6	32
10	12	1	6	7	5
11	0	2	20	21	0
		5	4	2	270
11	1	0	11	9	90
		1	15	13	93
		3	19	16	94
		4	8	6	278
		5	6	6	256
11	2	1	12	12	162
		2	14	13	173
		3	15	11	357
		5	6	7	341
11	3	0	20	18	270
		3	8	5	275
		4	16	12	103
11	4	1	13	15	6
		3	12	10	192
11	5	0	17	15	90
		3	4	4	276
		4	13	12	255
11	6	1	8	7	187
		2	13	11	12
		3	12	9	0
11	7	0	12	10	270
		3	11	10	73
		4	5	4	105
11	8	1	10	3	153
		2	13	14	191
11	9	1	9	7	264
		3	7	7	275
12	0	0	12	9	180
		1	9	8	90
		2	9	4	0
		3	10	10	270
		4	9	6	0
12	1	0	17	14	180
		1	9	7	284
		2	8	5	146
		3	8	7	55
		4	10	8	5
12	2	0	7	4	0
		1	13	9	237
		2	9	9	89
		3	8	8	110
		4	4	4	192
12	3	0	9	6	0
		1	8	9	158
		3	13	10	204
		4	7	4	154
12	4	1	8	7	343
		2	11	13	278
12	5	1	9	8	15
		2	8	8	93
		3	13	9	333
		4	6	5	205
12	6	1	10	8	121
		2	6	7	93
12	7	0	12	8	180
		1	6	5	218
12	8	0	8	6	0
		1	8	7	290
13	0	1	10	12	90
13	1	1	4	3	136
13	2	1	8	6	243
		2	8	2	177
13	3	0	10	2	270
13	4	0	10	8	90
		1	9	2	39
		2	6	2	281
13	6	0	12	10	270
14	0	0	14	11	180
14	1	0	6	4	0
		1	5	6	260
14	2	1	5	6	151
14	3	0	2	1	0

TABLE 5.

Progress of the structure analysis

Patterson syntheses

↓

Br atom

↓

1st F calculation ($R = 29{\cdot}6\%$)
1st three-dimensional F_o synthesis

↓

Br, N, O(1), O(2), C(1), C(2), C(3), C(7), C(9) (9 atoms)

↓

2nd F calculation ($R = 25{\cdot}6\%$)
2nd three-dimensional F_o synthesis

↓

Br, N, O(1), O(2), C(1) · · · C(10) (14 atoms)

↓

3rd F calculation ($R = 23{\cdot}5\%$)
3rd three-dimensional F_o synthesis
1st three-dimensional F_c synthesis

↓

4th F calculation ($R = 19{\cdot}5\%$)
4th three-dimensional F_o synthesis
2nd three-dimensional F_c synthesis

↓

5th F calculation ($R = 15{\cdot}1\%$)
5th three-dimensional F_o synthesis
3rd three-dimensional F_c synthesis

↓

6th F calculation ($R = 15{\cdot}0\%$)
6th three-dimensional F_o synthesis
4th three-dimensional F_c synthesis

↓

Five rounds of least-squares refinement of co-ordinates and anisotropic temperature factors
($R = 11{\cdot}1\%$)

↓

Isotropic B values
Final F calculation ($R = 12{\cdot}5\%$)

↓

Final three-dimensional F_o synthesis

The final atomic co-ordinates are listed in Table 1 while details of the progress of the structure analysis are shown in Table 5.

The final three-dimensional electron-density distribution was evaluated on the basis of the phase constants of Table 4 and is shown in Fig. 1 by means of superimposed contour sections drawn parallel to (010). The corresponding atomic arrangement is illustrated in Fig. 2.

For the structure-factor calculations theoretical atomic scattering factors were used: those of Berghuis *et al.*[9] for carbon, nitrogen and oxygen, and the Thomas–Fermi values[10] for bromine, were chosen.

The standard deviations of the final atomic co-ordinates were derived from the least-squares residuals by application of the equation

$$\sigma^2(x_i) = \sum_j w_j(\Delta F_j)^2/[(n - s) \sum_j w_j(\partial F_j/\partial x_i)^2]$$

The results are listed in Table 3.

The extensive calculations were performed on the Glasgow University DEUCE computer, with programmes devised by Dr. J. S. Rollett and Dr. J. G. Sime. We are grateful to Dr. Stotherd Mitchell for supplies of (—)-2-bromo-2-nitrocamphane. The awards of an I.C.I. Research Fellowship (to T. A. H.) and a Fulbright Scholarship (to D. A. B.) are gratefully acknowledged.

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[9] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

[10] Internationale Tabellen zur Bestimmung von Kristallstrukturen," Borntraeger, Berlin, 1935, Vol. II, p. 572.