during which time the Dry Ice sublimed and the reaction mixture slowly warmed to ambient temperature. The resultant yellow solution was poured into about 100 ml of ice–water. The aqueous solution was extracted thrice with 30-ml portions of *n*-BuOH, and the butanol solvent was removed by distillation under reduced pressure. The residue weighed 0.573 g and was chromatographed on silicic acid (160 g, Mallinckrodt, 100 mesh) using MeOH as the solvent. This procedure removed the last traces of DMSO from the product, and the resultant homogeneous oil (0.379 g, 16%) crystallized during storage. The product, **2**, was soluble in 1 *N* NaOH, acetone, or methyl isobutyl ketone, but was insoluble in water, benzene, or hexane. It was recrystallized from methyl isobutyl ketone and benzene: mp 135.0–135.5°; ir (Nujol) 3400, 3260 (NH,OH), 1743–1715 (carboxyl C═O), 1670 (amide C═O), 1538 (amide NH); nmr (acetone-d_6) 4.12 (m, 2, methylene H), 5.1 (m, 2, methine H and amide H), 6.9 (broad, 1, amine H), 8.0 (broad, 1, carboxyl H).

Anal. Calcd for $C_{10}H_6F_{12}N_2O_4$ (**2**): C, 26.92; H, 1.36; F, 51.10; N, 6.28. Found: C, 26.88; H, 1.47; F, 48.47; N, 6.32.

Reaction of Glycylglycine Ethyl Ester with Hexafluoroacetone. Preparation of 3 and 8.—A solution of 0.983 g (5.0 mmol) of the hydrochloride of glycylglycine ethyl ester in 25 ml of DMSO was treated with 0.535 g (5.3 mmol) of triethylamine. This mixture was then treated with an excess of hexafluoroacetone in exactly the same manner as that described above for glycylglycine. An oil was obtained which weighed 0.444 g (18.8%), bp 96–110° (0.23 mm).

Anal. Calcd for $C_{12}H_{10}F_{12}N_2O_4$ (**3** or **8**): C, 30.40; H, 2.13; F, 48.08; N, 5.91. Found: C, 30.60; H, 2.27; F, 47.08; N, 5.81.

In a later run, the above oily product was found to contain two isomers, **3** and **8**. The minor product (**8**) was obtained in only 2.8% yield, tlc R_f 0.8 [C_6H_6–EtOAc (9:1), silica gel]. The major oily product (**3**) was isolated in 12.7% yield, R_f 0.4 [C_6H_6–EtOAc (9:1), silica gel]. The ir, nmr, and mass spectra of both of these isomers were consistent with the proposed structures.

Reaction of Glycylglycylglycine Methyl Ester Hexafluoroacetone. Preparation of 4.—The hydrochloride of glycylglycylglycine methyl ester[7] (mp 196–197°) was treated with hexafluoroacetone according to the same procedure that was used on glycylglycine ethyl ester hydrochloride (see above). The yield of crystalline product (**4**) was 27.8%: mp 150.5–151.0° (from hot CH_2Cl_2 or benzene); ir (Nujol) 3484, 3356, 3165 (NH), 1757 (ester C═O), 1689, 1667 (amide C═O), 1536 (amide NH), 1227 (C-F), 1183 (C–O–C); nmr (acetone-d_6) 2.8 (s, 2, amide, H_2O), 3.67 (s, 3, methyl), 4.02 (m, 4, methylene), 4.95 (broad, ~1, methine), 5.2 (broad, ~1, NH, partly exchanged); mass spectrum *m/e* (rel intensity) 517 (3, M^+), 486 (26, $M^+ - OCH_3$), 448 (60, $M^+ - CF_3$), 429 (7, $M^+ - NHCH_2CO_2CH_3$), 402 (100, $M^+ - CONHCH_2CO_2CH_3$), 351 (4, M^+ − hexafluoroacetone), 344 (21, $M^+ - CONHCH_2CONHCH_2CO_2CH_3$), 173 (100, $CONHCH_2CONHCH_2CO_2CH_3$), 88 (29, $NHCH_2CO_2CH_3$), 85 (25, $NH{=}CHCONH{=}CH_2$).

Anal. Calcd for $C_{13}H_{11}F_{12}N_3O_5$ (**4**): C, 30.12; H, 2.14; F, 44.08; N, 8.12. Found: C, 29.98; H, 2.08; F, 43.82; N, 8.14.

Reaction of Glycine Ethyl and Methyl Esters with Hexafluoroacetone. Preparation of 5 and 6.—The hydrochlorides of glycine ethyl and methyl esters were treated with hexafluoroacetone in separate experiments according to the procedure used on glycylglycine ethyl ester hydrochloride. The ethyl ester product, **5**, was obtained in 16.3% yield, bp 84° (23 mm).

Anal. Calcd for $C_{10}H_7F_{12}NO_3$ (**5**): C, 28.79; H, 1.69; F, 54.65; N, 3.36. Found: C, 28.60; H, 1.79; F, 54.44; N, 3.54.

The methyl ester product, **6**, was obtained in 44.5%, bp 78° (25 mm). The ir and nmr spectra of both of these products were consistent with the proposed structures.

Reaction of α-Methylalanyl-α-methylalanine (9) with Hexafluoroacetone. Preparation of 10.—A mixture of 0.37 g (1.80 mmol) of α-methylalanyl-α-methylalanine[8] and 5 ml of DMSO was treated with an excess of hexafluoroacetone in the same manner as that described above for glycylglycine. A solid precipitated when the reaction mixture was poured into ice–water. It weighed 0.31 g and was crystallized from aqueous acetone to afford 25 mg (4.1%) of pure **10**, mp 88.5°. The ir and nmr spectra supported structure **10** for this product. It was insoluble in water, but soluble in 1 *N* NaOH solution.

Anal. Calcd for $C_{11}H_{14}F_6N_2O_3$ (**10**): C, 39.29; H, 4.20; F, 33.90; N, 8.33. Found: C, 39.05; H, 4.13; F, 34.15; N, 8.32.

Registry No.—**2**, 36871-69-9; **3**, 36871-70-2; **4**, 36901-03-8; **5**, 36871-71-3; **6**, 36871-72-4; **8**, 36871-73-5; **10**, 36871-74-6; hexafluoroacetone, 684-16-2.

Acknowledgment.—Support of this work under a National Institutes of Health Research Project Grant No. AM 12761-03 is gratefully acknowledged.

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Crystal and Molecular Structure of 5a,11a-Dibromojanusene

WALTER M. MACINTYRE* AND ALAN H. TENCH

Chemistry Department, University of Colorado, Boulder, Colorado 80302

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The crystal structure of 5a,11a-dibromojanusene has been solved by the heavy-atom method. The strain between the apposed aromatic rings results in corresponding carbon atoms in the two rings being separated by amounts ranging from 2.99 Å for 11b and 12b to 4.09 Å in the case of 14 and 19. The dihedral angle between the apposed rings is 26.6°. The molecular geometry is discussed in detail.

Janusene (5,5a,6,11,11a,12-hexahydro-5,12:6,11-di-*o*-benzenonaphthacene) was first synthesized by Cristol and Lewis in 1967.[1] The compound was synthesized in order to study the physical and chemical effects arising from the π-electron interactions between two apposed aromatic rings, forced by the rigidity of the system to approach each other very closely. The structural formula, and the atom numbering system, are shown in Figure 1. A Dreiding model of janusene shows that the apposed or face (F) rings (in the terminology of Cristol and Lewis) would be parallel to each other and separated by about 2.5 Å, in the absence of any repulsion between the two π-electron clouds. Considerable repulsion is, of course, to be expected. The X-ray analysis of 5a,11a-dibromojanusene (DBJ) (Figure 2) was undertaken in order to determine how the molecular structure accommodates the strains imposed by the π-electron interaction.

Discussion

The bond lengths and angles in DBJ, as determined in this analysis, are given in Tables I and II, respectively, together with the corresponding standard deviations. Since none of the hydrogen atoms was located, data are given only for the bonds involving the carbon atoms and the bromine atoms.

The carbon–carbon bond lengths are all well within the expected limits. The carbon–bromine bond length

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(1) S. J. Cristol and D. C. Lewis, *J. Amer. Chem. Soc.*, **89**, 1476 (1967).

TABLE I

BOND LENGTHS IN DIBROMOJANUSENE AND THEIR ESTIMATED STANDARD DEVIATIONS (σ)[a]

Bond		Length	σ	Bond		Length	σ
C8	C9	1.388	0.020				
C9	C10	1.401	0.019	C1	C2	1.402	0.019
C10	C10a	1.407	0.016	C1	C12a	1.396	0.016
C6a	C10a	1.392	0.016				
C10a	C11	1.518	0.015	C12	C12a	1.523	0.015
C11	C11b	1.526	0.015	C12	C12b	1.510	0.015
C11	C11a	1.557	0.014	C11a	C12	1.568	0.015
C11b	C20	1.380	0.017	C12b	C13	1.383	0.017
C6b	C11b	1.406	0.015				
C19	C20	1.401	0.021	C13	C14	1.418	0.021
C18	C19	1.402	0.023				
C5a	C11a	1.572	0.014				
C11a	Br	1.992	0.010				

[a] Data are presented in ångstroms.

TABLE II

BOND ANGLES IN DIBROMOJANUSENE AND THEIR ESTIMATED STANDARD DEVIATIONS (σ)[a]

Atoms defining angle			Angle	σ	Atoms defining angle			Angle	σ
8	9	10	120.8	1.1	1	2	3	121.3	1.0
9	10	10a	118.3	1.1	12a	1	2	117.8	1.1
10	10a	6a	120.3	0.9	1	12a	4a	121.5	0.9
6a	10a	11	113.5	0.8	12	12a	4a	113.4	0.8
10	10a	11	126.1	0.9	12	12a	1	125.1	0.9
11	11b	6b	113.0	0.8	12	12b	5b	113.5	0.8
11	11b	20	125.2	0.8	12	12b	13	125.3	0.8
6b	11b	20	121.3	0.9	5b	12b	13	121.0	1.0
11b	20	19	118.5	1.0	12b	13	14	118.0	1.2
20	19	18	120.6	1.2	13	14	15	120.5	1.3
10a	11	11a	106.4	0.8	11a	12	12a	106.3	0.8
11b	11	11a	110.1	0.8	11a	12	12b	109.7	0.8
11b	11	10a	104.0	0.8	12b	12	12a	104.5	0.8
11	11a	Br	104.1	0.7	12	11a	Br	102.9	0.7
11	11a	5a	109.5	0.7	5a	11a	12	109.0	0.7
11	11a	12	116.1	0.8					
5a	11a	Br	115.2	0.6					

[a] Values are given in degrees.

TABLE III

SOME INTRAMOLECULAR DISTANCES IN DIBROMOJANUSENE AND THEIR ESTIMATED STANDARD DEVIATIONS (σ)[a]

Atoms		Distance	σ	Atoms		Distance	σ
C10a	C12a	4.920	0.015	C16	C20	4.424	0.018
C11	C12	2.651	0.015	C5b	C11b	3.247	0.015
C11b	C12b	2.987	0.015	C6b	C12b	3.353	0.015
C13	C20	3.513	0.019	C6	C11	2.604	0.015
C14	C19	4.094	0.023	C10a	C11a	2.461	0.015
C15	C19	4.283	0.025	C10a	Br11a	3.097	0.011
C14	C18	4.371	0.023	C11	Br11a	2.812	0.011
C13	C17	4.603	0.019	Br5a	Br11a	3.269	0.002

[a] Data are in ångstroms.

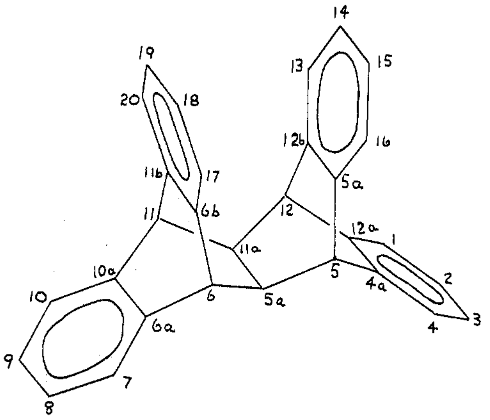

Figure 1.

is somewhat longer than might be expected. The average value of the length of the bond between a bromine atom and an aliphatic carbon atom has been quoted as 1.94 Å.[2] The value found by us, 1.99 Å (σ 0.018), is larger by an amount that is possibly significant. The slight lengthening of the C–Br bond probably is one result of the considerable steric hindrance between the two bromine atoms. The distance between the two bromine atoms (Table III) is 3.269 Å (σ 0.0028), compared with a nonbonded van der Waals contact of ~4 Å. The bond angles around C-11a and C-5a reflect this hindrance also. For example, the angle C-5a–C-11a Br, at 115° (σ 0.6°), is much larger than the tetrahedral value, whereas the angle C-11–C-11a Br is only 104° (σ 0.7°). The mutual repulsion of the bromine atoms leads to an increase in the C-5a–C-11a Br angle relative to the strict tetrahedral angle. This in turn causes a decrease in the C-11–C-11a Br and C-12–C-11a Br angles.

The major effects of intramolecular overcrowding are apparent not so much in the bond lengths and angles, but in the selected intramolecular distances listed in Table III. The closest approach of two nonbonded carbon atoms in the molecule is the 2.461 Å (σ 0.015 Å) found between C-10a and C-11a and between C-4a and C-5a. A nonbonded distance of 2.651 Å (σ 0.015 Å) separates C-11 and C-12, and C-6 and C-5, which are substituents on the apposed face rings of the mole. The rings themselves are bent outwards, away from each other, as indicated by the increase in distance between corresponding atom from 2.987 Å (σ 0.015 Å) for C-11b and C-12b to 4.094 Å (σ 0.023 Å) for C-19 and C-14.

It should be observed that the aromatic systems retain their planarity, despite the severe intramolecular overcrowding. The least-squares plane through atoms C-11b, C-6b, C-17, C-18, C-19, and C-20 has the equation $-0.06558X - 0.23031Y + 0.97090Z + 4.72903 = 0.0$, where X, Y, and Z are coordinates in ångstroms relative to an orthogonal system of axes. These coordinates are related to the fractional atomic coordinates (xyz), relative to the crystallographic axes, given in Table V, by the transformation

$$X = x \cdot a \sin \beta$$

$$Y = y \cdot b$$

$$Z = z \cdot c + x \cdot a \cos \beta$$

where a, b, c, and β are the unit cell dimensions of the crystal. The deviations of the ring atoms, and of some other selected atoms, are listed in Table IV. The six atoms in the ring are coplanar. The substituents, C-11 and C-6, are significantly out of the plane, in the same direction.

The two face rings have a dihedral angle of 26.6° (σ ~1°).

The side rings are also planar with the substituents C-6 and C-11 lying in the plane. This plane has the

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(2) "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 18, The Chemical Society, London, 1965.

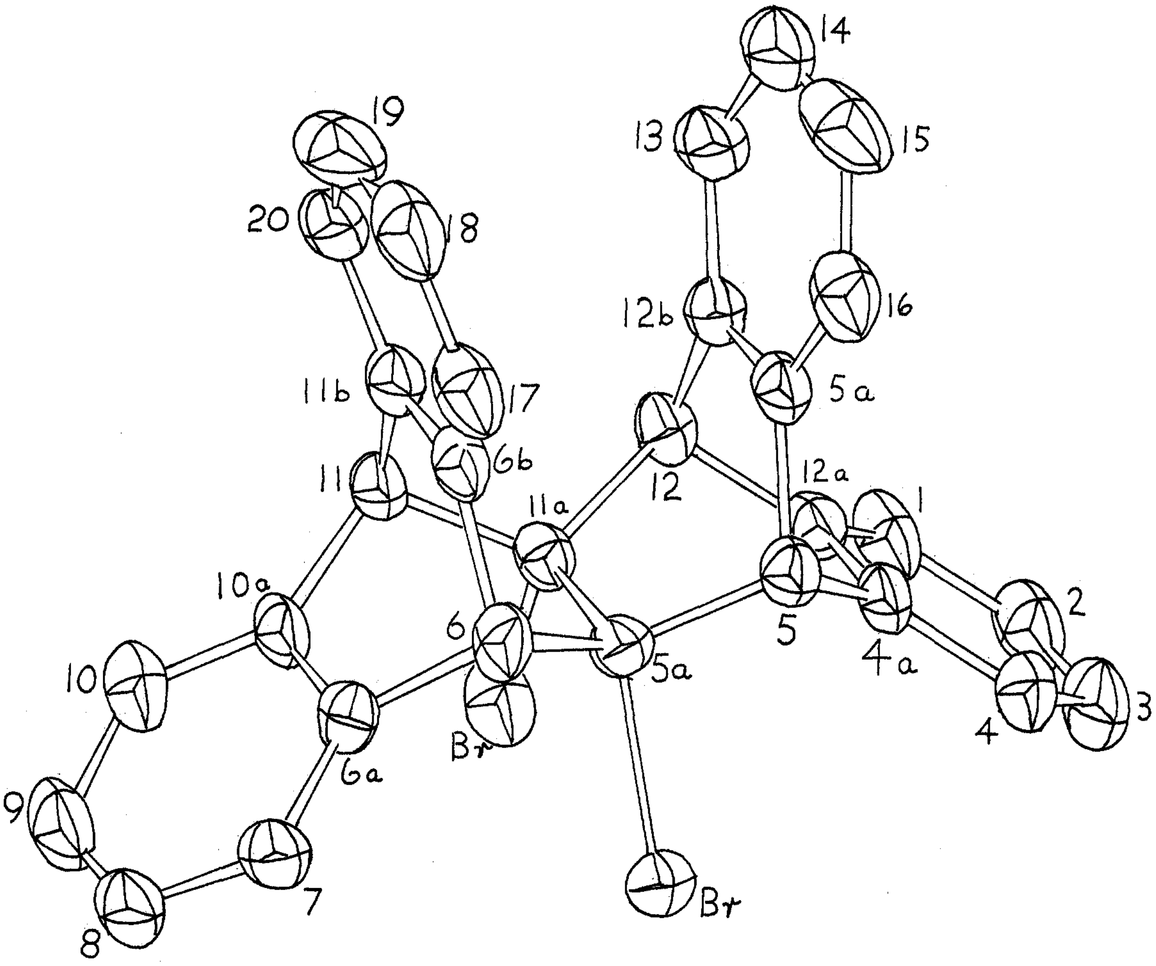

Figure 2.—An ORTEP plot showing the anisotropic thermal ellipsoids in dibromojanusene.

TABLE IV

LEAST-SQUARES PLANE THROUGH THE FACE RING OF DIBROMOJANUSENE

Atom	Distance from plane, Å	Atom	Distance from plane, Å
C11b	−0.004147	C6b	0.010930
C20	−0.006369	C17	−0.007174
C19	0.010096	C18	−0.003339
C11	0.162718	C6	0.157287
C11a	−0.964632	C5a	−0.996286

equation $-0.66354X + 0.81534Y + 0.57517Z - 1.94107 = 0.0$, where X, Y, and Z are the coordinates in Å relative to the orthogonal system of axes defined above.

Intermolecular distances in DBJ are not remarkable. The smallest distance between two atoms on neighboring molecules is 3.60 Å between C-2 on one molecule and C-10 on another molecule, related to the first by the *c* glide. The shortest intermolecular distance involving bromine is 3.74 Å (σ 0.002 Å), which is the distance between the bromine atoms and C-19 and C-14 on the molecule down the *b* axis in the next cell.

The molecule in Figure 1 has three elements of symmetry. There is a twofold axis normal to the C-5a–C-11a bond, bisecting it. Furthermore, the axis lies in the plane defined by C-5a, C-11a, and the hydrogen atoms on these two carbon atoms. This plane is a plane of symmetry in the molecule. Another plane of symmetry includes the twofold axis and is normal to the C-5a–C-11a bond. DBJ should possess the same symmetry, provided that the strain resulting from the eclipsed bromine atoms is not too great.

The crystal does not make use of all the molecular symmetry. The molecular twofold axis coincides with a crystallographic twofold axis. However, there is no crystallographic mirror plane corresponding to either of the molecular planes of symmetry. It is important, therefore, to establish from the bond lengths and angles whether the molecule has the expected symmetry.[3] The data in Tables I and II are arranged such that those bond lengths and bond angles are opposite each other which should be equal if the molecule has a plane of symmetry defined by the twofold axis and the C-5a–C-11a bond. Inspection of the tables indicates at once that the corresponding bond lengths and angles are equal within experimental error. It would appear, then, that the dibromojanusene molecule possesses that plane of symmetry. The other symmetry plane normal to the C-5a–C-11a bond, is generated automatically by the combination of the twofold axis and the first plane of symmetry.

Curiously, other observations can be made which are at variance with this highly symmetrical picture. In Table V the atomic coordinates are arranged so that the coordinates of atoms, related by the symmetry plane including the C-5a–C-11a bond, are grouped together. Such pairs of atoms should have the same *y* coordinates. The *y* coordinates are different, how-

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[3] Crystallographic theory does not require that the symmetry of a crystal reflect the full symmetry of the constituent molecules.

TABLE V

ATOMIC COORDINATES FOR DIBROMOJANUSENE[a]

Atom	x	y	z
C9	3070 (74)	29490 (80)	3374 (45)
C2	7998 (67)	29193 (75)	50651 (41)
C10	9362 (58)	37176 (76)	10733 (39)
C1	13254 (61)	36579 (72)	47522 (37)
C10a	4138 (52)	44793 (60)	13850 (34)
C12a	6975 (50)	44264 (61)	40200 (33)
C11	9516 (48)	53607 (59)	21716 (33)
C12	11294 (50)	53137 (65)	36005 (33)
C11b	4395 (50)	68687 (61)	18998 (34)
C12b	6846 (51)	68291 (62)	35256 (34)
C20	9763 (63)	81397 (72)	19608 (40)
C13	12901 (65)	80751 (73)	38821 (41)
C19	3749 (91)	94038 (73)	15849 (48)
C14	7446 (84)	93842 (83)	38252 (48)
C11a	6275 (44)	46308 (57)	27270 (32)
Br11a	13044 (5)	26627 (7)	29692 (4)

[a] The standard deviations in the coordinates are given in parentheses. All values are expressed as fractions of the corresponding cell edge × 10^5.

ever, the differences ranging from three standard deviations in the case of C-2 and C-9 and of C-14 and C-19 to nine standard deviations in the case of C-10a and C-12a. Such differences are significant and indicate that the molecule does depart somewhat from the perfect $2mm$ symmetry indicated by the bond lengths and angles. However, the maximum difference in y coordinates of nine standard deviations corresponds to a difference of only 0.1 Å in the y coordinates of atoms C-10a and C-12a. This is a relatively small effect, probably arising from the effects of the mutual repulsion of the bromine atoms being transmitted through the length of the molecule.

Thus dibromojanusene must be regarded as having very slightly distorted $2mm$ symmetry.

The question arises as to why this distortion does not appear in the bond length and bond angle data. The most probable answer is that at any one atomic center the effect is too small to be significant. However, the effects at each atomic center should be additive and should begin to be noticeable in quantities, such as atomic coordinates, which represent vector sums, but not in quantities such as bond lengths, which represent differences in vectors and where the effects will tend to subtract out.

Experimental Section

Crystal Data.—Crystals of DBJ were supplied by D. C. Lewis. They were recrystallized from an alcohol–acetone mixture. The crystals were colorless and prismatic in habit.

The unit cell is monoclinic. The cell dimensions, determined from Weissenberg and precession photographs, are $a = 14.900$ Å (σ 0.012 Å), $b = 9.157$ Å (σ 0.011 Å), $c = 19.500$ Å (σ 0.051 Å), and $\beta = 123.2°$ (σ 0.4°), where σ means standard deviation. The cell volume is 2227 Å^3.

The density of the crystals was determined by flotation in potassium iodide solution and found to be 1.626 g/cm^3. This density, together with the above cell volume, implies that the cell contains four DBJ molecules. The density calculated assuming four molecules per cell is 1.615 g/cm^3, in satisfactory agreement with the observed value.

The X-ray photographs showed the following systematic extinctions: hkl absent with $l + k$ odd; $h0l$ absent with h odd or with l odd; $0k0$ absent with k odd. In the monoclinic system these extinctions are consistent with two space groups, Cc and $C2/c$. The space group $C2/c$ has a center of symmetry while Cc does not. The crystal was shown to contain a center of symmetry by the Foster–Hargreaves test[4] and so the space group $C2/c$ was chosen. This assignment of space group was confirmed during the structure refinement. The space group $C2/c$ has eight equivalent positions. The asymmetric unit contained therefore one-half molecule, or 15 carbon atoms, 1 bromine atom, and the associated hydrogen atoms.

Intensities were collected on our automatic single crystal diffractometer CASCADE,[5] operated in the manual mode. Cu Kα radiation was used. There were 2380 independent reflexions accessible to the copper radiation. Of these 1770 had intensities higher than twice background and were regarded as being observed. The data were corrected for Lorentz and polarization effects. An absorption correction, based on a program by Moseley,[6] was also applied and resulted in increases of intensity of up to 30%. The crystal used in the intensity collection had dimensions 0.35 × 0.17 × 0.14 mm.

Structure Analysis.—The position of the bromine atom in the cell was determined from Harker sections to be (0.129, 0.250, 0.295). With a y coordinate of 0.25, bromine atom contributes nothing to the intensity of any plane with $(k - l)$ odd. Thus the first Fourier synthesis, using the phases of the bromine atoms only, was calculated using as coefficients only those structure factors with $(k - l)$ even. The electron density distribution, so calculated, showed spurious lattice-centering, giving twice the number of peaks which would have been obtained otherwise. It was rather difficult to select from the electron density distribution that set of peaks corresponding to the carbon atoms. However, once the carbon atoms had been correctly identified, Fourier refinement proceeded smoothly. During the refinement, the bromine atom moved slightly away from $y = 0.25$ and began therefore to contribute to the phases of the planes with $k - l$ even. This contributed to the convergence of the Fourier refinement.

The Fourier refinement was followed by several cycles of least squares refinement, using, for the first three cycles, individual isotropic temperature factors, and thereafter individual anisotropic temperature factors. The function minimized was $\Sigma\omega(|F_o| - k|F_c|)^2$. The final value of the R factor over the 1770 observed planes was 0.05. The atomic coordinates, anisotropic thermal parameters, and their corresponding estimated standard deviations, from the final cycle of refinement, are given in Tables V and VI.[7] The estimated radial standard deviation in the position of each of the atoms in the asymmetric unit are listed in Table VII.[7]

The least squares refinement was carried out on the CDC 6400 computer at the University of Colorado Computing Center, using the ORFLS program of Busing, Martin, and Levy.[8] The other calculations were carried out on our IBM 1620 computer in our laboratory.

Registry No.—**1,** 23646-39-1.

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[4] F. Foster and A. Hargreaves, *Acta Crystallogr.*, **16**, 1124 (1963).

[5] J. P. Cowan, W. M. Macintyre and G. J. Werkema, *ibid.*, **16**, 221 (1963).

[6] J. D. Moseley, M.S. Thesis, University of Colorado, 1964.

[7] Tables VI and VII will appear following these pages in the microfilm edition of this journal. In addition there will be included in the microfilm edition a diagram showing the contents of the unit cell of the crystal projected down the b axis, a diagram illustrating the distortion of the molecule from 2-mm symmetry, and a table of observed and calculated structure factors. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JOC-72-130. Remit check or money order for $5.00 for photocopy or $2.00 for microfiche.

[8] W. R. Busing, K. O. Martin, and H. A. Levy, ORNL-TM-305, Oak Ridge National Laboratory, Tenn., 1962.