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THE MOLECULAR AND CRYSTAL STRUCTURE OF 2α-BROMOARBORINONE

THE STRUCTURE OF THE TRITERPENE ARBORINOL

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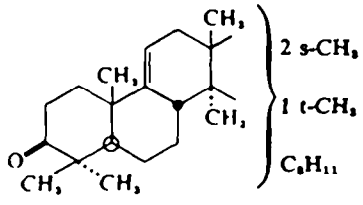
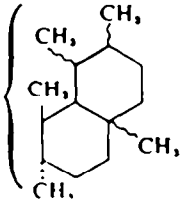
Abstract—The molecular structure and stereochemistry of the triterpene arborinol was obtained from a three-dimensional X-ray diffraction study of 2α-bromoarborinone. The molecule is shown to be pentacyclic with a 13β, 14α*trans* configuration of the methyl groups at the C/D ring junction, not previously found among pentacyclic triterpenes. The space group is $P2_12_12_1$, with four molecules in the unit cell: $a = 12{\cdot}84$ $b = 8{\cdot}68$ $c = 22{\cdot}46$ Å. The value of $R = (\Sigma||Fo| - |Fc||)/\Sigma|Fo|$ is 12·4% for 1719 observed reflections.

The implications of the structure for the fernene-group of triterpenes are discussed.

RECENTLY, two new triterpene alcohols, arborinol together with its 3-epimer isoarborinol were isolated from the leaves of *Glycosmis arborea* (Rutaceae) by Djerassi *et al.*[1] On basis of chemical reactions and a variety of physical measurements including NMR, ORD and mass spectroscopy they deduced that it was a pentacyclic compound with ring structure A, B and C as indicated in 1 and showed by NMR evidence the



I



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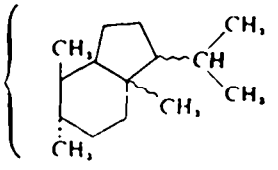

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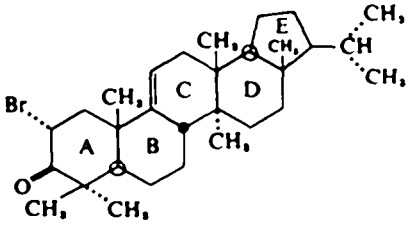

IV 2α-Bromoarborinone

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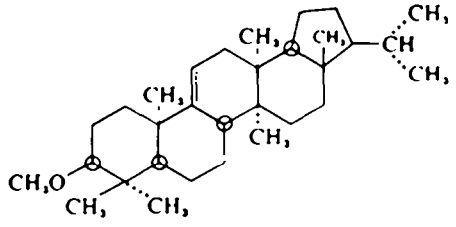
[1] H. Vorbrüggen, S. C. Pakrashi and C. Djerassi, *Liebigs Ann.* **668**, 57 (1963).

presence of two secondary and a t-methyl groups in rings D and E. The 13β/14α *trans* configuration of the methyl groups at the C/D ring junction deduced by these authors represents an arrangement not previously observed amongst pentacyclic triterpenes and is of considerable biogenetic interest. Since there was insufficient material available to elucidate the full structure of the molecule, we undertook at Professor Djerassi's suggestion the investigation of the structure of arborinol through a three-dimensional X-ray diffraction analysis of the heavy atom derivative 2α-bromoarborinone, prepared for us by Dr. H. Vorbrüggen. The X-ray analysis required only a few milligrams of material. It was deliberately designed to involve minimal assumption about the chemical structure of the molecule so as to provide evidence independent of previous suggestions about the structure of this group of triterpenes.

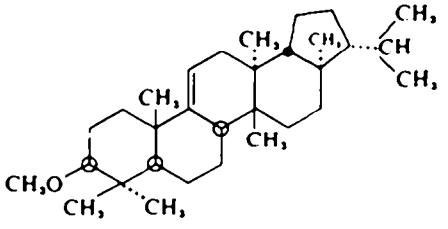
The X-ray analysis fully confirmed the structure proposed by Djerassi *et al.*[1] and established the position of the remaining atoms in the molecule of 2α-bromoarborinone as indicated in IV. The unusual 13β, 14α *trans* configuration at the C/D ring junction was verified and interatomic distances accurate to about $\pm$0·05 Å obtained. A preliminary report on the more chemical aspects of this investigation has already been published.[2]

Since cylindrin[3,4] has been shown to be the 3-methyl ether of isoarborinol its full structure can now be written as V.

Cylindrin was obtained by Natori *et al.*[3,4] from the rhizomes of *Imperata cylindrica* together with a stereoisomeric triterpene arundoin (VI) which was also isolated by Eglinton *et al.*[5] from *arundo conspicua*. The occurrence of cylindrin (V) and arundoin (VI) in the same plant is biogenetically interesting, since the compounds have an



V Cylindrin



VI Arundoin

[1] O. Kennard, L. Riva di Sanseverino, C. Djerassi and H. Vorbrüggen, *Tetrahedron Letters* 3433 (1965).

[2] K. Nishimoto, M. Ito, S. Natori and T. Ohmoto, *Tetrahedron Letters* 2265 (1965)

[3] T. Ohmoto, K. Nishimoto, M. Ito and S. Natori, *Chem. Pharm. Bull. Japan* **13**, 224 (1965).

[4] G. Eglinton, R. S. Hamilton, M. Martin-Smith, S. Smith and G. Subramanian, *Tetrahedron Letters* 2323 (1964).

"antipodal" configuration of rings C, D and E. This "antipodal" steric arrangement of the ring skeleton present in arundoin is also found in fernene (VII), isolated by Ageta *et al.*[6] from *Dryopteris Crassirhizoma* Nakai (Aspidiaceae), and davallic acid (VIII), isolated by Nakanishi *et al.*[7] from the rhizomes of a fern *Davallia divaricata*. It is obvious that the spacial relationships in rings C, D and E as derived from our X-ray determination can be compared with those of the corresponding rings of the "antipodal" fernene-group of triterpenes.

Biogenetically, arborinols can be postulated to be formed by a squalene cyclization process involving an intermediary precursor (IX) with ring B in the boat form, followed by a concerted rearrangement to the arborinols (X). Such a boat form is indeed present in the antibiotic fusidic acid (XI) whose correct structure was deduced by Godtfredsen *et al.*[8,9] and firmly established by an X-ray analysis of the crystal structure of fusidic acid bromobenzoate methyl ester by Cooper.[10]

EXPERIMENTAL

A heavy atom derivative of arborinol, 2α-bromoarborinone, was prepared by Dr. H. Vorbrüggen at the Woodward Research Institute, Basel, using a method described previously.[1] It was recrystallized from hexane, needles m.p. 217–220°., which were homogeneous on TLC (silica plate, benzene–hexane (1:1) R_f = 0·58). Slow evaporation of a solution of pure bromo-ketone in methylene chloride–hexane resulted in the larger crystals, which were used for the X-ray determination.

Crystal data. 2α-Bromoarborinone, $C_{30}H_{47}OBr$, mol. wt = 503·3, m.p. 219–220°. Provenance: see Ref. 1. Orthorhombic, thick dipyramidal. Twinning common. $a = 12{\cdot}84 \pm 1$, $b = 8{\cdot}68 \pm 1$, $c = 22{\cdot}46 \pm 4$ Å. V = 2513 Å^3. Density measured by flotation 1·39 gm. cm^{-3}. $Z = 4$. $D_{calc} = 1{\cdot}34$ gm. cm^{-3}. Ni filtered Cu radiation: $\lambda\alpha_1 = 1{\cdot}5403$ Å $\lambda\alpha_2 = 1{\cdot}5443$ Å. Cell dimensions calculated from the separation of $\alpha_1\alpha_2$ doublets on Weissenberg photographs.[11] Space group $P2_12_12_1$ from absences. $\mu = 27{\cdot}2$ cm^{-1}. F(000) = 1080.

Intensity data were collected from an approximately cylindrical crystal 0·60 mm long and 0·40 mm in cross-section, prepared by manual grinding. A series of equi-inclination Weissenberg photographs for layers 0–6 were taken about the *b* axis, which enabled the exploration of 76% of the copper sphere. Intensities from multiple film packs were matched visually against a scale prepared from the same crystal. Different layers were put on a common scale by comparison with the 0kl reflections. Altogether 1719 non-zero reflections were observed representing 62% of the total number of possible reflections obtainable with Cu radiation.

The observed intensities were corrected for spot-shape and Lorentz-polarization factors using a programme by Dr. H. J. Milledge. The square roots of these values, on the appropriate scale, were used in the subsequent structure factor calculations. No absorption corrections were applied.

STRUCTURE DETERMINATION

The gross structure was solved by the application of the heavy atom method. Conventionally, using this method, the heavy atoms are first located from a Patterson map, the observed structure factors are phased and a Fourier map is calculated. Such a map will contain in addition to large peaks due to the heavy atoms smaller peaks some of which may correspond to the lighter atoms in the molecule. A number of

[6] H. Ageta, K. Iwata and S. Natori, *Tetrahedron Letters* 1447 (1963).

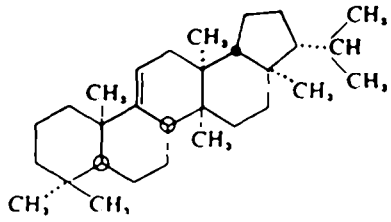
[7] K. Nakanishi, Y. Y. Lin, H. Kakisawa, H. Y. Hsü and H. C. Hsin, *Tetrahedron Letters* 1451 (1963).

[8] D. Arigoni, W. von Daehne, W. B. Godtfredsen, A. Maleia and S. Vangedal, *Experientia* **20**, 347 (1964).

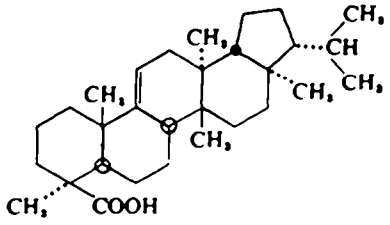
[9] W. O. Godtfredsen, W. von Daehne, S. Vangedal, A. Marquet, D. Arigoni and A. Melera, *Tetrahedron* **21**, 3505 (1965).

[10] A. Cooper, *Tetrahedron* **22**, 1379 (1966).

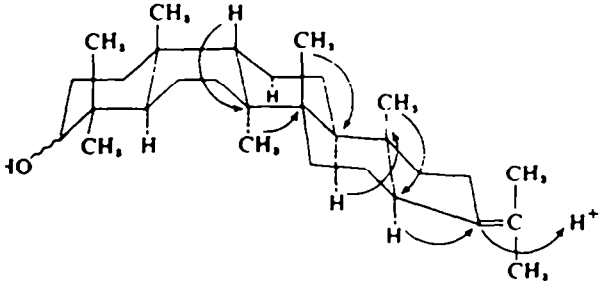
[11] P. Main and M. M. Woolfson, *Acta Cryst.* **16**, 731 (1963).



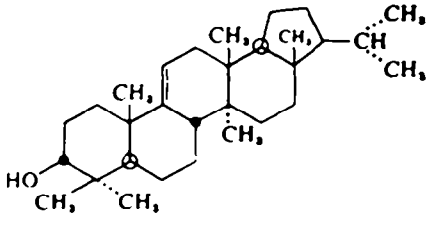
VII Fernene



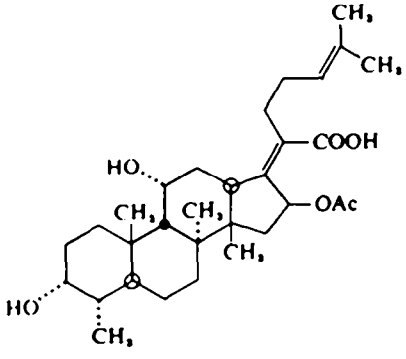
VIII Davallic acid



IX



X Arborinol



XI Fusidic acid

peaks are selected using various criteria, including the known or probable chemical features of the molecule, and a new set of phase angles is calculated. The progress of the analysis is indicated by a decrease in the value of the disagreement factor R, defined as $(\Sigma |Fo| - |Fc|)/\Sigma |Fo|$ which is about 59% for a random non-centrosymmetric arrangement of atoms.[12]

The above method was condensed and made more objective by the use, in the present investigation, of the series of calculations embodied in the computer programme "FATAL" which will be described more fully elsewhere, in connection with

TABLE 1. FLOWSHEET SHOWING LAYOUT OF "FATAL" CALCULATIONS

Input "O"

Unit cell dimensions, symmetry, form factors
Instructions for computing Fourier map
Scale factor K for structure factors F_o
List of scattering amplitudes with their indices (planes list)
Value of electron density $\rho(xyz)$ minimum
Values of constants a and b for F_o output
Co-ordinates of heavy atom

Calculations		*Output*
1. Structure factors F_c	→	F_o & F_c if $\Delta F > a$ or $\Delta F/F > b$ Values of K and R for batches of 120 reflexions and totals
2. F_o synthesis with phases of F_c from 1 above. Store		
3. Scanning of electron density peaks	→	Coordinates x, y, z and peak heights $\rho(xyz)$ if $\rho(xyz) > \rho_{min}(xyz)$
4. Distances (d) between peaks $\rho(xyz)$	→	d if < 3 Å

Input "O" + 1

Data as in input O, but with coordinates selected from output 3 with appropriate form factors and new K and B from output 1.

their work on automatic heavy-atom analysis, by Hodgson, Rollett and Stonebridge. This approach involves minimal chemical assumptions other than the existence of discrete atoms. The flowchart of the calculations is shown in Table 1. Essentially the programme supplies the user at each stage of the calculation with a list of co-ordinates corresponding to peaks above a preset minimum value and the distances between neighbouring peaks. Atomic sites to be included in the next stage of the calculation are selected from this list using as chief criteria the peak heights and inter peak distances. If a true atomic site is chosen the electron density will probably increase—false peaks remain stationary or actually decrease in value. The scale factor K relating experimental and calculated values of structure factors is gradually improved and so is the disagreement factor R. The cyclic process is repeated till all atoms are located.

In the present investigation the position of the Br atoms was determined from a FATAL Patterson calculation obtained by placing a hypothetical atom at (000) for the phasing calculation. Three peak positions, lying in the Harker sections $\frac{1}{2}$, y, z; x, $\frac{1}{2}$, z; and x, y, $\frac{1}{2}$; were obtained giving as fractional bromine co-ordinates $x = 0{\cdot}030$, $y = 0{\cdot}25$, $z = 0{\cdot}041$. However, structure factor calculations with these parameters gave $R = 58\%$ which dropped to 45% when the fractional y co-ordinate was changed

[12] A. J. C. Wilson, *Acta Cryst.* 3, 397 (1950).

to 0·21 on the assumption that the peaks indicating $y = 0{\cdot}25$ were due to the superposition of pairs of vector peaks on either side of the symmetry planes.

When the peak positions from this calculation (F1) were plotted out the molecular skeleton was not evident, and an apparently unrelated set consisting of 10 of the highest peaks (those above 3e/A^3) was selected for the next cycle F2, (B = 3·5, K = 450, R = 41%). One of these was later shown to be a spurious atom (Peak S, Fig. 1).

At this stage the main outline of the molecular skeleton emerged as three six membered rings and a five membered ring with some substituents (Fig. 1). The peak

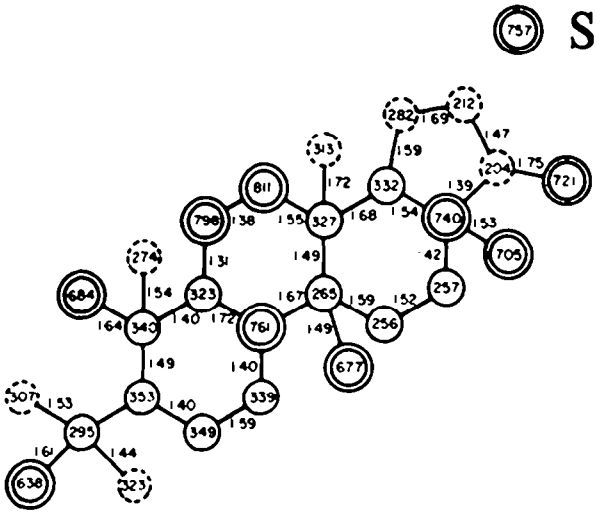


FIG. 1. The molecular skeleton of 2α-bromoarborinone as seen from the plot of peak positions obtained from the Fourier map phased on 1 Br and 10 carbon atoms in FATAL cycle F2.

● Carbon atoms used as input for F2.
○ Additional carbon atoms used as input for F3.
○ Additional atoms used in input F4–F6.

Interpeak distances in Å units.
Peak height, inside circle in arbitrary units of electron/A^{-3}.
The peak representing bromine is omitted.

heights defining the five membered ring were comparatively low and to avoid any bias in the calculation, these were not included in the next cycle. However, they still reappeared in F3 (B = 5·5, K = 450, R = 38%), and the highest peak position of this set was now added together with two peaks completing the last six membered ring and some further substituents. At F4 (B = 5·5, K = 390, R = 31·6%) two positions were removed from the calculation one of which was a false atom (S, Fig. 1 which had decreased in height from 7·6 to 5·1 e/A^3 and was not close to any other site selected) while the other reappeared together with the two remaining atoms of the isopropyl group in F5. In F5 were also included the two atoms completing the five membered ring and one further atom attached to ring A. This was recognised to be an oxygen atom from the short distance to the nearest peak and the planarity of the surrounding group. With all atoms of the molecule accounted for the reliability factor was

26·4%, and there were no peaks above 2 e/A^3 in height except those at sites used for the phases of Fcalc, where all peaks were above 4·5 e/A^3.

It would be a hindrance to lay down exact rules for analyses of this type. In the present case no site was accepted unless the peak found was higher than 2·5 e/A^3, until the last stage when two methyl carbon atoms were included because of peaks of 2·0 and 2·4 e/A^3. This (flexible) rule, and rejection of sites unless they were at acceptable distances from their nearest and next nearest neighbours, sufficed to prevent the selection of any new false peaks from F2 onwards.

STRUCTURE REFINEMENT

After the 32 heavier atoms in the molecule had been located their positions were refined by a series of least squares diagonal matrix calculations, using a programme written by R. Diamand. The progress of these calculations is shown in Table 2.

TABLE 2. PROGRESS OF REFINEMENT OF 2α-BROMOARBORINONE

Cycle	Scale factor	Reliability factor, R (%)	$\omega\Delta^2 \times 10^{-8}$	Max shift (Å)
Iso 1	350	27·2	1172782215	C(3)*y* 0·235
Iso 2	320	28·0	1082318101	C(24)*y* 0·214
Iso 3	355	25·9	1006399487	C(25)*y* 0·169
Iso 4	320	23·9	766084120	C(27)*y* 0·118
Iso 5	346	22·3	734069537	O *y* 0·092
Iso 6	340	22·1	688852110	C(3)*y* 0·063
Iso 7	339	21·8	677333193	O *y* 0·035
Aniso 1	317	17·1	240096564	C(23)*y* 0·067
Aniso 2	321	17·5	263332132	C(3)*y* 0·062
Aniso 3	295	13·8	111873680	C(1)*x* 0·053
Aniso 4	299	12·7	89860201	C(3)*y* 0·031
Aniso 5	293	12·4	83587421	O *y* 0·029

TABLE 3. FINAL ATOMIC CO-ORDINATES FOR 2α-BROMOARBORINONE

	x	*y*	*z*		*x*	*y*	*z*
Br	0·02946	0·21444	0·04082	C(15)	0·39406	−0·38954	0·28967
O	0·22925	0·37538	0·06142	C(16)	0·37517	−0·48034	0·34420
C(1)	0·13969	0·03086	0·11744	C(17)	0·28794	−0·58727	0·34007
C(2)	0·15776	0·12055	0·06319	C(18)	0·19368	−0·48889	0·32125
C(3)	0·23944	0·24598	0·06996	C(19)	0·10075	−0·59951	0·32619
C(4)	0·34357	0·17207	0·08964	C(20)	0·13155	−0·69276	0·38031
C(5)	0·32601	0·06751	0·14053	C(21)	0·24224	−0·64703	0·39583
C(6)	0·42598	−0·01295	0·15869	C(22)	0·21164	−0·49720	0·21439
C(7)	0·40692	−0·08646	0·21855	C(23)	0·26012	−0·18649	0·09006
C(8)	0·32388	−0·21125	0·21547	C(24)	0·29345	−0·78384	0·42734
C(9)	0·22578	−0·14173	0·18986	C(25)	0·23158	−0·82101	0·47963
C(10)	0·23955	−0·06104	0·13356	C(26)	0·40664	−0·73972	0·44382
C(11)	0·13321	−0·17342	0·21009	C(27)	0·31554	−0·72289	0·30267
C(12)	0·11316	−0·28785	0·25719	C(28)	0·28605	−0·15766	0·31852
C(13)	0·20803	−0·39521	0·26697	C(29)	0·39732	0·09740	0·03709
C(14)	0·30291	−0·28615	0·27303	C(30)	0·41775	0·31278	0·10872

In all these calculations scattering factors, as listed in the International Tables for X-ray crystallography,[13] were used. The weighting scheme was: $w = 1$ if $F_0 < F^*$, $w = F^*/F_0$ if $F_0 > F^*$. $F^* = 30$ (isotopic) $F^* = 20$ (anisotropic). A fudge-factor of 0·7 was introduced for cycles Aniso 2–5.

TABLE 4. COMPONENTS OF THERMAL VIBRATION COEFFICIENTS (*bij*); ANISOTROPIC REFINEMENT, CYCLE ANISO 5

	*b*11	*b*22	*b*33	*b*12	*b*23	*b*13
Br	0·00885	0·04661	0·00446	−0·00119	0·01554	0·00241
O	0·01341	0·01962	0·00285	−0·00089	0·00568	0·00227
C(1)	0·00731	0·03234	0·00175	0·00153	0·00770	0·00253
C(2)	0·00640	0·03510	0·00231	0·00130	0·01122	0·00451
C(3)	0·00861	0·01966	0·00148	−0·00030	0·00131	−0·00301
C(4)	0·01088	0·01652	0·00103	0·00105	0·00160	0·00104
C(5)	0·00779	0·01357	0·00105	0·00007	0·00003	−0·00044
C(6)	0·00651	0·02107	0·00271	0·00014	0·00585	0·00429
C(7)	0·00730	0·01191	0·00211	−0·00097	0·00218	−0·00302
C(8)	0·00405	0·00643	0·00181	−0·00027	−0·00198	−0·00188
C(9)	0·00583	0·01748	0·00161	0·00006	0·00025	−0·00115
C(10)	0·00582	0·01653	0·00191	0·00086	0·00199	0·00050
C(11)	0·00507	0·02253	0·00267	0·00077	0·00047	0·00301
C(12)	0·00562	0·02238	0·00294	−0·00194	0·00567	−0·00539
C(13)	0·00390	0·01911	0·00184	−0·00105	0·00029	−0·00075
C(14)	0·00655	0·01331	0·00112	0·00039	−0·00082	0·00202
C(15)	0·00484	0·01545	0·00256	0·00029	0·00200	0·00130
C(16)	0·00627	0·03193	0·00203	0·00075	0·00566	0·01043
C(17)	0·00691	0·00896	0·00150	−0·00035	−0·00028	−0·00154
C(18)	0·00560	0·01675	0·00160	0·00000	0·00176	−0·00110
C(19)	0·00784	0·02263	0·00261	−0·00103	0·00413	0·01048
C(20)	0·00543	0·02738	0·00255	0·00060	0·00270	0·00262
C(21)	0·00825	0·02271	0·00130	0·00021	0·00378	−0·00648
C(22)	0·00995	0·02346	0·00121	−0·00227	−0·00265	−0·01063
C(23)	0·01278	0·02164	0·00207	0·00141	−0·00181	−0·00085
C(24)	0·00828	0·02039	0·00180	0·00257	0·00157	−0·00165
C(25)	0·01994	0·03212	0·00262	−0·00433	0·00900	−0·00857
C(26)	0·01254	0·02869	0·00324	0·00308	0·00775	−0·00116
C(27)	0·01088	0·01301	0·00201	−0·00108	−0·00183	−0·00426
C(28)	0·01560	0·01336	0·00171	−0·00083	−0·00565	−0·00423
C(29)	0·01118	0·02717	0·00170	0·00201	0·00230	0·00775
C(30)	0·00985	0·02653	0·00246	−0·00148	−0·00056	−0·00980

The results of these calculations are recorded in the following Tables, 3: atomic positions; 4: thermal vibration parameters; 5: observed and calculated structure factors. The final reliability factor was 12·4% and the magnitudes of the shifts suggested by the last cycle were below the estimated standard deviations in atomic positions.

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

TABLE 5. OBSERVED AND CALCULATED STRUCTURE FACTORS AND PHASE ANGLES FOR 2α-BROMOARBORINONE. EACH GROUP OF THREE COLUMNS AFTER THE INDEX NUMBER CONTAINS 10 × Fo, 10 × Fc AND PHASE ANGLE IN MILLICYCLES

0,0,L

4	97	146	0
6	394	442	999
8	957	1038	0
10	394	474	0
12	615	657	0
14	141	143	0
16	316	256	0
18	159	143	0
20	78	62	0
22	88	54	999

1,0,L

3	416	444	750
5	752	757	249
7	564	520	749
8	588	639	750
10	195	183	249
11	433	408	749
12	159	138	749
13	118	92	750
14	427	384	749
15	408	372	249
17	318	278	749
18	195	167	749
19	83	67	249
23	164	146	249
24	59	52	749
25	72	48	749

2,0,L

1	358	298	0
2	880	1274	0
3	83	88	999
4	632	735	0
5	390	429	999
6	302	347	999
8	138	81	0
9	226	256	999
10	761	683	0
11	128	101	999
12	578	534	0
13	106	89	0
14	575	520	0
15	476	473	999
16	232	220	0
17	182	152	999
19	156	128	0
20	174	168	999
24	161	162	999
26	41	43	999

3,0,L

1	563	598	249
2	78	119	750
3	414	415	750
4	754	911	750
5	360	395	249
6	278	323	750
7	241	158	249
8	576	620	249
9	164	116	750
10	507	503	750
11	156	180	749
12	206	183	750
13	264	288	749
14	51	60	249
15	517	530	749
16	255	241	749
18	186	164	749
19	59	53	249
20	287	291	749
22	51	48	749
24	83	105	249
27	51	71	249

4,0,L

0	308	453	999
2	851	1062	999
3	182	208	0
4	247	288	999
5	228	270	0
6	93	52	999
7	319	405	999
8	465	492	0
9	169	248	999
10	232	265	999
12	78	81	0
13	66	64	0
14	132	147	999
15	41	62	0
17	51	52	999
18	114	86	0
19	210	213	999
21	118	108	999
22	125	90	999
24	66	86	0

5,0,L

1	562	735	249
2	680	712	750
3	230	267	249
4	311	356	249
5	150	180	750
6	531	614	249
7	66	56	249
8	232	302	249
9	458	489	749
11	324	329	749
13	269	247	749
14	128	107	249
15	132	80	749
16	219	174	749
19	51	41	249
20	29	13	749
21	41	51	249
22	72	78	749
24	59	62	749
25	72	85	249

6,0,L

0	322	199	0
2	102	128	999
3	387	427	0
4	174	204	999
5	618	746	999
7	618	736	999
9	289	319	0
10	136	129	999
11	153	166	0
12	217	193	0
15	93	73	999
17	126	142	999
19	159	142	999
21	78	84	999
22	93	90	999

7,0,L

1	515	564	249
3	315	376	249
4	66	69	249
5	135	128	249
8	147	151	249
9	193	203	249
10	157	183	249
11	304	333	749
13	202	180	749
15	206	176	749
16	202	167	749
17	51	79	749
18	114	93	749
19	106	130	249

8,0,L

0	189	202	0
1	118	115	0
2	210	220	999
3	425	496	0
4	147	138	999
5	421	452	999
6	114	118	0
7	399	434	0
8	66	69	999
9	241	270	0
10	41	9	0
11	72	98	0
12	102	96	0
13	114	129	999
14	66	62	999
15	114	101	999
17	225	228	0
20	72	70	999
23	83	81	999
24	29	31	0

9,0,L

1	484	542	249
2	179	219	249
3	210	234	750
4	221	194	249
5	144	175	249
7	278	292	749
9	286	293	749
10	114	120	749
11	174	164	749
12	114	114	749
13	118	132	749
14	41	62	749
16	118	137	249
17	29	44	249
18	83	74	749
19	93	107	749
20	29	62	249
21	41	39	249
24	29	36	249

10,0,L

1	347	406	0
2	371	373	999
3	174	197	0
4	191	193	999
5	304	336	0
6	29	30	999
7	138	128	0
8	51	64	0
9	150	153	0
11	159	198	0
12	167	75	999
14	66	11	999
16	66	37	0
17	78	58	0
18	41	69	999

11,0,L

2	280	255	749
3	377	378	249
6	177	171	749
8	125	138	749
9	51	63	749
11	93	70	749
13	250	249	749
17	59	62	749

12,0,L

0	191	179	0
1	88	95	999
3	110	97	0
4	156	147	999
6	51	33	0
7	156	141	0
9	102	102	0
10	88	75	999
11	118	120	999
13	141	156	0
14	88	85	999
15	78	81	0
17	29	40	999
19	41	52	999

13,0,L

1	159	169	750
4	110	73	749
6	93	74	749
8	51	39	749
9	66	55	749
10	66	74	749
11	159	153	749
14	51	60	749
15	41	34	749
18	29	113	249

14,0,L

0	150	106	999
2	83	71	999
3	78	97	0
4	83	89	999
7	93	89	0
8	29	30	999
11	59	48	999
14	59	25	999

15,0,L

1	41	53	249
4	72	77	749
6	72	56	749
8	72	79	749

16,0,L

0	51	48	0
2	51	68	999

0,1,L

3	706	803	750
5	200	171	750
6	762	916	0
7	283	179	750
8	726	699	999
9	437	392	249
10	308	275	0
11	398	352	750
12	419	340	0
13	106	107	249
14	51	55	999
16	389	408	999
17	195	185	249
19	200	180	749
20	225	233	0
21	195	153	749

1,1,L

4	732	842	102
5	438	376	172
6	381	342	128
7	345	352	766
8	416	392	189
10	468	492	291
11	308	223	137
12	570	542	762
13	329	315	983
14	255	238	163
15	114	120	818
16	177	173	834
17	184	189	921
18	78	95	183
19	144	127	23
20	88	99	919
21	153	152	236
22	51	68	799
23	110	99	791
24	41	40	226
25	29	38	242

2,1,L

0	348	302	249
1	363	381	864
2	741	852	946
3	626	699	43
4	649	699	25
5	423	461	813
6	549	605	6
7	482	475	91
8	447	527	974
9	475	458	43
10	462	444	973
11	352	319	986
12	482	459	54
13	153	102	866
14	172	148	28
15	51	80	884
16	118	101	58
17	307	270	219
18	359	328	19
19	72	71	808
20	97	101	113
22	150	146	770
23	88	81	857
26	51	70	870

3,1,L

0	765	906	249
1	280	293	880
2	694	748	822
3	716	546	008
4	417	404	239
5	213	198	924
6	639	648	993
7	388	388	790
8	416	414	175
9	308	261	240
10	424	404	206
11	338	349	119
12	250	257	797
13	164	156	890
14	279	269	236
15	286	307	795
16	128	108	235
17	370	367	926
18	236	218	828
19	128	135	164
20	213	214	856
21	202	205	247
22	132	133	79
23	97	88	823
24	72	85	267
26	66	37	213
27	41	62	762

4,1,L

0	304	213	249
1	413	419	13
2	177	206	989
3	462	471	17
4	323	391	938
5	344	347	145
6	757	838	31
7	305	279	829
8	431	413	994
9	248	243	98
10	215	182	883
11	283	324	15
12	273	243	957
13	259	282	84
14	299	275	990
15	226	218	985
16	221	192	986
17	125	126	184

TABLE 5. (*contd.*)

18	88	82	803
19	114	101	847
20	41	46	158
21	97	130	58
22	135	125	124
23	51	84	6
24	29	32	172

5,1,L

0	656	636	249
1	260	242	858
2	641	640	209
3	380	321	754
4	501	467	233
5	818	904	806
6	334	308	756
7	501	520	230
8	210	201	104
9	327	354	203
10	352	353	226
11	93	88	179
12	289	283	182
13	153	141	843
14	217	245	178
15	114	123	913
16	114	95	814
17	225	220	246
18	97	106	198
19	72	95	35
20	83	91	47
21	72	82	856
22	59	64	233
23	66	53	230
27	41	55	168

6,1,L

0	359	227	749
1	839	836	990
2	477	429	864
3	456	389	932
4	426	371	956
5	189	162	825
6	182	158	846
7	277	273	959
8	272	260	945
9	286	283	984
11	315	300	14
13	210	188	967
14	189	161	208
15	41	65	940
16	132	106	915
17	150	125	963
18	121	119	798
19	41	77	7
20	110	97	986
21	78	73	139
24	51	69	957
25	66	79	972

7,1,L

0	247	212	249
1	302	255	857
2	234	203	182
3	247	229	789
4	245	216	86
5	381	394	751
6	93	87	976
7	409	388	223
8	159	146	53
9	172	189	761
10	177	164	759
11	191	180	59
12	135	106	233
13	66	38	238
14	72	59	774
15	66	56	233
16	88	120	785
18	41	64	929
19	273	276	161
20	59	57	79
24	97	15	766
25	41	49	846
26	29	48	218

8,1,L

0	348	318	750
1	512	421	992
3	236	252	33
4	315	311	773
5	295	294	952
6	215	214	49
8	59	89	183
9	189	160	985
10	141	134	918
11	240	222	76
12	114	127	928
13	380	371	5
14	83	90	867
15	150	146	910
16	41	71	71
17	41	36	164
18	72	66	196
19	59	31	798
20	51	70	175
21	88	84	188

9,1,L

0	118	69	749
1	208	152	222
2	102	96	912
3	304	243	181
4	359	271	107
5	408	411	230
6	110	88	5
7	255	209	807
8	41	22	822
9	240	237	770
10	161	169	891
11	72	84	835
12	83	91	940
13	41	56	835
14	41	61	31
15	66	86	231
17	147	136	202
19	72	85	39
21	97	96	90
22	29	28	197

10,1,L

0	219	232	249
1	409	351	107
2	78	72	899
3	365	330	981
4	208	179	938
5	121	87	81
6	241	227	181
8	128	138	6
9	240	216	990
10	159	144	76
11	191	176	16
15	141	129	996
16	93	82	853
18	29	37	195
21	51	57	949

11,1,L

0	106	108	749
2	308	274	248
3	250	223	777
4	106	86	127
5	114	92	206
6	161	125	975
7	314	254	765
8	66	57	36
9	208	165	108
10	66	101	808
11	93	107	948
13	41	62	122
14	106	125	829
15	59	54	854
16	83	76	927
17	59	55	194
18	29	36	243
19	29	48	202
20	29	27	839

12,1,L

0	41	61	749
1	259	210	879
2	41	67	223
3	41	61	95
5	66	73	124
6	221	158	967
10	135	125	14
11	141	111	841
13	135	117	924
14	29	44	52
15	59	68	181
16	83	92	116

13,1,L

0	102	100	749
2	41	65	209
3	41	66	196
5	93	107	211
6	41	76	132
7	88	103	229

14,1,L

4	66	84	28
6	66	78	988
8	72	89	992
9	59	67	816
11	72	71	2

15,1,L

0	97	115	749
2	29	45	779
4	29	73	213
8	59	71	767
9	29	53	957

16,1,L

2	41	56	95
4	39	54	968
6	29	44	979

0,2,L

3	347	367	750
4	723	889	999
5	238	299	249
6	1031	1072	999
7	753	744	249
8	649	599	0
9	736	558	749
10	182	80	999
11	241	147	750
12	349	366	999
13	386	407	749
14	241	228	0
15	334	309	749
17	110	87	749
18	51	35	999
19	29	44	749
20	72	52	0
22	51	58	0
25	29	48	249
26	51	52	0

1,2,L

2	604	613	138
3	215	196	151
4	793	850	124
5	440	413	977
6	1081	1142	782
7	184	220	882
8	823	788	174
9	591	519	873
10	319	317	997
11	360	319	179
12	159	149	761
13	144	108	44
14	204	216	817
15	191	168	213
16	202	198	165
17	83	89	143
18	215	191	128
19	29	53	771
20	177	152	163
22	29	34	957
23	29	49	895
24	29	30	184
25	51	50	906
26	29	20	945

2,2,L

0	308	391	0
1	551	603	249
2	572	550	54
3	625	615	240
4	193	164	983
5	370	385	758
6	195	212	0
7	307	348	893
8	189	164	192
9	604	567	971
10	626	598	956
11	398	343	175
12	530	511	999
13	125	121	222
14	318	291	19
15	141	102	827
16	29	56	141
17	97	72	131
19	226	240	151
20	208	208	155
21	29	33	996
22	121	120	912
23	72	69	922
24	66	82	976
26	29	55	137
28	29	29	69

3,2,L

0	616	652	999
1	293	328	161
2	563	528	138
3	394	447	60
4	633	660	774
5	311	287	156
6	230	246	228
7	161	182	14
8	367	411	852
9	144	176	41
10	380	373	778
11	391	324	887
12	114	96	65
13	198	193	762
14	184	166	89
15	66	96	937
16	223	211	242
17	116	113	197
18	309	279	171
19	174	157	955
20	106	102	85
21	97	98	973
22	66	63	781
23	29	48	763
24	29	19	85
25	29	24	213
26	51	75	242
27	29	14	856

4,2,L

0	630	659	0
1	945	780	954
2	942	881	100
3	159	93	21
4	387	301	787
5	604	669	90
6	240	247	206
7	416	410	8
8	398	401	921
9	164	186	235
10	348	327	945
11	135	140	905
12	164	168	856
13	144	121	134
14	195	173	904
15	184	172	229
16	88	81	999
17	223	233	112
18	169	65	955
19	85	145	761
20	153	92	779
25	29	25	45
26	51	73	976
27	29	42	173

5,2,L

0	539	363	0
1	652	582	185
2	500	377	214
3	482	439	778
4	652	587	69
5	198	177	834
6	295	313	114
7	469	461	952
8	208	183	150
9	247	237	841
10	269	25	116
11	164	297	826
12	293	173	999
13	182	342	811
14	93	162	128
15	213	92	246
16	138	193	136
17	83	136	909
18	51	101	786
19	184	54	151
20	66	154	161
21	83	86	837
22	78	78	879
23	51	83	10
24	51	72	878
26	29	37	941
27	29	30	751

6,2,L

0	292	247	999
1	669	523	862
2	369	275	188
3	715	634	999
4	451	436	180
5	299	300	973
6	204	164	157
7	415	410	999
8	150	146	919
9	267	282	9
10	200	212	816
11	102	128	785
12	223	220	895
14	106	95	180
15	217	228	913
16	164	168	955
17	161	134	99
18	164	143	772

TABLE 5. (*contd.*)

19	153	140	59
20	41	66	786
22	72	76	844
24	72	75	990
26	29	13	839

7,2,L

0	691	549	0
1	572	463	801
2	295	277	883
3	298	379	173
4	204	173	875
5	236	210	104
6	51	67	769
7	150	159	914
8	41	24	763
9	184	158	235
10	135	117	806
11	320	287	238
12	29	59	863
13	298	278	192
14	118	117	98
15	204	188	139
16	29	63	896
17	59	89	67
18	153	133	218
20	29	46	988
21	29	40	811
22	41	62	3
23	66	75	232
24	41	55	874

8,2,L

0	141	73	0
1	144	120	14
2	102	116	225
3	340	313	37
4	193	179	757
5	388	338	957
6	225	239	245
7	304	290	996
8	331	328	775
9	182	158	60
10	102	114	852
11	29	32	975
12	51	77	49
13	144	135	61
14	72	60	100
15	159	180	142
16	78	98	872
17	106	109	866
18	41	54	235
19	29	38	944
20	51	60	780
21	41	65	35
22	29	18	995
23	29	26	966
24	41	67	753

9,2,L

0	66	67	0
1	406	332	786
2	200	181	936
3	240	243	789
4	88	109	123
5	128	125	801
6	179	179	93
7	309	269	181
8	128	132	177
9	283	260	823
10	66	89	123
11	232	223	181
13	41	90	35
14	97	85	74
15	29	52	848
16	66	69	32
17	97	106	197
18	29	39	801
19	41	57	842
20	29	18	831
21	29	43	855
22	29	31	82
23	29	30	100

10,2,L

0	110	103	999
1	206	191	955
2	29	46	33
3	138	119	980
4	156	167	786
5	305	270	10
6	66	83	102
7	234	230	94
8	150	157	161
9	198	168	808
10	51	78	792
11	51	59	130
12	29	75	244
13	29	44	148
15	88	85	956
16	72	75	987
17	59	83	49
18	29	50	225
19	29	26	940
20	41	41	803
22	29	20	155

11,2,L

0	132	152	0
1	193	180	175
2	72	94	230
3	29	34	847
4	200	183	892
5	29	55	768
6	179	168	195
7	114	127	827
8	41	67	977
9	241	214	182
11	93	95	805
12	97	89	6
13	128	114	154
14	29	52	958
15	51	37	180
16	59	65	16
18	29	45	860
19	29	39	216
21	29	55	130

12,2,L

0	110	89	0
2	114	101	874
3	125	117	974
4	110	86	150
5	118	112	989
6	132	152	756
7	106	99	783
9	118	103	0
10	106	99	79
12	83	71	44
13	51	61	845
15	51	58	945
17	29	39	838
18	29	38	919
19	29	56	52

13,2,L

1	83	93	770
2	88	87	865
3	41	50	248
4	83	79	778
5	29	24	85
6	88	88	839
7	78	85	218
8	29	49	105
10	59	58	189
11	29	45	180
12	41	59	142
13	41	55	106
14	29	41	801
17	29	35	858

14,2,L

0	118	113	999
1	29	42	797
2	29	27	953
4	41	71	973
5	59	73	947
6	51	60	212
7	59	40	979
9	29	24	926
10	29	47	48
12	29	35	953
14	29	35	89

15,2,L

2	41	46	896
4	66	85	757
5	41	47	68
9	41	14	997

16,2,L

2	41	63	977

0,3,L

3	106	99	249
4	125	119	999
5	479	507	249
6	78	125	999
7	961	926	249
8	358	344	999
9	210	175	750
11	206	204	749
13	221	211	749
14	59	67	999
15	284	242	749
16	335	322	0
18	132	142	0
19	128	143	249
20	29	47	0
21	225	218	249
22	29	38	999
23	41	58	249
25	29	50	749
27	29	44	249

1,3,L

2	573	651	777
3	114	86	7
4	184	182	184
5	219	238	906
6	436	347	988
7	223	213	948
8	797	699	971
9	270	221	865
10	507	489	158
11	260	232	93
12	327	300	227
13	210	184	899
14	232	212	201
15	269	214	955
16	59	90	164
17	221	200	170
18	221	193	990
19	29	42	894
20	66	67	192
22	159	124	215
23	29	36	930
24	29	53	791
25	29	44	94
26	29	49	838
27	29	50	912

2,3,L

0	102	127	249
1	535	466	101
2	377	337	28
3	289	292	792
4	480	545	899
5	432	439	845
6	656	655	934
7	193	157	72
8	210	222	151
9	742	664	177
10	138	93	965
11	200	178	166
12	236	233	832
13	198	183	920
14	208	199	38
15	41	86	197
16	208	167	914
17	195	194	863
18	102	84	963
19	102	98	764
21	83	85	33
22	29	28	63
23	29	41	119
24	29	58	118
25	41	61	224

3,3,L

0	367	366	749
1	394	398	949
2	573	537	231
3	475	429	917
4	314	323	905
5	273	282	831
6	495	482	62
7	66	108	234
8	652	616	144
9	51	53	197
10	277	220	172
11	132	101	69
12	240	218	211
13	280	286	895
14	179	184	856
15	267	242	37
16	150	123	818
17	343	332	816
18	102	101	933
19	29	56	904
20	161	154	137
21	29	57	827
22	93	76	986
23	83	73	934
24	59	59	834

4,3,L

0	356	332	749
1	463	402	912
2	727	644	890
3	377	358	958
4	376	355	46
5	193	170	822
6	200	211	51
7	307	275	177
8	385	326	968
9	396	372	80
10	159	146	67
11	396	381	13
12	121	111	960
13	179	177	184
14	340	317	923
15	307	285	916
16	202	149	801
17	191	172	952
18	135	128	972
19	66	61	88
21	78	87	188
22	29	29	892
23	41	68	163
25	51	52	67

5,3,L

0	986	827	749
1	360	280	794
2	407	325	758
3	444	414	880
4	225	209	865
5	382	375	792
6	78	64	81
7	232	222	195
8	238	228	5
9	243	236	218
10	311	295	157
11	125	105	988
12	265	213	78
13	326	278	842
14	29	43	871
15	93	115	769
16	128	135	853
17	59	80	975
18	186	182	174
19	29	47	946
20	88	77	25
21	51	54	173
22	78	71	220
24	29	50	989
26	29	33	914

6,3,L

0	476	441	249
1	428	372	904
2	332	245	67
3	339	298	896
4	347	357	961
5	210	185	131
6	371	326	873
7	169	128	64
8	128	126	858
9	174	175	45
10	88	89	785
11	121	115	990
12	114	102	235
13	284	285	16
14	252	231	776
15	144	154	9
16	191	172	866
17	141	126	788
18	93	89	915
20	29	37	771
23	29	56	41

7,3,L

0	83	38	249
1	88	78	63
2	234	169	792
3	284	268	845
4	174	196	6
5	336	305	788
6	215	224	46
7	284	269	755
8	247	240	91
9	172	109	87
10	238	215	980
11	206	165	977
12	93	87	813
13	144	158	229
14	83	80	938
15	232	232	249
17	93	107	763
18	29	53	991
19	114	117	750
21	29	16	844
22	29	46	982

8,3,L

0	198	157	749
1	206	149	18
2	262	260	792
3	88	77	66
4	174	170	240
5	121	106	978
7	114	111	172
8	41	56	882
9	72	69	74
10	202	200	809
11	255	242	961
12	72	73	910

TABLE 5. (*contd.*)

13	29	32	145
14	106	96	793
15	153	165	87
17	29	38	841
18	97	94	138
19	78	102	115
20	41	48	931

9,3,L

0	97	62	249
2	215	201	953
3	283	233	144
4	193	162	95
5	132	101	872
6	72	84	952
7	245	208	178
8	106	117	990
9	191	173	792
11	41	62	133
12	164	174	954
13	29	74	819
14	29	49	174
15	51	59	775
16	29	57	140
17	41	67	197
18	29	32	985
19	29	46	218
20	29	48	996
21	41	49	196

10,3,L

1	202	157	23
2	88	81	191
3	164	145	936
4	270	274	179
5	88	120	770
6	97	96	79
7	97	81	41
8	66	75	751
9	138	126	980
11	78	77	990
12	138	157	774
13	97	80	961
14	41	44	35
15	88	66	811
16	88	91	789
18	29	77	215
20	29	57	19

11,3,L

0	121	129	249
3	106	100	865
5	264	236	121
6	135	106	35
7	114	105	871
8	121	102	894
9	29	39	922
10	182	170	994
13	110	102	180
14	29	43	246
15	59	52	220
17	29	41	129
19	29	21	241

12,3,L

1	153	128	48
2	78	98	240
4	29	67	960
5	59	51	836
6	88	83	987
7	102	115	835
8	83	79	33
9	97	65	925
11	78	79	934
12	29	61	220
13	66	58	939
14	41	60	205
18	29	51	982

13,3,L

0	51	57	249
2	88	81	176
3	83	84	68
4	83	74	78
5	59	47	840
6	51	50	954
7	66	64	123
10	51	65	199
12	41	50	828
13	29	43	246

14,3,L

1	29	43	960
2	41	49	157
3	29	49	807
4	83	84	976

15,3,L

2	72	75	243

0,4,L

3	228	222	249
4	51	11	999
5	51	83	749
6	66	78	999
7	72	48	249
8	88	105	0
9	78	92	249
10	293	319	999
11	110	131	249
12	114	134	0
13	323	271	249
15	141	147	249
17	88	79	249
18	93	134	999
19	72	72	249
20	29	37	999
21	29	45	749
24	66	69	999
26	29	30	999

1,4,L

2	255	307	137
3	226	245	923
4	397	463	187
5	273	290	989
6	226	292	774
7	345	425	43
8	138	154	163
9	456	410	81
10	195	200	978
11	144	161	957
12	210	227	921
13	118	121	988
14	191	186	822
15	191	177	171
16	200	213	181
17	102	84	112
18	102	118	206
19	179	187	913
20	114	101	80
21	88	87	115
22	29	18	982
23	29	52	947
25	29	29	28

2,4,L

0	342	392	0
1	382	422	759
2	358	341	28
3	338	353	750
4	254	258	803
5	265	288	199
6	114	133	149
7	72	65	120
8	230	270	902
9	78	120	850
10	364	376	927
11	319	312	850
12	51	76	962
13	83	59	203
14	206	199	985
15	219	179	191
17	210	208	203
18	72	74	49
19	29	71	0
20	164	170	960
21	86	72	24
22	51	71	919
23	29	33	867
24	29	51	177
25	41	62	97
26	41	66	808

3,4,L

0	88	89	0
1	128	143	100
2	121	138	829
3	243	268	992
4	260	264	98
5	304	339	36
6	238	272	246
7	150	129	949
8	174	225	844
9	273	251	829
10	135	128	246
11	132	138	29
12	102	115	858
13	186	166	840
14	277	299	142
15	66	89	877
16	132	138	143
17	159	164	927
18	72	69	55
19	29	10	809
21	93	96	924
22	41	69	59
23	51	60	911
24	51	70	237

4,4,L

0	83	84	0
1	245	231	161
2	161	159	926
3	125	105	194
4	293	344	171
5	503	541	41
6	169	188	852
7	78	75	191
8	295	310	888
9	59	69	834
10	72	84	899
11	234	248	784
12	378	377	819
13	335	324	128
14	135	136	881
15	83	99	131
16	29	40	193
17	29	57	977
18	51	74	837
19	72	73	101
20	78	74	750
22	29	44	944
23	29	42	148
24	66	85	915

5,4,L

0	504	447	999
1	287	290	756
2	97	111	925
3	106	88	999
4	147	157	119
5	51	54	868
6	301	293	67
7	198	186	916
8	198	210	839
9	200	215	821
10	252	265	880
11	240	250	922
12	334	369	86
13	121	116	7
14	29	40	963
15	72	72	811
16	72	66	964
18	59	70	129
19	66	83	890
20	66	54	32
21	41	71	878
22	29	40	973
24	29	35	980

6,4,L

0	287	243	999
1	128	139	786
2	264	287	869
3	270	275	136
4	83	90	105
5	41	51	128
6	195	223	247
7	267	299	991
8	118	110	909
9	125	136	778
10	219	215	106
11	204	216	837
12	186	179	80
13	114	132	193
14	164	166	843
15	156	175	159
17	114	116	32
18	78	100	832
20	29	44	827
21	29	32	243
22	66	87	993

7,4,L

0	135	118	999
1	174	120	217
2	304	346	45
3	193	195	811
4	59	97	990
5	88	67	26
6	88	126	206
7	128	134	936
8	184	197	797
9	147	155	831
10	147	174	765
11	267	297	177
12	125	142	863
13	66	61	201
14	198	207	27
16	144	147	66
17	41	58	921
18	29	40	92
19	41	77	805
21	59	67	230
23	29	50	757
24	29	23	936

8,4,L

0	138	144	0
1	97	90	195
2	78	77	993
3	213	209	937
5	169	146	907
6	226	235	786
7	83	86	78
8	217	214	184
10	138	167	864
11	132	147	144
12	72	79	151
15	121	155	984
17	29	32	988
18	29	44	205
19	29	42	893
20	29	55	815
23	29	56	57

9,4,L

0	78	73	0
1	161	158	804
2	141	175	35
3	138	101	198
4	93	115	36
5	29	82	828
6	51	49	963
7	93	119	224
9	83	95	805
10	41	61	981
11	51	57	130
12	102	127	155
13	110	119	808
14	102	109	917
15	29	47	980
17	29	46	237
18	59	80	989
20	29	65	206

10,4,L

1	83	96	846
3	41	64	11
4	125	141	776
5	106	106	69
6	29	68	841
7	72	70	833
8	102	120	775
9	29	31	100
10	29	59	143
12	29	67	125
13	59	87	25
15	29	43	872
16	29	56	828
17	51	54	908
18	29	30	795
20	29	26	233

11,4,L

0	66	109	999
1	78	80	64
2	29	61	953
3	29	45	248
4	78	77	909
7	29	87	184
9	29	69	92
10	66	69	50
11	59	72	804
13	51	50	75
15	41	50	933
16	29	52	915
18	29	34	202

12,4,L

7	83	75	900
8	83	66	192

15,4,L

0	29	32	0
1	41	74	8

0,5,L

3	315	326	249
4	97	113	0
5	232	229	249
6	29	4	1
7	299	273	249
8	29	8	999
9	41	21	249
10	125	80	0
11	29	56	749
12	41	36	999

TABLE 5. (*contd.*)

13	153	171	249
14	106	93	0
15	128	119	249
16	132	133	999
17	102	117	749
18	78	54	999
19	78	56	749
20	29	24	999
21	41	32	749
22	41	43	0
23	66	80	749

1,5,L

2	51	54	906
3	260	227	55
4	88	79	38
5	66	88	123
6	102	120	210
7	217	211	222
8	144	136	905
9	182	150	202
10	156	122	782
11	240	216	978
12	97	127	140
13	377	259	958
15	141	135	910
16	29	40	909
17	138	140	141
18	128	107	214
19	29	40	880
20	88	91	165
22	66	66	764
23	29	41	64
24	41	50	207
25	29	47	37

2,5,L

0	106	91	249
1	186	193	980
2	97	113	820
3	156	130	907
4	128	155	861
5	29	80	936
6	51	145	911
7	401	382	144
8	102	96	980
9	208	190	766
10	118	107	934
11	223	219	767
12	269	213	880
13	125	117	913
14	232	213	926
15	114	117	799
16	144	120	884
17	118	79	129
19	128	113	182
21	114	99	234
23	29	38	75
24	51	62	82

3,5,L

0	177	195	249
1	195	165	54
2	114	118	825
3	260	245	887
4	72	62	214
5	225	234	915
6	41	43	69
7	182	177	5
8	360	334	107
9	121	139	800
10	223	204	179
11	243	183	29
13	156	157	851
14	97	78	39
15	206	168	896
16	118	118	224
17	156	132	873
18	29	47	135
20	88	80	209
21	29	60	945
23	41	46	968
24	51	57	954
25	29	65	759

4,5,L

0	314	309	249
1	144	123	840
2	200	204	806
3	326	297	808
4	223	190	12
5	326	290	181
6	179	166	926
7	172	137	223
8	184	193	860
9	267	257	203
10	132	128	996
11	255	276	957
12	102	95	785
13	29	68	855
14	147	129	779
15	78	75	159
16	141	124	825
17	51	55	167
18	29	58	64
19	93	95	89
21	51	68	59
22	29	29	904
24	29	72	804

5,5,L

0	141	113	249
1	167	130	953
2	83	58	114
3	114	104	928
4	322	288	929
5	210	213	164
6	193	199	142
7	316	292	944
8	255	254	38
9	516	498	946
11	217	199	146
12	29	46	852
13	41	39	978
15	97	88	892
16	29	47	154
17	29	43	192
18	41	77	146
19	29	19	39
20	88	76	57
24	29	19	55

6,5,L

0	78	67	249
1	88	88	48
2	144	151	818
3	51	12	808
4	240	232	223
5	184	150	778
6	156	157	800
7	78	65	869
8	210	180	888
9	267	254	65
10	121	104	145
11	125	131	785
12	204	215	873
13	41	61	903
14	114	125	880
17	93	83	210
18	59	83	781
19	72	73	193
21	29	55	94
22	29	56	816

7,5,L

0	141	96	249
1	93	63	244
2	118	116	946
3	121	113	241
4	83	97	852
5	78	92	51
6	273	284	2
8	59	77	110
9	153	161	879
10	132	149	7
11	118	122	971
12	128	117	23
13	78	95	838
15	97	103	796
17	29	56	237
18	59	74	40
19	29	62	799
20	29	51	76
21	29	31	904
22	51	85	995

8,5,L

0	128	107	249
2	114	107	889
3	106	88	981
5	110	86	88
6	135	111	821
7	83	65	110
8	93	93	941
9	110	107	780
10	59	78	881
11	118	115	91
12	41	53	174
14	78	73	223
15	41	21	811
16	29	50	758
18	59	60	249
20	29	60	940

9,5,L

1	102	53	967
2	121	129	55
4	141	114	6
5	114	104	769
6	83	73	974
7	121	99	53
10	114	104	974
13	51	84	230
15	41	53	161
16	29	45	96
17	29	50	226
18	41	59	963
19	29	52	952

10,5,L

0	59	57	249
1	102	63	71
2	114	108	132
4	93	85	228
5	29	56	227
6	51	61	105
7	59	74	998
8	66	55	225
9	41	44	947
10	41	67	750
11	72	65	774
13	51	52	886
14	29	46	156
15	29	25	103
16	51	79	200
17	29	54	919

12,5,L

0	97	74	249

0,6,L

3	147	154	249
4	51	68	0
5	88	81	249
6	110	103	999
7	29	16	749
8	97	62	0
9	110	115	749
10	347	329	999
11	177	145	749
12	78	106	999
13	248	264	749
14	221	208	999
16	114	87	0
17	51	48	749
18	78	82	0
20	41	40	0
21	41	33	249
22	29	42	0
23	29	27	249

1,6,L

1	72	125	35
2	97	110	120
3	83	81	129
4	141	153	760
5	186	183	945
6	29	33	766
7	213	219	92
8	59	67	9
9	118	123	908
10	179	159	188
11	135	117	944
12	118	112	906
13	93	87	779
14	125	125	175
15	110	106	916
16	88	87	849
17	135	122	902
19	114	112	101
21	51	33	20
22	59	63	199
23	29	51	966
24	29	64	925

2,6,L

0	83	69	0
1	159	197	849
2	88	74	238
3	135	134	108
4	83	102	179
5	88	71	893
6	78	66	22
8	182	180	973
10	167	147	131
11	208	170	92
12	51	67	51
13	102	104	929
14	106	94	960
15	121	137	176
16	93	70	841
17	78	62	225
18	78	70	980
20	41	43	967
22	93	91	919
23	72	78	210
24	29	41	788

3,6,L

0	78	82	0
1	72	67	773
2	29	14	28
3	184	175	34
4	78	71	887
5	118	118	79
6	78	63	199
7	121	91	820
8	102	109	978
9	195	177	0
10	93	78	918
11	125	120	192
12	150	148	227
13	29	29	877
14	102	107	131
16	88	77	104
17	59	64	89
18	59	63	38
19	93	88	840
22	29	34	77
21	78	82	907
23	29	44	135

4,6,L

1	169	139	76
3	147	127	205
4	164	169	894
5	179	164	888
6	110	114	85
7	128	133	907
8	213	209	756
9	200	184	752
10	93	74	954
11	106	107	152
12	121	99	157
13	66	53	137
14	83	72	928
15	88	84	157
16	29	51	985
17	51	58	946
18	88	94	841
20	59	65	864
21	29	51	94
22	29	32	4
23	29	14	825

5,6,L

0	110	124	0
1	78	93	907
2	118	134	103
3	93	86	74
4	156	143	985
5	88	82	760
6	29	45	781
7	213	193	879
8	153	159	973
9	41	41	949
10	83	81	766
11	78	81	965
12	110	110	52
14	59	51	953
15	41	58	855
17	51	42	859
19	51	50	968
21	29	25	128

6,6,L

1	138	94	778
2	78	94	244
3	29	30	916
4	59	76	879
5	144	140	904
6	247	251	231
7	110	128	819
8	41	39	919
10	41	48	838
11	29	22	218
13	121	118	102
14	29	39	888
15	97	86	72
16	29	66	840
17	29	47	192
18	29	30	768
20	51	95	906
21	29	64	770

7,6,L

0	88	80	0
2	118	112	895
3	29	74	83
5	102	73	23
6	59	61	121
7	29	43	121
8	78	76	795
9	125	97	813
10	51	75	977
11	29	20	222

TABLE 5. (*contd.*)

12	106	106	994
14	51	57	148
16	78	88	24
17	59	61	814
18	29	36	913
19	41	56	185
20	29	43	145
21	29	79	863

8,6,L

1	51	47	67
5	102	90	2
6	59	52	215
7	83	76	841
8	83	74	829
9	51	39	990
10	110	104	797
11	41	32	165
12	66	54	160
13	83	82	24
16	29	42	858
17	59	85	907
18	41	65	777
19	29	23	928

9,6,L

0	66	83	0
1	72	57	218
2	66	66	1
4	51	60	124
5	72	55	791
6	88	82	773
9	78	67	199
11	41	61	131
12	59	64	53
14	66	76	12
15	29	49	949
16	51	61	905
17	29	66	202
18	29	20	178

10,6,L

2	66	67	860
3	59	18	876
4	66	68	197
6	41	41	822
8	72	77	226
10	29	31	951
11	59	71	996
13	51	60	981
14	29	55	787
15	29	40	831
16	29	50	50

11,6,L

0	72	86	0
4	59	48	784

DISCUSSION

The stereochemical features of the molecule, as established in the present investigation, are shown in Fig. 2. The electron density distribution computed from the final least squares parameters is illustrated in Fig. 3.

Table 6 lists the interatomic distances obtained after the last FATAL cycle and at the end of the analysis. Average values from the final refinement for the carbon carbon bond are: sp^3–sp^3 1·514 Å (over 28 values) and sp^2–sp^3 1·502 Å (over 5 values). The C=O bond is comparatively short but similar distances of 1·15 Å and 1·20 Å were found in giberellic acid[14] and in 4-bromoestrone[15] respectively.

[14] J. A. Hartsuch and W. N. Lipscomb, *J. Amer. Chem. Soc.* **85,** 3414 (1963).
[15] D. A. Norton, G. Kartha and C. Tang Lu, *Acta Cryst.* **16,** 89 (1963).

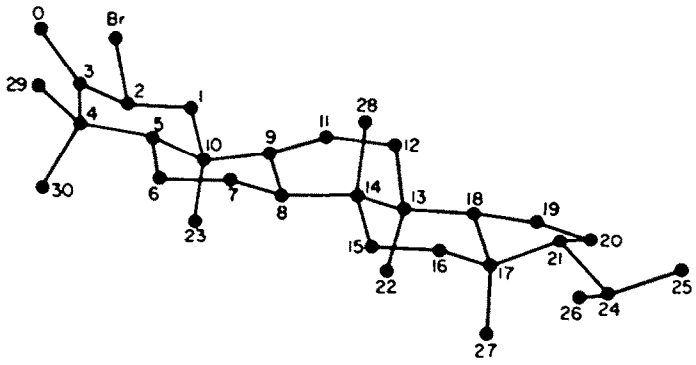


FIG. 2. The molecule of 2α bromoarborinone. Numbering of atoms relates to Tables 3, 4, 6, 7.

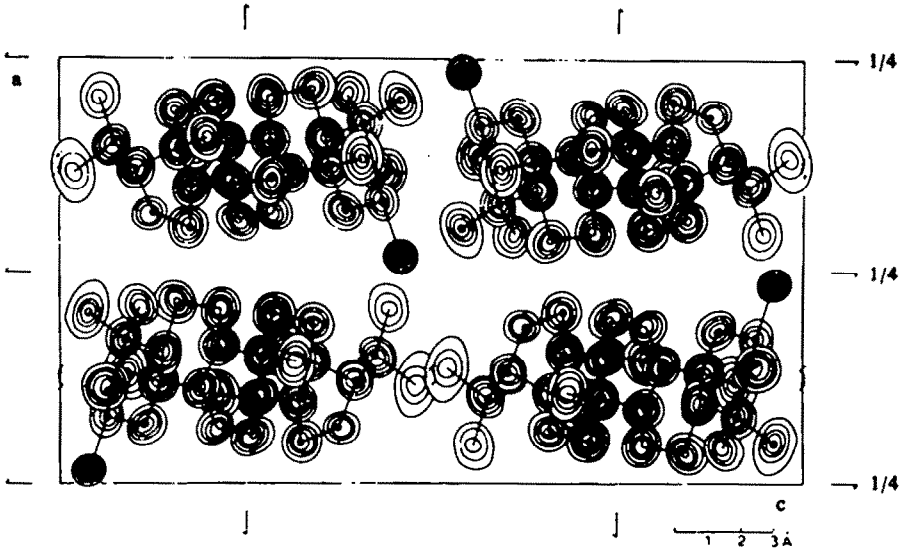


FIG. 3. Composite electron density map showing the four molecules of 2α-bromoarborinone related by the three sets of screw axes in the unit cell. Contours at intervals of 1e/Å³ except around the bromine atoms, which are indicated by solid centres. Lowest contour 1e/Å³.

Rings A, B and D are in the chair form and C(22) and C(28) in the *trans* configuration. Atoms C(22), C(13), C(14), C(28) are coplanar.

The bromine atom is coplanar with C(2), C(3), C(4) and O to within 0·05 Å and is 2·96 Å distant from the oxygen atom. There is some distortion of bond angles around the oxygen atom in the direction of maximal O–Br separation. In ring C atoms 8, 9, 11 and 12 are coplanar to 0·02 Å.

Four of the five carbon atoms in ring E are coplanar to within 0·05 Å with C(17) displaced 0·74 Å from the mean plane. It is interesting to note that as a rule in molecules containing fused five- and six-membered ring systems four atoms of the five-membered ring are strictly coplanar while one of the two atoms common to the two

TABLE 6. INTERATOMIC DISTANCES FOR 2α-BROMOARBORINONE

	Final FATAL Cycle R = 26·5%	Final L.S. Cycle R = 12·2%
Br –C(2)	2·02 Å	1·91 Å
C(1) –C(2)	1·31	1·46
C(1) –C(10)	1·62	1·55
C(2) –C(3)	1·45	1·52
C(3) –C(4)	1·47	1·55
C(4) –C(29)	1·56	1·51
C(4) –C(30)	1·57	1·61
C(4) –C(5)	1·49	1·49
C(5) –C(10)	1·55	1·57
C(5) –C(6)	1·47	1·51
C(6) –C(7)	1·53	1·51
C(7) –C(8)	1·43	1·52
C(8) –C(9)	1·57	1·51
C(8) –C(14)	1·57	1·47
C(9) –C(10)	1·45	1·46
C(9) –C(11)	1·35	1·30
C(10)–C(23)	1·39	1·49
C(11)–C(12)	1·46	1·47
C(12)–C(13)	1·54	1·55
C(13)–C(22)	1·54	1·51
C(13)–C(14)	1·55	1·55
C(13)–C(18)	1·55	1·48
C(14)–C(28)	1·49	1·53
C(14)–C(15)	1·53	1·52
C(15)–C(16)	1·51	1·48
C(16)–C(17)	1·44	1·46
C(17)–C(18)	1·57	1·54
C(17)–C(27)	1·48	1·49
C(17)–C(21)	1·40	1·48
C(18)–C(19)	1·57	1·54
C(19)–C(20)	1·54	1·51
C(20)–C(21)	1·52	1·52
C(21)–C(24)	1·58	1·53
C(24)–C(25)	1·48	1·45
C(24)–C(26)	1·53	1·55
C(3) –O	1·33	1·15

ring systems is out of plane by a distance close to that found in 2α-bromoarborinone. Hartsuch and Lipscomb[14] find such a displacement of 0·71 Å in giberellic acid, Abrahamsson[16] 0·71 Å in prostalglandin $F_{\alpha-1}$ and the present authors 0·70 in tomatidine hydrobromide.[17] We have also calculated from published co-ordinates the geometry of such systems in 7-bromocholesteryl chloride[18] where the four atoms are coplanar to 0·10 Å and the fifth displaced by 0·7 Å; while in lanosteryl iodoacetate[19] the displacement is 0·5 Å and the remaining atoms are coplanar to 0·03 Å.

[16] S. Abrahamsson, *Acta Cryst.* **16**, 409 (1963).
[17] O. Kennard, L. Riva di Sanseverino and J. S. Rollett, to be submitted to *J. Chem. Soc.*
[18] H. Burki and W. Nowacki, *Z. Kristallog.* **108**, 206 (1956).
[19] J. Friedrichson and A. McL. Mathieson, *J. Chem. Soc.* 2159 (1953).

TABLE 7. 2α-BROMOARBORINONE BOND ANGLES

Br –C(2) –C(1)	108·05	C(12)–C(13)–C(14)	105·27
Br –C(2) –C(3)	108·35	C(12)–C(13)–C(18)	110·49
C(2) –C(1) –C(10)	109·63	C(12)–C(13)–C(22)	106·61
C(1) –C(2) –C(3)	114·00	C(14)–C(13)–C(18)	111·23
C(2) –C(3) –C(4)	109·09	C(14)–C(13)–C(22)	115·06
C(2) –C(3) –O	127·43	C(18)–C(13)–C(22)	108·04
C(4) –C(3) –O	123·46	C(8) –C(14)–C(13)	109·67
C(3) –C(4) –C(5)	110·23	C(8) –C(14)–C(15)	109·61
C(3) –C(4) –C(30)	105·87	C(8) –C(14)–C(28)	106·93
C(5) –C(4) –C(29)	113·72	C(13)–C(14)–C(15)	105·41
C(5) –C(4) –C(30)	110·94	C(13)–C(14)–C(28)	113·05
C(29)–C(4) –C(30)	105·25	C(15)–C(14)–C(28)	112·15
C(4) –C(5) –C(6)	111·06	C(14)–C(15)–C(16)	113·09
C(4) –C(5) –C(10)	117·76	C(15)–C(16)–C(17)	114·40
C(6) –C(5) –C(10)	108·23	C(16)–C(17)–C(18)	105·56
C(5) –C(6) –C(7)	107·08	C(16)–C(17)–C(21)	118·31
C(6) –C(7) –C(8)	111·98	C(16)–C(17)–C(27)	110·89
C(7) –C(8) –C(9)	108·52	C(18)–C(17)–C(21)	96·62
C(7) –C(8) –C(14)	113·75	C(18)–C(17)–C(27)	118·06
C(9) –C(8) –C(14)	110·99	C(21)–C(17)–C(27)	107·20
C(8) –C(9) –C(10)	114·93	C(13)–C(18)–C(17)	115·70
C(8) –C(9) –C(11)	122·98	C(13)–C(18)–C(19)	120·05
C(10)–C(9) –C(11)	121·05	C(17)–C(18)–C(19)	104·14
C(1) –C(10)–C(5)	104·35	C(18)–C(19)–C(20)	100·91
C(1) –C(10)–C(9)	110·45	C(19)–C(20)–C(21)	106·91
C(1) –C(10)–C(23)	111·69	C(17)–C(21)–C(20)	105·51
C(5) –C(10)–C(9)	109·64	C(17)–C(21)–C(24)	119·53
C(5) –C(10)–C(23)	116·89	C(20)–C(21)–C(24)	107·84
C(9) –C(10)–C(23)	103·87	C(21)–C(24)–C(25)	108·05
C(9) –C(11)–C(12)	123·52	C(21)–C(24)–C(26)	108·77
C(11)–C(12)–C(13)	111·70	C(25)–C(24)–C(26)	112·02

The consistency of the bond distance values is reasonably satisfactory, particularly since the main aim of the analysis was to establish the gross chemical structure and the individual intensity readings on which the analysis was based were of moderate accuracy only. The convergence of the refinement is probably due to the comparatively high percentage of the reflections within the reciprocal sphere which were measured. There was little change in the bond distances (Table 6) and in atomic positions during the least squares refinement, except for atoms nearest to Br. The average co-ordinate changes were 0·031 Å in the x, 0·05 Å in the y and 0·033 Å in the z direction. The maximum movement was 0·147 Å in the y co-ordinate of C(3). Essentially the structure was solved with the FATAL group of calculations and the least squares computations were mainly concerned with refining the amplitudes of the thermal vibrations.

The list of bond angles is given in Table 7. The average tetrahedral angle over 29

measured values excluding those of ring E was 110·1°. The strain imposed on the D/E ring junction was evident from the bond angles, particularly around C(18).

The molecules in the crystal are held by van der Waal's attractions only. Distances less than 4 Å are given below.

C(26) . . . C(29) 3·50 Å	Br . . . C(25) 3·74 Å
C(3) . . . C(23) 3·64 Å	Br . . . C(29) 3·87 Å
C(2) . . . C(23) 3·97 Å	Br . . . C(16) 3·99 Å
C(29) . . . C(23) 3·97 Å	O . . . C(29) 3·35 Å
C(25) . . . C(21) 3·99 Å	O . . . C(23) 3·47 Å
	O . . . C(2) 3·80 Å

Taking the van der Waal's radius of the methyl group as 2·0 Å and that of oxygen as 1·40 Å the shortest distances are that from one of the methyl groups attached to ring A (C29) to the neighbouring isopropyl methyl group C(26) and that from C(29) to a neighbouring oxygen atom.

CALCULATIONS

The following computers were used in the calculations described in this paper.

Data reduction	"Pegasus"	University College, London
"FATAL"	"Mercury"	Computing Laboratory, Oxford
Least squares	"Atlas"	Institute of Computer Science, London
	"Atlas"	Science Research Council, Harwell
Molecular geometry	"Titan"	Mathematical Laboratory, Cambridge
Fourier synthesis	"IBM 7090"	Imperial College, London

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