# Crystal Structure and Absolute Configuration of an Anilide Hydrobromide: (+)-N-[(2-Benzylmethylamino)propyl]propionanilide Hydrobromide

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The crystal structure of (+)-N-[(2-benzylmethylamino)propyl]propionanilide hydrobromide, C<sub>20</sub>H<sub>27</sub>N<sub>2</sub>OBr, has been determined by the heavy atom method and refined by block-diagonal least-squares to an R index of 0.049 for the 1569 observed reflexions. The unit cell is monoclinic, space group P2<sub>1</sub>, with a=9.487, b=12.071, c=9.247 Å,  $\beta=107^{\circ}32'$ , Z=2. The six atoms of the amide group,

-N-C-C, are slightly nonplanar with a maximum deviation of 0.07 Å occurring at N, but the four

atoms identified with letters are planar. The mean plane of the six atoms makes an angle of  $71.3^{\circ}$  with the adjoining phenyl ring, and only  $6.0^{\circ}$  with the second phenyl ring. The amido-nitrogen is separated from the protonated nitrogen, N<sup>+</sup>, by only 2.972 Å which is approximately the sum of their van der Waals radii. The *s*-methyl is well removed from the phenyl rings and is not shielded by either of them. There is strong evidence in support of a hydrogen bond between N<sup>+</sup> and Br<sup>-</sup>, which are 3.23 Å apart. The absolute configuration of the molecule in this hydrobromide derivative is found to be *R* in terms of the sequence rule nomenclature, thus confirming the absolute configuration determined chemically for the free base.

# Introduction

The compound (+)-N-[(2-benzylmethylamino)propyl] propionanilide is an optically active salt of the base I(a)which belongs to a group of potent analgesics discovered recently by Wright, Brabander & Hardy (1959), and known as basic anilides. The most active member of this group is diampromid, I(b). Basic anilides I(a and b) have structural features similar to methadone, I(c),

at the asymmetric carbon, C\*, since these three compounds have the groupings  $>N-C*H(CH_3)-R$ . According to Beckett & Casy (1965), the more active enantiomorphs of several analgesics [including (-)-methadone] containing this structural feature relate to R-(-)alanine, but it was found from chemical procedures by Portoghese & Larson (1964) that the more active forms of the anilides related to S-(+)-alanine, where the R and S designations refer to the absolute configuration according to the convention of Cahn, Ingold & Prelog (1956). Also, it was reported by Casy & Hassan (1967*a*) that methadone and the anilides differed in their stereospecificities, and it appeared likely, therefore, that 3-amino-1,1-diphenylpropyl and basic anilide analgesics differed in their modes of binding to the analgesic receptor site. A detailed structure analysis of these compounds has been considered, therefore, to be of significance in the understanding of these binding differences.

An X-ray study of the crystal structure and absolute configuration of d-methadone hydrobromide was carried out in this laboratory by Hanson & Ahmed (1958). A probable conformation of N-[(2-benzylmethylamino)propyl]propionanilide hydrochloride in solution, based on spectroscopic data, was proposed by Casy & Hassan (1967b). The present X-ray crystal structure analysis of the corresponding hydrobromide derivative has been carried out in order to determine independently the molecular structure and its absolute configuration, and to provide the relevant quantitative data similar to that of methadone. A schematic drawing of the molecule giving the numbering of the atoms (Br and H excluded) is shown in II.

### Crystal data

Crystals of (+)-*N*-[(2-benzylmethylamino)propyl]propionanilide hydrobromide are colourless, transparent, thin prisms with one of the long directions parallel to the monoclinic unique axis *b*. The chemical formula is  $C_{20}H_{27}N_2OBr$  with F.W.=391.4. The unit cell is monoclinic with dimensions a=9.487, b=12.071, c=

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9.247 Å ( $\sigma$ =0.003 Å for each),  $\beta$ =107°32′ ( $\sigma$ =3′), U=1009.8 Å<sup>3</sup>. The density,  $D_m$  (flotation in carbon tetrachloride, n-hexane mixture)=1.290 g.cm<sup>-3</sup> at 22°C, and  $D_x$ =1.287 g.cm<sup>-3</sup> for Z=2. Since the compound is optically active and the systematic absences are for 0k0 when k is odd, the space group is uniquely determined as P2<sub>1</sub>. Linear absorption coefficients are  $\mu$ (Cu K $\alpha$ )=31.1 cm<sup>-1</sup> and  $\mu$ (Mo K $\alpha$ )=21.7 cm<sup>-1</sup>. F(000)=408.

# **Data collection**

The crystal selected for data collection was of irregular shape with approximate dimensions  $0.30 \times 0.23 \times$ 0.05 mm. Preliminary examination of the crystal, the unit-cell constants, and the space group was carried out with precession photographs. The cell dimensions and the intensity data were measured on a General Electric XRD 5 diffractometer equipped with a scintillation counter, with Cu radiation ( $\lambda(K\alpha_1)=1.54051$  Å,  $\lambda(K\alpha_2)=1.54433$  Å) and Ni filters. The crystal was mounted with its crystallographic b axis along the  $\varphi$  axis of the instrument. The cell dimensions were measured with narrow slits (0.02°-0.05°) at small take-off angles (1.0°-1.5°) utilizing only the medium and high order axial reflexions. The integrated intensities were measured at a take-off angle of 2.5°, by the  $\theta$ -2 $\theta$  scan as described by Furnas (1957), for all the *hkl* and *hkl* reflexions within the range of the instrument ( $2\theta_{max} = 165^{\circ}$ ,  $\sin\theta/\lambda = 0.64$ ), and the background was measured separately for each reflexion at the beginning and end of each scan. The scan was over 2° in 2 $\theta$  for the low-angle reflexions.

Appropriate attenuation of the primary beam for the very strong reflexions was achieved by reducing the X-ray tube current. The intensity of the 004 reflexion was measured every 40 to 60 minutes for scaling purposes. Of the 2319 reflexions scanned, only 1569 had a significant count above background.

The net intensity counts were reduced to the same relative scale, modified by the appropriate  $(Lp)^{-1}$  corrections, and at a later stage corrected for absorption. The absorption corrections,  $\exp(\mu R)$ , were calculated on an IBM 360 computer with a program written by the authors in FORTRANIV to perform the Gaussian quadrature approximation described by Busing & Levy (1957). The three-dimensional grid used in this approximation was made up of  $6 \times 6 \times 6$  points. The minimum and maximum absorption corrections to the intensities were 1.15 and 2.22 for the 101 and  $1,15,\overline{1}$  reflexions, respectively. The data were not corrected for extinction but the effect of these errors on the atomic parameters was minimized by the weighting function employed in the least-squares refinement.

For the purpose of establishing the absolute configuration from violations of Friedel's law, resulting from

Table 1. Fractional coordinates, vibration tensor componets (Å<sup>2</sup>) for the expression  $T = exp - 2\pi^2(U_{11}a^{*2}h^2 + ... + 2U_{23}b^*c^*kl + ...)$ , and their e.s.d.'s (all quantities × 10<sup>4</sup>)

					<b>T</b> 7	211	211	<b>0</b> <i>T</i> I
x	У	z	$U_{11}$	$U_{22}$	$U_{33}$	2023	$20_{13}$	$2U_{12}$
1770 (1)	0 (2)	1351 (1)	1051 (6)	554 (4)	938 (6)	523 (12)	-114 (9)	-164 (14)
5427 (8)	1955 (6)	1418 (7)	1585 (63)	1303 (61)	652 (37)	140 (79)	1072 (81)	615 (105)
4681 (7)	2282 (5)	3461 (6)	704 (42)	623 (36)	475 (33)	-115 (59)	495 (59)	27 (69)
1617 (7)	2670 (5)	1472 (6)	692 (41)	622 (38)	346 (28)	95 (59)	195 (53)	147 (68)
4704 (8)	2042 (6)	4983 (7)	592 (48)	658 (47)	387 (34)	- 247 (71)	391 (64)	16 (77)
3804 (8)	1231 (7)	5268 (8)	680 (50)	724 (51)	592 (43)	-103 (88)	382 (75)	- 56 (94)
3827 (10)	1016 (8)	6754 (9)	1066 (73)	899 (66)	676 (53)	273 (99)	748 (100)	291 (113)
4722 (11)	1610 (9)	7930 (9)	1316 (80)	974 (72)	517 (46)	85 (95)	436 (101)	570 (133)
5598 (11)	2423 (8)	7637 (9)	1075 (73)	990 (69)	644 (53)	- 695 (101)	-101(100)	673 (122)
5631 (9)	2646 (7)	6170 (9)	652 (51)	820 (61)	642 (49)	-431 (88)	226 (81)	10 (89)
5352 (9)	1648 (8)	2657 (8)	923 (61)	1005 (67)	411 (39)	-282(85)	427 (80)	-104 (108)
6048 (10)	552 (7)	3336 (9)	957 (67)	855 (61)	701 (53)	-122(93)	422 (97)	248 (106)
6747 (10)	-99 (12)	2283 (10)	1224 (75)	1106 (73)	1108 (67)	- 390 (176)	1347 (119)	121 (184)
4121 (9)	3385 (7)	2878 (9)	850 (60)	603 (49)	647 (49)	106 (82)	305 (88)	-281(91)
2482 (9)	3549 (7)	2532 (8)	687 (52)	695 (51)	502 (42)	129 (77)	281 (76)	-159 (86)
2030 (10)	4747 (6)	1990 (9)	1260 (76)	443 (58)	832 (57)	103 (74)	428 (106)	-24 (89)
1742 (12)	2791 (8)	-118(10)	1225 (80)	896 (68)	634 (54)	- 52 (101)	616 (106)	258 (123)
1 $(11)$	2650 (7)	1339 (9)	1088 (72)	603 (52)	658 (51)	152 (84)	- 139 (96)	271 (99)
- 289 (9)	2669 (7)	2875 (10)	677 (56)	604 (51)	905 (60)	80 (91)	167 (92)	93 (86)
-880(13)	3589 (8)	3358 (12)	1498 (99)	683 (62)	1124 (78)	28 (113)	1272 (146)	374 (133)
-1112(14)	3605 (9)	4722 (14)	1421 (101)	867 (80)	1582 (106)	-108(152)	1178 (174)	382 (151)
-767 (11)	2725 (11)	5705 (12)	726 (64)	1743 (127)	1090 (78)	-90 (162)	730 (117)	372 (148)
-210(11)	1794 (10)	5252 (13)	939 (72)	1322 (94)	1226 (82)	1103 (143)	994 (125)	703 (137)
10 (10)	1762 (8)	3842 (11)	872 (65)	721 (56)	1060 (70)	479 (103)	740 (110)	422 (101)
	x 1770 (1) 5427 (8) 4681 (7) 1617 (7) 4704 (8) 3804 (8) 3827 (10) 4722 (11) 5598 (11) 5631 (9) 5352 (9) 6048 (10) 6747 (10) 4121 (9) 2482 (9) 2030 (10) 1742 (12) 1 (11) - 289 (9) - 880 (13) - 1112 (14) - 767 (11) - 210 (11) 10 (10)	x $y$ 1770 (1)0 (2)5427 (8)1955 (6)4681 (7)2282 (5)1617 (7)2670 (5)4704 (8)2042 (6)3804 (8)1231 (7)3827 (10)1016 (8)4722 (11)1610 (9)5598 (11)2423 (8)5631 (9)2646 (7)5352 (9)1648 (8)6048 (10)552 (7)6747 (10) $-99$ (12)4121 (9)3385 (7)2482 (9)3549 (7)2030 (10)4747 (6)1742 (12)2791 (8)1 (11)2650 (7) $-289$ (9)2669 (7) $-880$ (13)3589 (8) $-1112$ (14)3605 (9) $-767$ (11)2725 (11) $-210$ (11)1794 (10)10 (10)1762 (8)	x $y$ $z$ 1770 (1)0 (2)1351 (1)5427 (8)1955 (6)1418 (7)4681 (7)2282 (5)3461 (6)1617 (7)2670 (5)1472 (6)4704 (8)2042 (6)4983 (7)3804 (8)1231 (7)5268 (8)3827 (10)1016 (8)6754 (9)4722 (11)1610 (9)7930 (9)5598 (11)2423 (8)7637 (9)5631 (9)2646 (7)6170 (9)5352 (9)1648 (8)2657 (8)6048 (10)552 (7)3336 (9)6747 (10) $-99$ (12)2283 (10)4121 (9)3385 (7)2878 (9)2482 (9)3549 (7)2532 (8)2030 (10)4747 (6)1990 (9)1742 (12)2791 (8) $-118$ (10)1 (11)2650 (7)2875 (10) $-880$ (13)3589 (8)3358 (12) $-1112$ (14)3605 (9)4722 (14) $-767$ (11)2725 (11)5705 (12) $-210$ (11)1762 (8)3842 (11)	xyz $U_{11}$ 1770 (1)0 (2)1351 (1)1051 (6)5427 (8)1955 (6)1418 (7)1585 (63)4681 (7)2282 (5)3461 (6)704 (42)1617 (7)2670 (5)1472 (6)692 (41)4704 (8)2042 (6)4983 (7)592 (48)3804 (8)1231 (7)5268 (8)680 (50)3827 (10)1016 (8)6754 (9)1066 (73)4722 (11)1610 (9)7930 (9)1316 (80)5598 (11)2423 (8)7637 (9)1075 (73)5631 (9)2646 (7)6170 (9)652 (51)5352 (9)1648 (8)2657 (8)923 (61)6747 (10)-99 (12)2283 (10)1224 (75)4121 (9)3385 (7)2878 (9)850 (60)2482 (9)3549 (7)2532 (8)687 (52)2030 (10)4747 (6)1990 (9)1260 (76)1742 (12)2791 (8)-118 (10)1225 (80)1 (11)2650 (7)1339 (9)1088 (72)-289 (9)2669 (7)2875 (10)677 (56)-880 (13)3589 (8)3358 (12)1498 (99)-1112 (14)3605 (9)4722 (14)1421 (101)-767 (11)2725 (11)5705 (12)726 (64)-210 (11)1794 (10)5252 (13)939 (72)10 (10)1762 (8)3842 (11)872 (65)	xyz $U_{11}$ $U_{22}$ 1770 (1)0 (2)1351 (1)1051 (6)554 (4)5427 (8)1955 (6)1418 (7)1585 (63)1303 (61)4681 (7)2282 (5)3461 (6)704 (42)623 (36)1617 (7)2670 (5)1472 (6)692 (41)622 (38)4704 (8)2042 (6)4983 (7)592 (48)658 (47)3804 (8)1231 (7)5268 (8)680 (50)724 (51)3827 (10)1016 (8)6754 (9)1066 (73)899 (66)4722 (11)1610 (9)7930 (9)1316 (80)974 (72)5598 (11)2423 (8)7637 (9)1075 (73)990 (69)5631 (9)2646 (7)6170 (9)652 (51)820 (61)5352 (9)1648 (8)2657 (8)923 (61)1005 (67)6048 (10)552 (7)3336 (9)957 (67)855 (61)6747 (10)-99 (12)2283 (10)1224 (75)1106 (73)4121 (9)3385 (7)2878 (9)850 (60)603 (49)2482 (9)3549 (7)2532 (8)687 (52)695 (51)2030 (10)4747 (6)1990 (9)1260 (76)443 (58)1742 (12)2791 (8)-118 (10)1225 (80)896 (68)1 (11)2650 (7)2875 (10)677 (56)604 (51)-880 (13)3589 (8)3358 (12)1498 (99)683 (62)-1112 (14)3605 (9)4722 (14)1421 (101)867 (80)-210 (11)1794 (10)5252 (13)9	xyz $U_{11}$ $U_{22}$ $U_{33}$ 1770 (1)0 (2)1351 (1)1051 (6)554 (4)938 (6)5427 (8)1955 (6)1418 (7)1585 (63)1303 (61)652 (37)4681 (7)2282 (5)3461 (6)704 (42)623 (36)475 (33)1617 (7)2670 (5)1472 (6)692 (41)622 (38)346 (28)4704 (8)2042 (6)4983 (7)592 (48)658 (47)387 (34)3804 (8)1231 (7)5268 (8)680 (50)724 (51)592 (43)3827 (10)1016 (8)6754 (9)1066 (73)899 (66)676 (53)4722 (11)1610 (9)7930 (9)1316 (80)974 (72)517 (46)5598 (11)2423 (8)7637 (9)1075 (73)990 (69)644 (53)5631 (9)2646 (7)6170 (9)652 (51)820 (61)642 (49)5352 (9)1648 (8)2657 (8)923 (61)1005 (67)411 (39)6048 (10)552 (7)3336 (9)957 (67)855 (61)701 (53)6747 (10)-99 (12)2283 (10)1224 (75)1106 (73)1108 (67)4121 (9)3385 (7)2878 (9)850 (60)603 (49)647 (49)2482 (9)3549 (7)2532 (8)687 (52)695 (51)502 (42)2030 (10)4747 (6)1990 (9)1260 (76)443 (58)832 (57)1742 (12)2791 (8)-118 (10)1225 (80)896 (68)634 (54)1 (11)2650 (7)2875 (	xyz $U_{11}$ $U_{22}$ $U_{33}$ $2U_{23}$ 1770 (1)0 (2)1351 (1)1051 (6)554 (4)938 (6)523 (12)5427 (8)1955 (6)1418 (7)1585 (63)1303 (61)652 (37)140 (79)4681 (7)2282 (5)3461 (6)704 (42)623 (36)475 (33)-115 (59)1617 (7)2670 (5)1472 (6)692 (41)622 (38)346 (28)95 (59)4704 (8)2042 (6)4983 (7)592 (48)658 (47)387 (34)-247 (71)3804 (8)1231 (7)5268 (8)680 (50)724 (51)592 (43)-103 (88)3827 (10)1016 (8)6754 (9)1066 (73)899 (66)676 (53)273 (99)4722 (11)1610 (9)7930 (9)1316 (80)974 (72)517 (46)85 (95)5598 (11)2423 (8)7637 (9)1075 (73)990 (69)644 (53)-695 (101)5631 (9)2646 (7)6170 (9)652 (51)820 (61)642 (49)-431 (88)5352 (9)1648 (8)2657 (8)923 (61)1005 (67)411 (39)-282 (85)6048 (10)552 (7)3336 (9)957 (67)855 (61)701 (53)-122 (93)6747 (10)-99 (12)2283 (10)1224 (75)1106 (73)1108 (67)-390 (176)4121 (9)3385 (7)2878 (9)850 (60)603 (49)647 (49)106 (82)2482 (9)3549 (7)2532 (8)687 (52)695 (51)502 (42)129 (77) </td <td><math display="block"> \begin{array}{c ccccccccccccccccccccccccccccccccccc</math></td>	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$

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the anomalous scattering by the Br atom, 19 pairs  $(hkl \text{ and } h\bar{k}l)$  of weak low-angle reflexions were measured. In space group  $P2_1$ , these violations result in the relationships:  $|F(hkl)| = |F(\bar{h}k\bar{l})|$ ;  $|F(h\bar{k}l)| = |F(\bar{h}k\bar{l})|$ ;  $|F(hkl)| = |F(\bar{h}k\bar{l})|$ ;  $|F(hkl)| = |F(\bar{h}k\bar{l})|$ ;  $|F(hkl)| = |F(\bar{h}k\bar{l})|$ ;  $|F(hkl)| = |F(\bar{h}k\bar{l})|$ . The average discrepancy in the measured intensities of the equivalent reflexions  $(hkl \text{ and } hk\bar{l}, \text{ or } h\bar{k}\bar{l} \text{ and } h\bar{k}l)$  was only 2.5%, while the average discrepancy in the intensities of the hkl and  $h\bar{k}l$  resulting from the effect of the anomalous scattering was about 19%.

# Structure determination and refinement

The structure was determined from Patterson and Fourier syntheses by the heavy atom method, and was refined by successive cycles of block-diagonal leastsquares. The x and z coordinates of the bromine atom



Fig. 1. Perspective view of the molecules showing the unit-cell axes and the nearest bromide atom.

were deduced from the Patterson synthesis, and its ycoordinate was set arbitrarily to zero since for space group  $P2_1$  the origin may be chosen anywhere on the b axis. In the first Fourier synthesis which was calculated with the structure amplitudes phased by the contributions of the bromine atoms alone, there were, as expected, false mirror planes of symmetry at v=0 and  $\frac{1}{2}$ . and hence twice the true number of peaks in the asymmetric unit. It was possible, however, from consideration of reasonable bond lengths and angles to separate the peaks belonging to the same molecule from those related to them by the false mirror symmetry. The deduced structure (excluding the hydrogen atoms, and assuming  $B \simeq 4 \text{ Å}^2$ ) corresponded to an R index of 0.34 which was reduced to 0.21 after the first isotropic least-squares cycle. A Fourier synthesis, which was calculated at this stage with the new phases, confirmed the assumed model and showed no spurious peaks or false symmetries. After two isotropic and one anisotropic least-squares cycles of refinement, the R index was reduced to 0.12.

The refinement became relatively slow after this stage until the data were corrected for absorption, the absolute configuration determined, and the anomalous scattering of the bromine atom included in the structure factor calculation. About 125 generally weak reflexions with high discrepancies were remeasured and corrected, but the 001 reflexion ( $|F_o| = 9.8$ ,  $|F_c| = 20.9$ ) could not be improved on remeasurement and was thereafter excluded from the refinement.

At different stages of the refinement, three unsuccessful attempts were made to locate the hydrogen atoms from difference maps. The first map was evaluated before correcting the data for absorption or inclusion of the anomalous scattering, the second after correcting for absorption and the third after inclusion of the anomalous scattering. Only a few of the hydrogenn atoms could have been accepted from the maps, but it was considered more reliable to calculate the positions of 17 non-methyl hydrogen atoms, include them

Table 2. Fractional coordinates ( $\times 10^3$ ) and isotropic temperature factors (Å<sup>2</sup>) of the hydrogen atoms included in the calculations, and their e.s.d.'s

	x	У	Z	В	Bonded to
H(1)	313 (6)	89 (5)	444 (6)	2.4 (1.5)	C(2)
H(2)	316 (8)	45 (6)	712 (8)	5.5 (2.2)	C(3)
H(3)	469 (7)	161 (7)	899 (8)	4.5 (1.9)	C(4)
H(4)	626 (10)	287 (8)	852 (10)	7.0 (3.0)	C(5)
H(5)	636 (7)	345 (6)	595 (7)	3.8 (1.7)	C(6)
H(6)	524 (6)	2 (8)	361 (6)	2.9 (1.3)	C(8)
H(7)	693 (8)	65 (6)	442 (8)	4.2 (1.8)	C(8)
H(8)	431 (8)	359 (6)	179 (7)	4.0 (1.8)	C(10)
H(9)	451 (7)	402 (6)	372 (7)	2.9 (1.6)	C(10)
H(10)	227 (8)	340 (6)	355 (7)	3.8 (1.7)	C(11)
H(11)	-72 (6)	174 (5)	79 (7)	2.5 (1.5)	C(14)
H(12)	-83(8)	301 (6)	65 (8)	4.2 (1.8)	C(14)
H(13)	-130(8)	417 (7)	265 (8)	4.6 (1.9)	C(16)
H(14)	-162(8)	414 (7)	493 (8)	5.0 (2.0)	C(17)
H(15)	- 90 (8)	261 (6)	673 (8)	4.9 (2.0)	C(18)
H(16)	5 (10)	112 (8)	596 (10)	7.0 (3.0)	C(19)
H(17)	45 (8)	109 (7)	333 (8)	5.0(2.0)	C(20)

Table 3. Observed and calculated structure amplitudes ( $\times$ 10) and calculated phase angles (°)

K FO FG ALPHA	K FO FC ALPHA	K FO PC ALPHA	K FO FC ALPHA	K FO FC ALPHA	K FO FC ALPHA	K FO FC ALPHA	K FO FC ALPHA
H= 0, L= 0 2 437 455 150 4 755 682 359 6 422 421 7 8 367 381 358	6 36° 24 143 7 41 34 302 8 29° 23 185 9 23° 5 307	0 370 365 2 1 317 317 238 2 250 256 319 3 356 358 281 4 233 240 38 5 157 157 288	8 37* 11 167 9 43 42 65 10 28* 21 239 11 21* 22 123 H= 9, L= 1	11 49 55 108 12 71 73 7 13 62 59 125 14 71 68 340 15 21• 30 153	10 44 30 18 11 22* 16 6 H= 7, L= -2 0 36* 24 1	i 11 136 139 266 i 12 51 46 93 13 63 60 279 14 31• 33 69 7 H= 2, L= 3	11 31 26 77 H= 6, L= -3 0 179 187 181 1 114 117 325
10 135 147 320 12 146 147 25 14 84 80 336 H= 1, L= 0	0 35* 5 177 1 57 47 309 2 34* 21 24 3 33* 20 217 4 32* 7 142	6 77 76 326 7 204 205 277 8 182 191 349 9 79 86 273 10 39* 20 4 11 67 69 263	0 38* 2 191 1 54 50 300 2 38* 14 75 3 52 46 248 4 36* 17 148	H= 3, L= 2 0 244 228 2 1 317 317 263 2 110 117 114 3 355 355 272	1 45 51 200 2 152 143 344 3 38* 12 164 4 93 93 5 5 40* 28 11 6 102 90 355	0 24* 15 5 1 319 326 272 2 196 213 338 3 378 383 263 4 39 47 6	2 81 89 187 3 130 126 271 4 51 57 164 5 82 84 302 6 76 81 161 7 49 47 298
0 36 58 167 1 426 451 111 2 554 542 295 3 353 377 106 4 314 306 35 5 175 182 95	5 200 25 302 6 200 9 16 7 25 24 242 H= 11, L= 0	12 49 47 9 13 46 47 273 14 24 24 335 H= 4, L= -1	5 54 44 309 6 34• 20 259 7 30• 20 250 8 25• 9 98 9 24 23 284	4 230 231 307 5 210 221 269 6 129 126 351 7 245 251 285 8 45 49 343 9 99 100 264	7 49 57 21 8 58 57 2: 9 38* 3 14 10 54 47 33: 11 29* 14 16 12 33 31 1	0         5         223         228         289           2         6         63         76         284           1         7         229         231         267           5         8         67         74         321           5         9         149         166         272           9         10         48         47         262	8 49 58 164 9 72 74 312 10 36* 34 121 11 29 33 286 12 27* 26 160 13 24 25 296
6 177 178 316 7 264 274 94 8 185 194 34 9 218 222 104 10 113 117 300 11 149 147 167	0 32 26 2 1 25• 5 171 2 24• 9 94 3 23• 15 282 4 20 18 338	0 474 474 182 1 174 172 305 2 184 193 135 3 111 116 256 4 479 502 175 5 99 101 358	H= 9, L= -1 0 68 62 183 1 41= 22 12 2 41= 11 189 3 404 27 89	10         38         32         358           11         110         116         272           12         52         52         322           13         64         61         288           14         24*         4         337	H= 8, L= 2 0 49 55 18 1 76 69 29 2 38 7 8	11 111 121 273 12 50 47 285 13 61 64 288 14 23• 9 285 14 23• 9 285	H= 7, L= 3 0 99 102 182 1 66 54 276 2 370 25 165
12 74 71 41 13 66 72 105 14 310 30 343 15 52 60 106 H= 2, L= 0	H= 0, L= 1 0 98 209 175 1 675 657 150 2 515 508 345 3 609 626 87	6 165 164 188 7 151 157 267 8 183 186 170 9 63 59 335 10 102 101 166' 11 78 74 290	4 54 54 180 5 38* 3 272 6 40 33 163 7 34* 18 65 8 30* 27 229 9 25* 5 231	H= 3, L= -2 0 110 96 181 1 387 384 103 2 213 2C5 42 3 208 224 90	3 50 46 26 4 48 44 20 5 81 68 26 6 35• 2 34 7 49 41 30 8 30• 21 21	0         396         396         3           2         1         101         92         341           3         2         381         372         347           3         148         141         232         5         4         417         411         23	3 86 78 267 4 47 50 202 5 58 49 261 6 35* 34 195 7 50 49 279 8 48 42 190
0 497 522 358 1 552 571 75 2 1125 1123 159 3 456 453 58 4 348 345 240	4 571 553 5 5 442 452 85 6 245 243 336 7 158 166 121 8 191 196 31 9 153 159 113	12 86 83 177 13 40 37 330 14 34 39 168 H= 5, L= 1	10 17• 19 139 H= 10+ L= 1 0 33• 18 6 1 33• 9 213	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	9 41 27 25 H= 8, L= -2 0 98 103 1 40= 40 12	5 5 218 204 254 6 146 145 357 7 42 51 163 8 236 238 2 2 9 111 109 260 2 10 98 98 29	9 37 30 262 10 23* 13 157 H= 7, L= -3 0 138 139 1
5 423 426 131 6 235 233 156 7 302 302 96 8 165 175 168 9 71 76 83 10 114 116 191	10 118 122 356 11 160 155 79 12 91 88 5 13 47 50 87 14 37 42 14 15 39 56 101	0 193 201 4 1 27 15 130 2 152 172 354 3 54 58 133 4 239 261 360 5 46 54 263	2 32* 13 332 3 31* 27 269 4 43 36 4 5 26* 7 261 6 22* 5 354	10 48 46 227 11 149 137 96 12 42• 40 264 13 59 51 96 14 30• 12 226	2 43 40 8 3 67 7C 7 4 72 79 34 5 48 55 15 6 40• 18 30 7 49 51 9	D 11 70 69 239 4 12 103 102 8 1 13 43 34 249 8 14 299 42 9 1 H= 3, L= 3	1 84 54 245 2 36 32 17 3 68 70 254 4 38 25 29 5 53 46 267 6 73 74 4
11 118 117 11 12 49 46 169 13 72 73 96 14 38 46 187 15 35 49 86	H= 1, L= 1 0 244 249 182 1 507 481 145 2 307 310 94	7         69         71         120           8         138         142         23           9         40         48         225           10         86         84         343           11         36*         21         73	0 37• 23 183 1 37• 19 213 2 36• 10 181 3 37 35 279 4 31• 27 179	0 173 184 5 1 174 184 314 2 380 401 8 3 91 103 130	9 330 25 18 10 280 14 11 220 26 10 H= 9, L* 2	0 286 283 4 7 1 202 201 285 1 2 322 330 11 3 181 183 270 4 211 212 354 5 99 108 290	8 41 39 37 9 36• 24 277 10 33• 12 52 11 49 48 266 12 22 24 56
0 573 573 182 1 313 315 12 2 193 213 160 3 244 237 245	4 146 137 129 5 266 251 134 6 298 293 188 7 407 403 78 8 88 91 163 9 134 135 149	13 27* 13 181 H= 5, 1= -1 0 77 73 0 1 199 194 301	5 32* 13 337 6 29* 5 159 7 25* 20 301 8 19* 1* 178	5 69 67 288 6 182 188 2 7 46 44 255 8 95 99 4 9 39* 18 217	0 36* 14 1 35* 30 25 2 35 33 3 41 34 29 4 33* 22 34 5 12* 28 24	9 6 217 224 11 9 7 103 103 264 6 8 112 115 345 3 9 54 57 313 6 10 116 114 35 291	H= 8, L= 3 0 36+ 23 5 1 56 53 280 2 44 39 8 3 60 63 274
5 122 123 318 6 279 293 194 7 37 43 332 8 194 201 176 9 81 91 32 10 134 134 135	10 54 63 122 11 218 213 89 12 54 58 184 13 61 60 111 14 29 21 178 15 50 56 99	2 188 184 261 3 231 231 254 4 126 134 48 5 217 220 292 6 81 89 132 7 121 117 304	0 21° 23 3 1 21° 14 23 2 19° 9 314 H= 11, L= -1	11 36* 17 334 12 67 66 2 13 28* 14 289 H= 4, L= -2	6 30° 31 4 7 26° 20 26 8 19° 8 31 H* 9, L* -2	4 12 62 70 0 9 13 27* 13 244 2 H= 3, L= -3 0 430 430 2	4 34* 10 359 5 45 40 297 6 34 30 12 7 34 33 241 8 26* 8 310 9 24 29 296
11 73 64 263 12 70 81 170 13 34* 12 302 14 62 63 187	H= 1, L= -1 0 788 745 2 1 119 104 74 2 386 394 328	8 85 68 303 9 91 85 274 10 43* 40 97 11 78 76 274 12 39* 11 138 13 34 35 283	0 28* 23 179 1 28* 23 317 2 27* 22 359 3 26* 11 185 4 24* 2 339	0 334 326 183 1 124 131 84 2 321 325 179 3 106 110 87 4 246 233 200 5 75 81 51	0 42 26 18 1 44 49 12 2 40° 28 21 3 40° 15 4 4 39° 20 13 5 38° 24 7	3         1         256         247         108           7         2         175         187         9           2         3         226         219         76           1         4         204         201         340           3         5         245         239         99           9         6         173         171         353	H= 8, L= -3 0 300 40 6 1 390 15 324 2 77 78 6
0 35 18 344 1 328 333 313 2 303 304 160 3 369 379 265 4 216 216 275	3         360         334         89           4         804         731         15           5         240         228         101           6         220         206         333           7         156         145         176           8         339         332         353	14 20* 18 57 H= 6. L= 1 0 121 129 2 1 200 204 112	5 20° 12 296 H= 0, L= 2 0 480 479 180 1 541 551 103	6 204 211 160 7 127 130 53 8 199 200 197 9 82 84 82 10 85 79 179 11 49 49 54	6 36* 24 21 7 34* 31 9 8 30* 15 18 9 26* 22 6 10 19* 18 24	7 7 99 91 96 1 8 91 92 352 2 9 172 173 98 7 10 121 123 312 4 11 69 65 123 12 75 52 358	3 52 57 199 4 55 62 2 5 47 40 21 6 36 33 19 7 35 40 218 8 35° 26 0
5 195 208 268 6 75 81 83 7 190 199 272 8 119 91 161 9 151 145 288 10 40 29 217	9 58 61 86 10 153 146 8 11 48° 16 161 12 107 103 1 13 44° 37 92 14 95 7C 338	2 46 44 240 3 144 147 37 4 157 157 39 5 179 181 126 6 84 79 208 7 135 133 86	2 193 178 143 3 450 445 67 4 133 132 178 5 303 301 130 6 103 101 162 7 388 395 82	12 68 63 194 13 36 29 86 14 26* 36 191 H= 5, L* 2	H= 10, L= 2 0 35 33 1 299 6 2 288 17 3 268 11 6	13 65 60 119 14 46 45 326 3 H- 4, L- 3 6 0 106 104 7	9 32* 21 120 10 39 35 340 11 21* 16 181 H* 9, L* 3
11 117 109 279 12 370 15 146 13 51 54 276 14 270 20 143 H= 5, L= 0	15 280 21 148 H= 2, L= 1 0 1066 1017 181 1 545 521 170	8 82 83 8 9 48 43 60 10 34* 3 254 11 61 57 102 12 28* 16 18	8         111         122         138           9         165         180         97           10         65         73         52           11         178         181         103           12         63         65         149           13         70         68         113	0 218 222 2 1 172 178 108 2 83 92 73 3 110 121 64 4 119 130 343 5 161 164 119	4 240 16 1 5 140 12 17 H= 10, L= -2 0 370 14 18	8 1 218 227 92 8 2 169 166 8 3 87 91 95 4 118 123 2 5 120 127 97 7 6 117 111 356	0 32* 35 5 1 32* 6 358 2 36 31 359 3 31* 7 210 4 29* 26 12 5 27* 3 116
0 314 312 2 1 253 251 302 2 163 163 17 3 141 143 225 4 191 196 27 5 101 97 32	3 120 136 346 4 552 546 172 5 73 59 82 6 317 325 175 7 34 43 24	0 187 196 3 1 127 125 279 2 160 174 342 3 89 84 224 4 107 119 22	15 59 71 92 H= 1, L= 2 0 228 228 186 1 437 407 95	7 105 108 66 8 79 72 22 9 84 85 100 10 49 51 15 11 75 65 103	2 38 38 18 3 36* 26 5 4 34* 19 21 5 32* 13 20 6 30* 20 16 7 24* 14	1         136         132         132           2         9         63         56         80           1         10         60         63         25           9         11         45         49         85           4         12         46         44         10           9         13         37         31         93	H= 9, L= -3 0 39* 20 3 1 39* 32 71 2 39* 14 143
0 110 110 525 7 178 191 252 8 103 113 21 9 40° 23 322 10 52 55 350 11 70 75 262	9         35+         16         111           10         196         204         170           11         32         27         110           12         82         81         182           13         33*         14         279           14         46         59         176	5 46 40 3 6 164 163 350 7 174 167 235 8 101 102 25 9 39* 18 298 10 60 48 340	2 697 706 177 3 284 254 40 4 443 428 195 5 288 275 154 6 198 201 159 7 186 188 80	H= 5, L= -2 0 405 411 181 1 127 129 301	8 21+ 8 20 H= 11, L= -2 0 30+ 11 35 1 29+ 15 22	2 H= 4, L= -3 0 52 53 185 8 1 249 251 80 1 2 173 166 236	3 36 34 101 4 38* 26 312 5 40 36 117 6 36* 22 298 7 33* 16 95 8 30* 9 32
12 61 53 28 13 30* 22 289 H= 6, L= 0 0 183 186 3	15 20* 5 114 H* 2, L* -1 0 155 158 178 1 493 479 125	11 50 44 246 12 56 38 29 13 22= 9 282 H= 7, L= 1	8 257 267 180 9 54 58 108 10 169 172 173 11 38* 13 197 12 66 67 194 13 34 39 102	2 36 27 93 3 191 196 290 4 233 232 191 5 70 55 259 6 35 38 184 7 98 99 260	2 29° 6 19 3 27° 15 26 4 25° 12 11 5 23° 9 33 6 18° 5 22	9 3 236 241 109 2 4 32 33 325 6 5 149 152 95 1 6 111 112 232 5 7 168 169 95 8 53 66 290	9 26° 16 116 10 19° 7 302 H° 10, L° 3 0 23° 11 4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2 654 628 28 3 543 545 100 4 41 48 354 5 260 261 85 6 140 132 297 7 280 277 81	0 56 59 186 1 111 98 112 2 111 99 198 3 86 87 93 4 84 87 179 5 399 22 37	14 61 68 160 15 20° 21 110 H= 1, L= -2 0 1031 1009 1	8 118 110 154 9 114 111 305 10 58 54 154 11 59 54 300 12 45 48 176 13 33 33 290	H= 12, L= -2 0 17= 2 17 H= 0, L= 3	9 72 73 112 10 42* 36 213 1 11 103 99 90 12 41 41 24* 13 46 45 87 14 23* 27 233	1 29 23 115 2 21= 8 359 3 15= 16 109 H= 10, L= -3
8 98 78 30 9 51 50 121 10 107 86 343 11 43 38 128 12 56 44 4	9 253 242 108 10 76 67 325 11 175 157 105 12 42 41 300 13 91 74 92	7 110 100 88 8 37* 24 177 9 35* 18 97 10 48 44 194 11 42 38 74	2 430 439 20 3 308 344 268 4 301 284 12 5 146 155 300 6 338 335 10 7 70 79 276	H= 6, L= 2 0 117 114 183 1 120 123 88 2 68 91 220	1 339 339 6 2 326 323 20 3 72 71 6 4 427 427 14 5 286 290 11	3     H=     5, L=     3       0     0     43     53     186       5     1     191     200     95       3     2     36*     28     231       3     3     150     151     81	1 36° 23 88 2 36° 7 138 3 35° 6 155 4 34° 13 192 5 32° 22 64 6 30° 7 222
H= 7, L= 0 0 53 47 1 1 106 100 94 2 64 54 193	15 250 54 109 H= 3, L= 1 0 248 244 183 1 349 355 272	H= 7, L= -1 0 102 93 4 1 58 67 72 2 74 79 13 3 68 65 122	8 195 196 11 9 123 131 289 10 98 93 360 11 60 62 232 12 110 111 7 13 55 60 266	3 202 197 97 4 119 115 173 5 66 65 112 6 46 37 114 7 107 101 78 8 64 60 203	7 112 117 10 8 164 175 17 9 85 91 10 10 148 160 16 11 58 64 12 12 59 67 17	7         4         79         80         153           8         5         163         160         101           15         6         64         59         101           17         7         118         119         88           55         8         44         52         201           2         9         80         61         96	7 26* 8 119 8 22* 12 188 H* 11. L= -3 0 30* 12 184
3 117 108 77 4 51 44 0 5 130 120 122 6 40* 14 220 7 60 54 104 8 39* 13 56	2 79 83 237 3 111 127 311 4 273 274 188 5 279 27C 274 6 113 118 141 7 137 137 286	4 112 116 13 5 39° 14 133 6 40° 16 224 7 87 82 86 8 76 72 343 9 47 40 151	14 44 50 27 15 24= 34 277 H= 2, L= 2 0 482 484 152	9 62 59 119 10 4C 37 167 11 43 41 82 12 27 18 149 H= 6, L= -2	13 57 61 11 14 45 54 15 H= 1, L= 3 0 379 372 10	8 10 35° 24 146 2 11 52 48 87 12 26° 12 118 H= 5, L= -3	1 30° 6 279 2 29° 11 167 3 28° 9 347 4 26° 15 201 5 23° 7 23° 6 19° 9 117
9 52 45 82 10 35* 19 235 11 44 32 119 12 21* 18 19	8 105 105 210 9 222 224 265 10 75 78 187 11 88 86 314 12 62 62 186 13 73 7C 277	10 52 47 16 11 30° 28 120 12 23° 17 307 H= 8, L= 1	1 434 442 283 2 69 66 106 3 164 168 296 4 375 352 182 5 329 332 267 6 157 162 182	D 191 192 1 1 136 135 273 2 63 54 122 3 151 148 281 4 35* 32 52	1 182 192 21 2 416 404 18 3 78 87 22 4 508 489 19 5 192 185 31 6 109 107 17	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	H= 12, L= -3 0 18* 1 355 1 18* 6 244 2 16* 3 95
0 62 60 185 1 39• 29 91 2 61 51 162 3 70 65 93 4 112 105 188	14 264 15 183 H= 3, L= -1 0 741 736 181 1 116 111 137	0 87 86 183 1 58 53 204 2 81 74 197 3 52 49 335 4 39* 21 156 5 38* 17 186	7         157         160         277           8         219         221         201           9         127         134         281           10         50         52         191           11         67         70         273           12         95         99         195	5 151 155 268 6 65 62 82 7 73 66 296 8 41 <sup>a</sup> 18 332 9 69 75 270 10 38 <sup>a</sup> 31 81	7 119 122 24 8 214 219 20 9 73 72 21 10 103 109 15 11 49 45 26 12 100 105 16	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	H= 0, L= 4 0 278 277 184 1 185 195 194 2 263 259 194
5 40° 28 21 6 42 31 165 7 38 39 73 8 43 43 203 9 33° 21 83 10 27 26 191 11 24 71	2 330 531 214 3 311 315 98 4 61 46 189 5 150 155 91 6 333 325 176 7 106 107 88 8 150 150 200	0 72 86 181 7 360 21 295 8 340 26 181 9 30 22 269 10 36 30 177 H= 8, L= -1	H= 2, L= -2 0 573 536 2 1 120 134 70	41 61 58 271 12 294 19 70 13 214 28 270 H= 7, L= 2 0 89 102 104	13 57 50 24 14 48 44 20 H= 1, L= -3 0 21= 6 14 1 408 420 24	12 13 28* 22 25 H= 6, L= 3 19 0 174 165 183 19 1 59 52 141	4 405 409 188 5 50 40 285 6 114 120 204 7 75 88 227 8 166 176 194 9 73 75 21
H= 9, L= 0 0 400 31 185 1 400 29 220 2 59 49 188	9         84         86         109         209           10         125         118         153           11         81         80         80           12         78         67         212           13         50         51         81           14         64         41         190	0 42 34 182 1 99 97 98 2 50 42 241 3 40 34 78 4 40* 12 174	2 522 490 323 3 287 275 112 4 437 410 342 5 168 161 93 6 393 380 11 7 130 127 132	1 66 61 204 2 88 77 161 3 66 65 27 4 106 108 198 5 37• 19 151 6 84 73 162	2 207 207 3 375 400 24 4 147 141 24 5 244 261 2 6 94 101 7 272 282 2	1         2         101         96         172           17         3         36         42         79           16         4         146         145         193           17         5         38*         28         40           14         6         83         79         193           16         7         29         23         140	10 120 119 18 11 50 52 26 12 87 92 194 13 25 29 225 14 39 45 200
3 33 27 308 4 36 30 229 5 38• 9 238	H= 4, 1= 1	5 77 74 100 6 41= 20 291 7 44 46 104	8 235 243 338 9 120 118 118 10 152 144 343	7 36 29 330 8 70 70 198 9 32• 9 200	8 108 112 9 138 140 2 10 76 80	18         8         66         66         183           10         9         33         7         125           10         10         44         46         175	H= 1, L= 4 0 40 40 184

\* Indicates unobserved reflexion with threshold amplitude,  $|F_{th}|$ , in place of  $|F_o|$ .

1904

Table 3 (cont.)

K FO FC	-	K FO FC	AL PHA	K FO FC #	L PHA	K FO FC ALPHA	K F0	FC A		X FO	FC ALPHA	K FO FC	AL PHA	K FO 1	C ALPHA
H= 1, L= 4 1 367 371 2 84 72 3 249 258 4 39 42 5 279 285 6 144 136 7 31	271 255 265 279 205	1 95 98 2 103 113 3 142 137 4 52 99 5 124 116 6 79 92 7 71 68 8 73 71	135 192 67 187 83 207 80 237	5 222 225 6 119 120 7 153 160 8 61 66 9 91 88 10 73 77 11 71 74 12 54 59 13 42 49	298 235 250 203 272 246 265 243 265	H*         5, 1*         -5           0         104         105         1           1         199         203         93           2         92         256         3         94           3         94         106         137           6         89         95         76           6         69         57         348	1 84 2 173 3 124 4 162 5 47 6 153 7 38 8 128 9 57	84 169 130 171 51 153 15 133 59	166 330 308 23 4 344 59 28 346	1 64 2 34 3 44 4 59 5 55 6 32 7 37 8 27	62 303 19 271 37 238 56 359 54 307 27 6 32 273 27 354	5 87 85 6 38* 19 7 75 74 8 47 42 9 60 61 10 28* 24 11 45 42 H= 2, L= -7	110 79 73 133 114 141 105	1 86 2 35 3 37 4 34* 5 23* 6 31* 7 29* 8 26* 9 21*	2 172 7 269 5 310 4 195 0 71 12 140 11 305 5 250 4 99
8 66 66 9 127 135 10 63 7C 11 79 85 12 52 51 13 78 75 14 23• 23	232 274 260 256 240 276 251	10 47 40 11 81 74 12 49 36 13 25* 25 H= 6, 1= 4	185 88 239 74	H# 1, L# 5 0 204 195 1 219 227 2 147 149 3 237 240	3 279 25 274	7 134 130 100 8 47 46 301 9 41* 34 127 10 52 56 288 11 41 50 94 12 29* 12 260 13 20* 29 108	10 60 11 35 12 72 He 1, L 0 135	56 36 74 - 6 150	330 360 15	H= 6, L= 0 34+ 1 6C 2 35 3 81 4 36+ 5 368	-6 28 360 50 57 44 213 82 116 32 27 30 265	0 78 79 1 118 111 2 51 45 3 51 72 4 95 90 5 101 83 6 127 124	185 119 162 296 163 50 220	H# 9, L# 0 34* 1 1 40 4 2 34* 1 3 33* 4 32*	-7 -0 182 -4 338 21 112 8 161 13 223
H= 1, L= -4 0 414 409 1 328 321 2 162 181 3 243 252 4 192 201	182 250 196 270 176	1 70 64 2 72 69 3 96 89 4 57 57 5 46 41 6 69 65 7 44 45	293 169 256 205 281 187 276	5 107 118 6 132 135 7 158 165 9 81 91 10 97 91 11 94 92	262 331 275 330 287 350 276	H* 6, 1= 5 0 37* 24 181 1 92 62 287 2 37* 20 323 3 92 87 280 4 36 30 182	2 106 3 190 4 130 5 94 6 120 7 218 8 42	111 193 14C 95 120 215 39	222 68 193 168 239 51 201	6 66 7 77 8 34 9 32 10 29 11 33 12 16	75 253 83 77 26 341 24 107 24 267 37 107 10 286	7 81 78 8 55 52 9 56 52 10 51 51 11 48 44 12 22* 28	91 194 217 76 203	5 30* 6 27* 7 24* 8 19* H= 10, 1*	0 293 .5 127 3 137 .6 148 -7
5 227 244 6 186 197 7 179 192 8 110 123 9 107 108 10 103 101 11 106 105 12 68 63	292 147 265 170 271 136 291 166	8 69 65 9 27 25 10 25 25 H= 6, L= -4 0 196 202 1 50 49	187 239 215 182 215	12 39 40 13 39 37 H= 1, L= -5 0 224 228 1 89 99 2 187 206	310 317 184 274 167	5 70 61 246 6 33* 24 313 7 66 65 267 8 28* 20 247 9 43 41 288 H= 6, L= -5	9 72 10 94 11 66 12 314 13 26 H# 2, 1	61 39 33	221 90 227 51	H= 7, L= 0 38 1 28 2 48 3 27 4 30	6 33 6 16 108 45 8 10 67 32 17	0 62 57 1 41 35 2 111 103 3 59 62 4 63 54 5 37* 12	187 352 172 133 189 171	1 30° 2 29° 3 32 4 26° 5 24° 6 20°	18 155 15 32 12 301 8 171 8 114 4 12
13 58 60 14 43 42 H= 2, L= 4 0 243 243 1 162 183 2 144 151	302 131 255	2 48 57 3 77 71 4 54 97 5 54 51 6 69 75 7 39 44 8 76 72 9 36* 5	179 96 190 294 190 358 171 190	3 53 48 4 209 323 5 88 99 6 139 143 7 55 56 8 220 219 9 76 76 10 82 84	34 181 308 150 69 204 304 166	0 33° 16 344 1 77 78 169 2 45 37 201 3 102 108 22 4 93 84 183 5 77 73 127 6 36° 18 163 7 36° 27 76	0 162 1 135 2 65 3 161 4 72 5 98 6 69 7 95	165 139 67 172 72 109 76 93	2 65 73 91 69 68 93	5 42 6 36 H= 7, L= 0 51 1 98 1 2 76	33 69 29 353 -6 42 184 C1 178 75 200	6 104 100 7 44 45 8 46 50 9 31 26 10 41 38 H= 3, L= -7	178 199 179 173	0 22* 1 22* 2 21* 3 19* H= 0, L=	4 4 15 2 17 262 16 175 8
3 195 202 4 209 217 5 126 139 6 206 212 7 102 105 8 112 122 9 82 88 10 84 87	293 344 272 346 288 357 284	10 330 32 11 300 36 12 40 44 13 160 19 H= 7, 1= 4	156 342 184 4	11 69 66 12 82 79 13 300 21 H= 2, 1= 5 0 167 191 1 320 12	41 186 350	8 50 50 217 9 34+ 20 53 10 45 46 217 11 43 39 75 12 22+ 20 236 H= 7, L= 5	8 62 9 71 10 50 11 50 12 30 H= 2, 0	63 66 57 49 32	16 57 51 85 71	3 99 4 37 5 37 6 48 7 35 8 33 9 21 10 26	97 44 16 258 30 155 35 167 30 353 33 188 21 121 29 201	0 132 130 1 71 79 2 128 116 3 40* 6 4 77 76 5 60 71 6 85 87 7 63 69	182 284 195 44 216 287 123 311	0 140 1 1 91 2 40* 3 40* 5 63 6 56	15 2 35 135 23 148 23 351 98 352 58 29 60 34
11 58 63 12 56 62 13 27* 18 H= 2, L= -4 0 195 177	302 348 312	1 87 87 2 36* 26 3 81 76 4 34* 5 5 65 55 6 32* 22 7 59 51	297 307 270 57 271 335 261	2 204 207 3 57 61 4 190 200 5 57 55 6 121 119 7 73 79 8 112 112 9 39 43	81 18 316 16 56 20	0 89 85 3 1 37 32 279 2 33 28 10 3 29 30 245 4 51 49 6 5 48 47 307 6 35 28 10 7 249 11 298	0 166 1 70 2 98 3 93 4 177 5 74 6 113	158 77 98 104 185 77 109	184 235 223 340 187 245 113 27	11 23 H= 8, L= 0 200 1 33 2 180	22 30 6 14 1 27 98 8 101	B 70 74 9 370 5 10 55 50 11 37 40 12 42 33 H= 4, L= 7	202 315 139 332 179	7 57 8 66 9 38 10 28 H= 1, L= 0 63	60 180
2 313 311 3 220 222 4 57 57 5 192 182 6 85 89 7 180 140 8 60 75	38 261 107 279 60 274 89	9 42 34 H= 7, L= -4 0 61 54 1 94 84 2 364 23	182 284 30	10 80 81 11 29 31 12 68 69 13 22* 18 He 2. Le -5	51 15 2	8 27 32 5 He 7, Le -5 0 130 126 182 1 40 32 206 2 56 59 133 3 54 58 284	8 128 9 64 10 86 11 39 12 58 13 21	124 63 74 48 52 23	213 291 164 347 183 329	H= 8, L= 0 37* 1 71 2 37* 3 37* 4 36* 5 35*	-6 27 183 74 316 28 81 36 119 22 123 37 291	0 64 69 1 47 50 2 38* 21 3 112 113 4 57 55 5 49 45 6 37 35 7 54 46	183 304 215 256 192 279 222 259	1 68 2 399 3 134 1 4 399 5 85 6 379 7 64 8 32	105         10         10         10         10         11         11         10         11         10         11         10         11         10         11         10
9 124 115 10 96 91 11 107 95 12 39* 35 13 45 44 14 25* 40 H= 3, L= 4	205 200 46 265 71	3 80 00 4 52 44 5 46 52 6 43 44 7 47 44 8 36* 24 9 54 56 10 40 31	143 269 112 279 194 300	1 333 336 2 47 43 3 185 184 4 171 174 5 117 123 6 46 57 7 197 200	215 147 294 187 293 130 286	4 80 89 201 5 43 46 298 6 44 43 172 7 36* 28 26 8 42 42 161 9 30 33 284 10 28* 14 119	0 154 1 169 2 379 3 69 4 131 5 111	147 190 2 65 134 110	182 127 320 80 163 83	6 47 7 320 8 290 9 250 10 200 He 9, Le	41 213 19 2 14 118 19 261 9 126 -6	8 29 29 9 23• 15 H• 4, L= -7 0 39• 9 1 79 73 2 40 73	210 279 177 238 25	9 38 10 21* H* 1, L* 0 77 1 64 2 123 1	31 99 26 107 -8 7C 4 61 137 03 352
0 248 239 1 94 101 2 220 219 3 107 114 4 246 245 5 47 42 6 101 103	3 100 4 77 18 102 9	11 200 20 12 190 2 H= 8, L= 4 0 62 64 1 330 16 2 42 32	273 193 329	9 55 51 10 75 76 11 57 57 12 37 36 13 67 60	273 125 290 146 290	H= 8, L= 5 0 28+ 15 10 1 28+ 18 122 2 34 32 353 3 26+ 28 63	с 30 7 90 8 69 9 59 10 48 11 47 н= 3,1	87 68 63 46 48	97 156 108 156 106	C 36* 1 36* 2 36* 3 35* 4 34* 5 33* 6 31* 7 2*	4 176 18 189 13 218 39 274 3 76 14 229 21 229 21 52 26 295	3 133 132 4 69 66 5 78 67 6 41* 19 7 130 124 8 50 56 9 54 58 10 32* 16	262 91 28 194 235 80 281 90	3 63 4 66 5 48 6 71 7 58 8 67 9 45 10 44	34         144           52         75           58         30           52         316           50         152           59         5           42         137           28         312
7 85 86 8 151 149 9 54 45 10 80 82 11 41 38 12 61 57 13 23• 21	83 62 13 83 22 21	3 32* 20 4 49 45 5 29* 10 6 27* 24 7 23* 11 H= 8, L= -4	219 9 319 271	0 340 9 1 190 198 2 51 47 3 188 190 4 360 23 5 174 175 6 97 100	24 91 14 84 268 99 47	3         22*         25         106           H#         6.         L=         -5           0         37*         34         160           1         37*         8         105           2         37*         28         55	0 64 1 209 2 103 3 114 4 120 5 170 6 71	61 209 106 116 118 169 60	182 277 86 291 165 255 152	8 244 9 184 H= 10, L= 0 324 1 50	6 212 3 123 -6 10 4 47 343	H= 5, L= 7 0 65 58 1 76 76	277 86 2 305	11 27 He 2, Le 0 40 1 78 2 76 3 38e	23 132 8 30 190 74 148 70 147 15 40
H= 3, L= -4 0 191 196 1 152 141 2 290 300 3 59 58 4 271 267 5 36 42	88 360 226 350 112	0 38° 2 1 38° 4 2 41 4 3 38° 1 4 38° 2 5 38 3 6 41 3 7 36° 2	290 316 214 114 276 19 268	7 118 121 8 36 28 9 76 75 10 51 51 11 71 65 12 25* 27 H= 3, L= -5	82 38 88 60 80 69	3         63         67         248           4         37*         31         22°           5         37*         25         200           6         41         49         59           7         34*         15         285           8         30         29         172           9         29         30         307           10         24*         21         98	7 130 8 56 9 48 10 40 11 60 12 28 13 42	133 60 40 45 56 32 37	87 264 116 274 108 277	2 320 3 310 4 290 5 270 6 240 7 200 H= 11, 1=	19 292 33 132 21 66 8 316 3 316 6 195 -6	3 40 34 4 48 48 5 51 48 6 299 17 7 46 38 H= 5, L= -7	247 8 288 334 268	4 63 5 36* 6 52 7 45 8 59 9 29	58 190 16 124 40 184 45 122 52 174 27 179 -8
6 205 204 7 69 69 8 181 184 9 42* 24 10 112 105 11 46 45 12 72 71 13 31* 27	358 186 350 112 25 215 354 186	8 29 21 9 30 11 10 24 21 11 20 24 H= 9, L= 4	346 213 59 275	0 82 89 1 208 198 2 158 157 3 226 221 4 123 126 5 128 114 6 171 179	5 308 18 231 2 311 49	11         16*         18         266           H*         9, L*         -5         0         38*         22         4           1         38*         17         271         2         47         46         13           3         37*         16         266         16         266	H= 4, 0 126 1 72 2 121 3 50 4 74 5 38	124 73 117 52 84	184 337 176 163 228 185	0 26* 1 26* 2 25* 3 23* 4 21* 5 17*	22 1 7 114 3 194 5 219 5 356 12 82	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2 325 89 183 1 305 28	0 42* 1 76 2 81 3 137 1 4 115 1 5 56	17 357 65 118 92 165 25 73 18 296 54 138
14 22+ 40 H= 4, L= 4 0 35 29 1 198 202 2 55 49 2 55 49	359 97 182	L 270 11 2 260 21 3 250 21 4 230 11 He 9, Le	89 352 9 17	7 114 115 8 42* 14 9 137 132 10 87 90 11 54 53 12 38 44 13 34 35	230 67 259 37 262 39 256	4 36° 4 95 5 35° 7 286 6 33° 26 6 7 31° 16 205 8 27° 13 2 9 23° 7 224 H= 10, L= -5	6 88 7 53 8 73 9 30 10 33 H+ 4,	82 58 72 8 31	179 214 195 178 181	H= 0, L= 0 131 1 79 2 76 3 54 4 141 5 55	7 126 4 88 290 73 311 60 6 140 28 62 224	7 48 34 8 384 31 9 354 27 10 42 46 11 34 26 He f, L= 7	261 354 162 31 220	7 84 8 37* 9 52 10 32 31 42	24 156 77 45 28 250 49 109 32 268 37 80
4 34 33 5 170 173 6 09 67 7 133 136 8 38* 22 9 88 91 10 35* 22 11 63 63	139 99 75 149 149 100 110 84	1 38* 24 2 42 3 3 38* 3 4 41 3 5 37* 2 6 35* 1 7 33* 1 8 29* 2	50 7 352 155 2 3 57 7 13 191 2 346	He 4, Le 5 0 126 134 1 97 106 2 42 38 3 135 129 4 150 152 5 75 73	183 116 159 93 174 104	0 34+ 18 3 1 34+ 22 145 2 34+ 18 106 3 33* 8 220 4 32* 25 296 5 30* 10 77 6 27* 12 10	0 36 1 81 2 64 3 93 4 113 5 79 6 69 7 41	• 29 83 64 97 115 71 66 • 21	168 6 342 222 6 272 20 212	6 96 7 64 8 86 9 37• 10 67 11 35 12 52	84 321 66 320 86 24 26 306 55 326 42 323 51 25	1 298 4 2 33 35 3 27* 6 4 54 47 5 34 30 6 19* 16	83 24 216 17 26 330	0 84 1 53 2 45 , 3 47 4 52 5 54 6 32• 7 14	85 183 49 295 40 198 46 261 48 226 47 233 37 199 41 251
12 32 24 H= 4, L= -4 0 57 61 1 139 134 2 208 215 3 205 214	62 49 356 117	9 25* 1 10 18* 1 H= 10, L* 0 36* 1 35* 2 35* 1	1 122 2 346 2 5 3 37 5 279	6 67 57 7 47 51 8 80 78 9 63 63 10 53 50 11 38 38 H# 4, L# -5	161 97 190 123 151 105	7 240 8 203 8 180 4 15 H= 11, L= -5 0 250 5 181 1 250 15 170 2 270 2 200	8 59 9 30 10 63 11 46 12 26 H= 5,	53 36 58 47 31 L= 6	256 39 241 24	0 210 1 86 2 31 3 120 4 133 5 83	218 2 93 90 32 99 113 102 141 24 79 40	0 36* 6 1 93 101 2 56 51 3 37 35 4 62 61 5 75 84	157 137 283 316 17 91	8 25* H= 3, L= 0 87 1 70 2 40 2 40	27 212 -8 93 183 57 42 47 300
4 108 121 5 110 113 6 78 82 7 93 94 8 57 60 9 107 106 10 75 76 11 38 37	108 335 111 330 122 309	3 340 1 4 330 1 5 310 1 6 290 1 7 250 1 8 210	90 7 46 1 146 5 246 7 309	0 235 236 1 84 83 2 117 125 3 72 59 4 63 61 5 83 94 6 112 116	2 152 341 36 115 345	3 266 19 50 4 246 6 23 5 218 6 135 6 168 8 244 H* 12, L= -5 0 168 10 358	0 52 1 70 2 38 3 136 4 62 5 45 6 43 7 78	42 59 18 137 66 40 36 67	183 283 12 265 176 283 268 252	6 39• 7 90 8 94 9 56 10 33 11 54 H= 1, L=	37 103 86 73 91 19 50 65 41 42 49 69 -7	6 35° 25 7 44 42 8 35 36 9 29° 7 10 29 30 11 19° 18 H= 7, L= 7	276 166 31 352 272 127	4 120 5 38 6 47 7 45 8 33 9 43 10 42	17 159 38 68 54 258 33 92 33 189 37 356 49 202
12 340 34 13 50 47 14 180 32 He 5, Le 4 0 159 160	306 112 316	C 29+ 1 1 29+ 1 2 28+ 1 3 27+ 4 25+ 5 23+ 6 16+	0 183 3 45 3 175 5 160 8 195 3 61 9 207	7 40+ 35 8 116 105 9 46 46 10 52 47 11 31 31 12 56 50 13 24+ 33	227 359 101 352 167 4 171	1 10° 8 166 He 0, Le 6 0 200 197 1 1 210 215 316 2 51 53 65 3 211 209 24	8 32 9 39 H= 5, C 173 1 38	27 36 L= -6 184 • 28 67	204 289 130 37	0 51 1 125 2 41 3 214 4 165 5 130 6 73	46 1 126 120 45 174 214 67 171 336 139 131 68 220	0 20* 10 1 24 27 2 19* 4 H= 7, 1* -7 0 93 92	89 319 360	H= 4, L= 0 41 1 54 2 330 3 55	8 43 1 50 266 11 263 52 280
1 09 7C 2 119 121 3 127 124 4 127 130 5 66 59 6 93 88 7 34 32 8 60 6C	193 100 179 94 191 130 184	H+ 12, L= - 0 18+ 1 1 18+ 2 16+ 1	4 3 182 1 335 1 299	H= 5, L= 5 0 156 151 1 56 54 2 93 88 3 66 64 4 99 98 5 13 3	183 304 173 239 212	4 97 98 34 5 128 135 29 6 38* 26 28 7 121 126 26 8 66 68 30 9 69 69 31 10 49 55 32 11 80 7	3 102 4 135 5 101 6 5 7 41 8 74 9 41	111 147 110 53 • 23 63 39	45 159 288 112 19 124	7 86 8 42* 9 60 10 44 11 63 12 22*	87 80 38 315 53 115 40 298 57 75 37 274 7	1 58 50 2 37* 20 3 52 53 4 36* 23 5 35* 10 6 34* 5 7 46 47 8 38 39	22 156 101 201 99 325 84 280	4 31° 5 43 6 29 7 35 H= 4, L# 0 52	7 73 38 285 20 318 27 260 -8 57 357
9 37 37 10 54 52 11 27* 28 H= 5, L= -4 0 112 116	114 166 98 183	C 202 19 1 343 34 2 105 9 3 203 20 4 60 6	6 182 2 307 9 227 3 224 9 271	6 78 72 7 34 32 8 81 80 9 316 23 10 30 31	245 191 215 201	12 300 29 28 13 190 32 29 He 1, L= 6 0 142 140	11 31 12 34 H= 6, 0 71	• 11 32 L• 0 74	182 349 3	0 92 1 113 2 50 3 127 4 40	57 181 114 121 45 257 124 80 44 145	9 260 10 10 210 15 H= 8, L= -7 0 58 50	69 239 182	1 56 2 88 3 52 4 58 5 71 6 61	52 255 77 154 49 288 56 227 64 266 68 97

Table 3 (cont.)

FO FC FO EC. FÓ FC ٤n FC FO FC AL PH 4. 1. - 8 34 28= 25= 20= 34 18 22 16 279 90 56 56 31\* 38 40 38\* 57 35\* 43 29\* 24\* 22 160 77 170 22 23 1, L--11 678 67 7 38 40 2 31 18 43 172 25 48 45 47 17 16 20 316 78 215 69 239 80 277 33\* 32\* 32\* 31\* 30\* 28\* 26\* 22\* 17\* 172 197 52 93 349 231 146 196 5 67 8 9 10 7 19 14 8 22 9 7 17 44 35• 31• 26• 25 50 37 8 23 29 329 224 165 123 304 25\* 41 25 22\* 19\* 36\* 36 35\* 41 32\* 37 26\* 25 15 38 18 13 10 182 306 59 115 252 20 306 59 262 343 239 83 234 3 24 25 32 20 26 16 21 01234 -10 5. L. 1, 1--9 -8 35+ 35+ 34+ 33+ 32+ 30+ 23+ 20+ 4 17 10 21 13 13 196 164 202 311 168 38 238 212 56 420 410 71 44 53 45 35 230 58 125 43 147 43 8 8 4 160 290 263 19 108 202 202 17 277 34+ 34+ 33+ 32 31+ 30+ 27+ 24+ 20+ 19 16 24 16 11 7 12 16 358 16 181 67 219 137 95 103 250 5, 1. 4. L= 8 н= 9 2. L. -11 23456780 61 290 270 56 220 31 26\* 25\* 24\* 37 29 19 15 13 42 65 15 11 6 54 19 3 249 43 30 2 348 01234 8. L. -9 27\* 26\* 25\* 51 22\* 18\* 012345 13 30 46 7 3 176 100 19 258 193 10 224 322 300 2. 1. 10 30\* 30\* 29\* 28\* 27\* 24\* 21\* 17\* 11 18 7 3 13 13 14 01234567 26\* 43 25\* 23\* 20\* 187 301 203 251 211 5 40 14 17 26 81 116 329 32 90 263 78 234 ~10 H= 6, L= 4. L -9 30\* 29\* 28\* 26\* 32 21\* 17\* 1 26 4 1 9 31 15 11 5. 6. -8 -8 2. 1. 9 189 303 230 118 185 238 62 325 на 9. L. ... н-3. 1. -11 63 51 39\* 35\* 36\* 35\* 32\* 33 29 61 29 17 35 15 13 34 27 182 346 214 75 199 212 264 333 185 65 35• 42 40 33• 22• 56 48 0123456789 68 84 50 56 39 57 50 37 24 27\* 30 26\* 25\* 23\* 19\* 310 310 290 280 280 280 280 280 280 280 280 183 194 51 52 179 2. 1. 01234567890 59 77 48 46 52 79 53 55 31 3 179 320 298 220 104 290 339 236 84 302 161 13 14 9 12 18 3 10 183 232 208 263 193 188 182 213 -10 62 12 31 40 29 16 48 38 012345 26 32 11 27 11 2 354 253 148 12 206 **H**= 9. L. -9 53 35\* 34\* 32\* 30\* 43 23\* 17\* 012345678 43 18 28 24 25 3 28 17 13 26\* 26\* 25\* 24\* 22\* 19\* 357 155 244 77 356 219 6 4 21 13 9 8 342 196 57 272 13 181 357 012345 1 228 334 7. 1= -10 ..... 4, L--11 270 270 270 27 23 25 170 2 5 10 22 19 28 8 13 184 350 238 133 22 51 н. 10. 1. -8 2, L= -9 280 270 260 250 230 28 11 20 2 4 3 27 134 229 92 83 59 5, L--9 012345 260 250 250 230 210 170 19 16 4 15 8 180 342 329 189 331 304 41\* 46 95 39\* 38\* 25\* 33\* 25\* 25\* 24 35 28 94 20 26 10 21 32 10, L. -9 012345 н. 6, L. 8 28 350 106 355 110 329 140 336 122 40\* 37 39\* 46 35 36\* 31\* 27\* 21 11 36 14 45 25 18 28 6 7 20 184 187 75 299 152 306 149 357 216 250 3, L= 10 0123454789 19\* 19\* 12\* 157 358 208 117 5 20\* 19 1 0 1 15 29 116 6 19• 18• ů 20 20 211 не 6, L= 8. L-~10 .... 5. 1. -11 н--8 10 н. 0, L= н-3. L. -10 0, L. 24\* 23\* 23 22 20 16 24\* 23\* 23\* 19\* 15\* 4 15 6 19 16 8 175 356 31 115 315 159 271 24 192 80 294 214 98 36\* 55 360 43 34\* 33\* 31\* 28\* 24\* 18\* 012345 012344 1 2 15 18 10 100 6 54 13 38 2 15 6 17 19 26 0 1 2 3 4 5 6 7 8 9 10 42 31 32• 31• 34 35 23• 17• 35 29 9 27 30 30 4 182 80 87 97 187 141 29 97 35\* 35\* 33\* 33\* 32\* 38 27\* 24\* 36 16 24 15 23 26 32 12 16 25 1 55 97 109 330 166 58 143 334 151 33 01234567 01234567 40\* 84 40\* 54 38\* 74 34\* 40 26\* 20\* 3 145 187 105 320 73 273 197 359 0123456789 67841 4836262317 24 8 131 27 60 62 85 118 86 26 85 3, L= , -9 6, L. 32\* 54 31\* 30\* 29\* 57 21\* 0123454 13 50 7 32 21 46 15 360 295 291 265 193 270 330 63 299 339 187 38 294 18 246 105 -10 1 30 16 20 7 15 20 29 11 8 9. 1= -11 18• 18• 16• 22\* 22\* 21\* 20\* 17\* 1 2 1 10 12 5 19 6 182 182 78 325 161 123 н. 1, L-10 71 н 4. 1. -10 32 30\* 29\* 31 26\* 23\* 31 26 2 19 27 20 3 29 н-7, L. -8 1, 1= 9 185 233 190 243 183 126 174 35\* 25\* 34\* 39 32\* 30\* 27 0123456 .... 0, L. u 0123454 3 19 19 30 5 8 29 201 54 173 90 45 91 221 3, L= -9 36+ 35+ 35+ 35+ 35+ 34+ 33= 177 46 311 155 55 37• 45 47 50 34• 184 88 179 100 190 15 32 28 12 36 46 18 31 47 46 31 0 1 2 3 34 31 20• 17• 32 31 8 15 183 344 251 154 01234 01234 40• 80 39• 39• 17 84 13 26 184 129 95 327 0123 19\* 19\* 17\* н. 690 180 7. 1. ....

in the refinement, and exclude the others. The most prominent peaks in the difference maps were indicative of residual thermal anisotropy of Br in the x, z plane.

In the final least-squares cycle, the R index was 0.049for the 1569 reflexions observed above threshold, the average shift was less than  $0.1\sigma$ , and the maximum shifts were  $0.3\sigma(x, y, z)$  and  $0.4\sigma(B_{ij})$ . The unobserved reflexions were excluded altogether from the refinement. The quantity minimized by the least-squares procedure was  $\Sigma w(|F_o| - |F_c|)^2$ , where  $w = 1/\{1 + [(|F_o| - p_2)/p_1]^n\},\$  $|F_0| = 1.6$  to 112.5,  $p_1 = 25$ ,  $p_2 = 30$ , and n = 2 for the early cycles and =4 for the final cycles. The exponent n=4 was employed in the final cycles in order to give nearly equal weights (0.5 to 1.0) to reflexions in range  $5 \le |F_o| \le 55$  and much reduced weights for the others, since the very strong reflexions were likely to suffer from extinction and the very weak reflexions were inaccurate because of poor counting statistics. The scattering factor curves of Br, O, N, C, H were those given by Hanson, Herman, Lea & Skillman (1964). The curves for Br<sup>-</sup> and N<sup>+</sup> were derived by slight modification of the Br and N curves in order to allow for their states of ionization. The  $\Delta f'$  and  $\Delta f''$  components for Br were taken from International Tables for X-ray Crystallography (1962). No special allowance was made for the slight error in the curve for hydrogen.

# Results

The final parameters and estimated standard deviations of the bromine and the non-hydrogen atoms of one molecule referred to a right-handed set of axes are listed in Table 1. The refined parameters and e.s.d.'s of the 17 non-methyl hydrogen atoms are given separately in Table 2, but as indicated by the high e.s.d.'s the accuracy of these parameters is considerably lower than for the other atoms. The e.s.d.'s were calculated from the least-squares matrices by the appropriate expression given in *International Tables for X-ray Crystallography* (1959, p. 330). The observed and calcu-





lated structure amplitudes, and the calculated phase angles based on the parameters in Table 1 and 2, are listed in Table 3. The phase angles of the hk0 reflexions are not exactly 0° or 180° since the anomalous scattering of the bromine atoms is included in the calculations. The discrepancies in the structure factor data are summarized in Table 4 according to the criteria described by Ahmed & Barnes (1963). The single observed reflexion listed in category 4 is the 001 reflexion, which could not be improved on remeasurement. The eight unobserved reflexions listed in categories 3 and 4 were all high-angle reflexions associated with very high background counts, resulting from unfavourable positions of the goniometer head with respect to the primary beam, and could not be measured accurately.

A perspective view of one molecule and its nearest bromine atom, relative to the unit cell axes, is presented in Fig. 1. The bond lengths and angles, not corrected for thermal vibration, and their e.s.d.'s [Ahmed & Cruickshank (1953) for the bond lengths, and *International Tables for X-ray Crystallography* (1959, p. 331) for the bond angles] are shown in Fig. 2. The mean C-H bond length is 1.05 Å.

#### Discussion

#### Absolute configuration

The absolute configuration of the molecule has been determined from the relative intensities of 19 pairs of reflexions of the types *hkl* and *hkl*. The corresponding observed and calculated structure amplitudes for the parameters given in Tables 1 and 2, and the ratios  $|F_o(h\bar{k}l)|$  / $|F_o(hkl)|$  and  $|F_c(h\bar{k}l)|/|F_c(hkl)|$  are listed in Table 5. From the consistent agreement of these ratios, it should be concluded that the atomic coordinates given in Table 1 correspond to the absolute configuration of the (+)-N-[(2-benzylmethylamino)propyllpropionanilide in the hydrobromide derivative. For further confirmation of this conclusion, the R index for all the observed data has been found to increase from 0.049 to 0.059 if the absolute configuration is reversed. In this analysis, the indices and the atomic coordinates have both been chosen to correspond to a righthanded set of unit-cell axes.

The view of the molecule down the N(1)-C(7) bond, presented in Fig. 3(*a*), shows that the absolute configuration is *R* in terms of the sequence rule nomenclature of Cahn, Ingold & Prelog (1956). This result is in agreement with the conclusions by Portoghese & Larson (1964) regarding the absolute configuration of the molecule in the free base as derived from chemical procedures. For comparison, a similar drawing of *d*-methadone (the less active form of methadone) in the form of the hydrobromide derivative, based on the coordinates reported by Hanson & Ahmed. (1958) is given in Fig. 3(*b*), and its absolute configuration is shown to be *S*.

## Interatomic distances and angles

In view of the importance of the amide and peptide groups to the structure of proteins, it would be appropriate to compare the dimensions of the amide group in this propionanilide molecule with the X-ray results (Brown & Corbridge, 1954) for acetanilide, and with the values calculated by Pauling (1960). A summary of this comparison is presented in Table 6. The two sets of results for propionanilide and acetanilide are in good agreement with each other except for one bond length, C(7)-C(8), and one angle, C(7)-N(1)-C(1), where the propionanilide results (1.526 Å and 123.8°) are in better agreement with Pauling's values (1.53 Å and 123°) than with the corresponding values for acetanilide (1.476 Å and 129.3°).

In the propionanilide molecule, the C(10)–C(11) single bond which lies between two C–N single bonds is found to be only 1.504 Å ( $\sigma$ =0.012 Å), which is rather on the short side, and its difference from the normal value of 1.54 Å is possibly significant. The C(14)– C(15) bond of the type C–C<sub>6</sub>H<sub>5</sub> which is found to be 1.526 Å ( $\sigma$ =0.012 Å) in this structure is not significantly different from the average value of 1.506 ± 0.005 Å reported by Sutton (1965) for this type of bond. The other two C–C single bonds in the structure are 1.548 Å each. The C–C aromatic bonds of the two phenyl rings have a weighted mean value of 1.378( $\sigma_{wm}$ =0.004) Å. The apparent shortening of these bonds can be attributed, at least partly, to the omission of the corrections for thermal vibration.

# Table 4. Agreement summary

	1569 observed reflexions $(1.6 \le F_o \le 112.5)$ R = 0.049	
Category	Limits	Number
1	$ \Delta F  \le 1.0  F_{th} $ , or $ \Delta F / F_0  \le 0.10$	1564
2	$1.0 F_{th}  <  \Delta F  \le 2.0 F_{th} $ , or $0.10 <  \Delta F / F_0  \le 0.15$	4
3	$2 \cdot 0  F_{th}  <  \Delta F  \le 3 \cdot 0  F_{th} $ , or $0 \cdot 15 <  \Delta F / F_o  \le 0 \cdot 20$	0
4	$3 \cdot 0 F_{th}  <  \Delta F $ , or $0 \cdot 20 <  \Delta F / F_o $	1
	750 unobserved reflexions ( $ F_{c_{\max}}  = 4.1$ )	
1	$ F_c  \leq 1.0  F_{th} $	687
2	$1.0 F_{th}  <  F_c  \le 1.5 F_{th} $	55
3	$1.5 F_{th}  <  F_c  \le 2.0 F_{th} $	7
4	$2 \cdot 0 F_{th}  <  F_c  \le 2 \cdot 5 F_{th} $	1

 $|F_{th}| =$  threshold amplitude = 1.3 to 4.3.

The three C-N<sup>+</sup>(2) bonds have a mean value of 1.509  $(\sigma_m = 0.006)$  Å which is significantly longer than the average value of  $1.479 \pm 0.005$  Å reported by Sutton (1965) for the C-N bonds at a 4-covalent nitrogen. The occurrence in amino acids of C-NH<sub>3</sub><sup>+</sup> bonds longer

than 1.47 Å has been discussed by Hahn (1957), where the mean value of a C-NH<sub>3</sub><sup>+</sup> bond is given as 1.503 Å. Also, Hamilton, Hamor, Robertson & Sim (1962) have deduced from a similar survey of alkaloids that the  $C(sp^3)$ -N<sup>+</sup> bond length is about 1.52 Å. It should,

 Table 5. Structure amplitudes and ratios of the reflexions examined for the effect of anomalous scattering by the Br atoms

h	k	l	$ F_o(hkl) $	$ F_o(hkl) $	$ F_c(hkl) $	$ F_c(hkl) $	$\frac{ F_o(hkl) }{ F_o(hkl) }$	$\frac{ F_{c}(h\bar{k}l) }{ F_{c}(hkl) }$
3	1	T	11.62	<b>9</b> ·78	11.14	9.27	0.84	0.83
4	1	ī	17.45	16.88	17.22	16.40	0.97	0.95
4	2	ī	18.41	20.62	19.35	21.72	1.12	1.12
5	1	1	2.73	2.38	1.55	1.35	0.87	0.87
1	1	2	8.10	6.34	10.48	7.89	0.78	0.75
2	1	2	11.99	12.48	13.42	14.50	1.04	1.08
3	2	2	10.97	10.10	11.71	10.57	0.92	0.90
4	1	2	12.40	12.38	13.13	13.23	1.00	1.01
5	1	2	12.69	11.93	12.86	12.11	0.94	0.94
5	2	2	3.62	4.94	2.74	4.70	1.37	1.71
2	1	3	10.11	9.05	9.18	7.90	0.90	0.86
2	2	3	19·6 <b>2</b>	19.48	21.26	21.18	0.99	1.00
4	2	3	17.30	16.79	16.61	15.97	0.97	0.96
0	1	4	18.49	19.22	19.51	20.43	1.04	1.05
1	2	4	8.40	7.91	7.25	6.60	0.94	0.91
1	2	4	16.23	15.65	18.14	17.39	0.96	0.96
3	1	4	15.20	15.52	14.12	14 <b>·2</b> 6	1.02	1.01
4	1	4	13.89	15.22	13.43	14.98	1.10	1.11
1	2	3	18.70	19.52	20.63	21.50	1.05	1.04



Fig. 3. Molecular structure and absolute configuration of (a) (+)-N-[(2-benzylmethylamino)propyl]propionanilide hydrobromide viewed along the amide bond, N(1)-C(7), (b) d-methadone hydrobromide viewed along the C(3)-C(4) bond.

(b)

C(7)-O(1) C(7)-C(8)	Propion- anilide 1·226 (10) 1·526 (13)	Acet- anilide 1·226 (6) 1·476 (6)	Pauling's values* 1·24, 1·26 1·53
C(7) - N(1) C(1) - N(1) C(10) - N(1)	1·353 (11) 1·430 (9) 1·474 (10)	1·330 (6) 1·426 (6)	1.32, 1.34 $1.47$
C(8)-C(7)-O(1) C(8)-C(7)-N(1) N(1)-C(7)-O(1) C(7)-N(1)-C(1) C(7)-N(1)-C(10) C(1)-N(1)-C(10)	120.5 (8) 118.7 (7) 120.8 (8) 123.8 (6) 119.2 (6) 116.1 (6)	120·4 117·7 121·7 129·3	121 114 125 123 123 114
C(8) $C(7)-N(1)$	C(10)	C(8) $C(7) - N(1)$	H ()
Propionanilic	le	Acetanil	ide

Table 6. Dimensions of the amide group

Bond lengths in Å, angles in degrees, and e.s.d.'s in parentheses.

\* First values are based on the X-ray results of amino acids, simple peptides and related substances. Second values are calculated values for 40:60 resonance structures.

therefore, be concluded that the mean value of 1.509 Å which has been found in this structure is a normal length for the  $C(sp^3)-N^+$  bonds.

An interesting intramolecular distance in the propionanilide structure is that between the two nitrogen atoms N(1) and N<sup>+</sup>(2) which are separated by only 2.972 Å. This shows that the two atoms are held as



Fig.4. The conformation proposed by Casy & Hassan (1967b) for N-[(2-benzylmethylamino)propyl]propionanilide from spectroscopic data, showing only part of the molecule.

close to each other as the van der Waals interactions between them will allow.

The  $Br^-$  and  $N^+(2)$  ions with the coordinates listed in Table 1 are only 3.230 Å apart. Also, the Br<sup>-</sup>... N<sup>+</sup>(2) vector makes angles of  $134.7^{\circ}$ ,  $92.6^{\circ}$ , and  $92.1^{\circ}$ with the N(2)-C(11), N(2)-C(13), and N(2)-C(14) bonds which, together with the angles of 112.1°, 107.4°, and  $114.0^{\circ}$  between the three C-N bonds, give a mean angle at N(2) of  $108.8^{\circ}$ . This evidence suggests the existence of a hydrogen bond,  $Br^- \dots H^+(2)$ , with the hydrogen atom lying off the Br...N(2) vector so that the three H-N-C angles are nearer to a tetrahedral configuration than the Br-N-C angles. A similar arrangement occurs in the structure of  $\beta$ -prodine HCl studied by Ahmed & Barnes (1963), where the Cl–N–C angles are  $125.8^{\circ}$ ,  $100.0^{\circ}$ , and  $98.4^{\circ}$ , while the H–N–C angles are  $111.6^\circ$ ,  $109.2^\circ$ , and  $104.3^\circ$ , and the H–N–Cl angle is  $14.3^{\circ}$ .

There are no particularly short intermolecular distances in this structure. The shortest contacts not involving hydrogen atoms are 3.118 Å for C...O and 3.572 Å for C...C. The nitrogen atoms are not involved in any intermolecular distances below 4.0 Å.

# Planarity of the amide group and phenyl rings

The four atoms C(8), C(7), O(1) and N(1) of the amide group are exactly planar within the accuracy of this determination. Their mean plane referred to the orthogonal set of axes  $(X'=ax+cz\cos\beta, Y'=by, Z'=cz\sin\beta)$  is

$$0.7669X' + 0.4659Y' + 0.4415Z' - 5.2945 = 0.$$
(1)

The displacements of the atoms from this plane are; C(8) 0.002; C(7) -0.007; O(1) 0.003; N(1) 0.002 Å, the corresponding  $\chi^2$  value is only 0.99, and  $P \simeq 0.29$ . Both C(1) and C(10), which are attached to N(1), lie on the same side of the plane at distances 0.151 and 0.113 Å, respectively, from it. The plane of the C(1)-N(1)-C(10) group makes a dihedral angle of 9.8° with plane (1), but the angle of rotation of this group round the N(1)-C(7) bond is only 0.6°, which is equivalent to 1.0 × e.s.d. of the angles in this structure. The angle of rotation has been calculated by the procedure described in the Appendix.

The mean plane through atoms C(8), C(7), O(1), N(1), C(1), and C(10) of the amide group is<sup>-</sup>

$$0.7940X' + 0.4468Y' + 0.4121Z' - 5.3190 = 0.$$
(2)

The displacements of these atoms from plane (2) are as follows: C(8) 0.009; C(7) -0.020; O(1) 0.026; N(1) -0.070; C(1) 0.035; C(10) 0.020 Å. The corresponding  $\chi^2$  value is 171, which shows that these six atoms deviate significantly from exact planarity.

Each of the two phenyl rings is found to be exactly planar. The equations of the mean planes of C(1) to C(6), and C(15) to C(20), are

0.7343X' - 0.6723Y' + 0.0942Z' - 1.0165 = 0, (3) and

0.8415X' + 0.3546Y' + 0.4077Z' - 1.2566 = 0, (4)

and the corresponding  $\chi^2$  values are 3.0 and 6.6, respectively. The dihedral angle between the two phenyl rings is 65.3°. Plane (2) of the amide group makes a dihedral angle of 71.3° with the adjoining phenyl ring, and a dihedral angle of 6.0° with the other phenyl ring.

# Conclusions

The molecular structure shown in Figs. 1 and 3(a) as determined from this X-ray analysis, closely resembles the conformation advanced by Casy & Hassan (1967b) on the basis of spectroscopic evidence, and reproduced here in Fig.4. The only difference between them is in the orientation of the anilo-phenyl and ethyl-carbonyl fragments relative to the aminoethyl side-chain. Their orientation is shown by the X-ray analysis to be rotated by about 90° from that assumed by Casy & Hassan. However, both models agree in the main particulars, namely, (a) the amide group and the adjoining phenyl ring are not coplanar (the angle between them has been determined as  $71.3^{\circ}$ ; (b) the two nitrogen atoms are held close to each other (they are actually separated by only 2.972 Å, which is equivalent to the sum of their van der Waals radii); (c) the s-methyl, C(13), is well removed from, and is not shielded by, either of the phenyl rings.

The X-ray analysis has shown that the six atoms of the amide group are not exactly planar, and that the maximum displacement of 0.07 Å occurs at N(1). However, the four atoms C(8), C(7), O(1), and N(1) of the group are planar within the accuracy of the determination, and the C(1)-N(1)-C(10) group is tilted by  $9.8^{\circ}$  off the plane of the four atoms and is rotated round the N(1)-C(7) bond by only  $0.6^{\circ}$ . The absolute configuration which was determined through chemical procedures by Portoghese & Larson (1964) has been confirmed by this X-ray determination.

#### **APPENDIX**

Calculation of the angel of rotation round a bond

. ....

Let

and

$$l_1 X + m_1 Y + n_1 Z - p_1 = 0, \qquad (1)$$

$$l_2 X + m_2 Y + n_2 Z - p_2 = 0 \tag{2}$$

represent the normal equations in cartesian coordinates of the mean planes of two groups of atoms linked together by a bond AB which lies in plane (1) and has the direction cosines  $(L_1, M_1, N_1)$ . In order to calculate the angle of rotation of the second group [represented by plane (2)] round AB, define a line CD normal to AB in plane (2). The direction ratios  $(L'_2, M'_2, M'_2)$  of CD can be calculated from the following expressions:

$$L'_{2} = m_{2}N_{1} - n_{2}M_{1};$$
  

$$M'_{2} = n_{2}L_{1} - l_{2}N_{1};$$
  

$$N'_{2} = l_{2}M_{1} - m_{2}L_{1}.$$
(3)

The angle of rotation ( $\varphi$ ) of the second group round the bond *AB* can then be calculated from the expression

$$\sin \varphi = (l_1 L_2' + m_1 M_2' + n_1 N_2') / [L_2'^2 + M_2'^2 + N_2'^2]^{1/2}, \quad (4)$$

where l,m,n are assumed to be direction cosines and not direction ratios. In this treatment, the angle of rotation is defined as that between the line *CD* and plane (1).

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