

## The Crystal and Molecular Structure of (+)-(R)-N-Methyl-1-[(1-naphthyl)ethyl]-(R)-O-methylmandelamide\*

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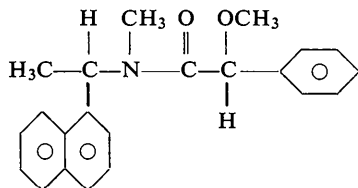
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The crystal and molecular structure of (+)-(R)-N-Methyl-1-[(1-naphthyl)ethyl]-(R)-O-methylmandelamide,  $C_{22}H_{23}NO_2$ , has been determined by X-ray diffraction. The crystals are monoclinic, space group  $P2_1$ , with cell dimensions  $a = 12.908$  (6),  $b = 8.022$  (5),  $c = 9.808$  (5) Å,  $\beta = 102.64$  (8)°. The structure was determined by statistical methods and refined to an  $R$  of 0.048 for 1983 reflections. Most of the dimensions of the molecule are unexceptional; however, the substituted naphthalene group is non-planar.

### Introduction

The reaction of excess racemic hydratropic acid and dicyclohexylcarbodiimide with optically active amines results in the asymmetric synthesis of diastereomeric hydratropamides. Cervinka (1966) has used this reaction as the basis of an empirical method for determining the absolute configurations of amines: the predominant enantiomer in the unreacted hydratropic acid being related to the configuration of the inducing amine.

As a test of this method, the absolute configuration of (+)-N-methyl-1-(1-naphthyl)ethylamine has been determined by examining the crystal structure of the (R)-O-methylmandelamide by X-ray diffraction. The absolute configuration of the amide molecule was fixed by comparison with the known asymmetry of the carbon atom in the acid moiety; the chirality of the asymmetric carbon atom in the amine was found to be (R). In a preliminary publication of this work (Mislow, Jacobus, Drew, Templeton & Zalkin, 1968),‡ we have shown that this result is in direct contradiction to the theory of Cervinka (1966). A detailed description of the crystal structure of (+)-(R)-N-methyl-1-[(1-naphthyl)ethyl]-(R)-O-methylmandelamide is given here.



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‡ Note added in proof:— After this work was completed, Cervinka & Fusek (1968) postulated that the (–)amine had the (S) configuration on the basis of asymmetric transformation. This was in agreement with our findings and this preliminary publication was withdrawn.

### Experimental

Crystals, colorless needles, were kindly provided by Professor K. Mislow of Princeton University. Preliminary photographs by the Weissenberg technique showed a monoclinic lattice. The cell dimensions were measured at room temperature ( $\sim 23^\circ\text{C}$ ) with a General Electric quarter-circle goniostat ( $\lambda = 0.71069$  Å for Mo  $K\alpha$ ) and are:  $a = 6.224$  (6),  $b = 8.022$  (5),  $c = 9.808$  (5) Å,  $\beta = 102.64$  (8)°. The errors in the last digits (in parentheses) are subjective estimates of the standard deviations. The calculated density, for  $Z = 2$ , is  $1.190$  g.cm $^{-3}$ , which agrees with the observed value (by flotation) of  $1.20$  g.cm $^{-3}$ . Reflections are absent for  $0k0$  if  $k = 2n + 1$ . These absences and the optical activity are characteristic of space group  $P2_1$ .

One crystal was used in the experiment, mounted about the needle  $b$  axis and with approximate size ( $0.1 \times 0.3 \times 0.1$  mm). Intensities were measured for 1983 reflections, each with  $2\theta \leq 140^\circ$ , using Cu  $K\alpha$  radiation filtered through Ni, at 35 kV and 20 mA. Each reflection was integrated by the  $\theta$ ,  $2\theta$  technique. Each scan extended from  $0.5^\circ$  (of  $2\theta$ ) below the  $\alpha_1$  peak to  $0.5^\circ$  above the  $\alpha_2$  peak, at a rate of  $1^\circ/\text{min}$ . The background was measured for 10 seconds at each end of the scan with crystal and counter stationary, and was assumed to be a linear function of  $2\theta$  between these points. The net intensity  $I$  is

$$I = C - (B_1 + B_2)(t_c/2t_b),$$

where  $C$  is the total counts recorded during the scan time  $t_c$ , and  $B_1$  and  $B_2$  are the background counts recorded each in time  $t_b$ . The standard deviation of the intensity was assumed to be:

$$\sigma(I) = [C + (t_c/2t_b)^2(B_1 + B_2) + (0.05I)^2]^{1/2}.$$

During the data collection, the intensity of the four standard reflections showed no significant change. No correction was made for absorption. 68 reflections with zero intensity were given zero weight in the subsequent refinement.

In the calculation of structure factors, atomic scattering factors for neutral C and H were taken from *International Tables for X-ray Crystallography* (1962). The isotropic temperature factors were defined as  $\exp(-B \sin^2 \theta / \lambda^2)$ . The anisotropic temperature factors used have the form:  $(-0.25 \sum_i \sum_j h_i h_j b_i b_j B_{ij})$ ,  $i, j =$

1, 2, 3 where  $b_i$  is the  $i$ th reciprocal cell length. Calculations were made with the CDC 6600 computer using unpublished programs for Fourier series, interatomic distances and angles, and structure-factor least-squares, all written by Dr A. Zalkin of this laboratory. The full-matrix least-squares program minimizes  $\sum w | \Delta F |^2 / \sum w | F_0 |^2$ .

### Determination and refinement of the structure

This structure was solved by means of a statistical method which has been described in some detail for a previous determination (Drew, Templeton & Zalkin, 1969). The normalized structure factor magnitudes  $|E|$  were calculated with the use of an unpublished program written by Maddox & Maddox (1965), and 135 reflections with  $|E|$  values over 1.50 were used in subsequent calculations. The origin was specified by assigning zero phase to three reflections, the 2 0 9, 13 0 2 and 0 1 1. The reflection 6 0  $\bar{2}$  was given the phase  $\pi$  from the  $\Sigma_1$  relationship (Karle & Hauptman, 1956). The phases of three other reflections were assigned symbols. The initial phase assignments are listed in Table 1.

Table 1. *Initial phase assignments*

| $h$           | $E_h$ | $\varphi_h$ |
|---------------|-------|-------------|
| 2 0 9         | 2.40  | 0           |
| 13 0 2        | 2.41  | 0           |
| 0 1 1         | 1.84  | 0           |
| 6 0 $\bar{2}$ | 3.09  | $\pi$       |
| 6 0 $\bar{8}$ | 2.71  | $a$         |
| 6 2 5         | 2.69  | $b$         |
| 5 2 $\bar{8}$ | 2.32  | $c$         |

The symbolic-addition equation (Karle & Karle, 1966) was then used:

$$\varphi_h \simeq \langle \varphi_k + \varphi_{h-k} \rangle_k \quad (1)$$

The value of the triple product  $|E_h E_k E_{h-k}|$  was required to exceed 8.0 if a single phase indication was to be accepted. The seven reflections were used as a starting set and the phases of 66 additional reflections were determined. For the remaining reflections, the contributing sums  $(\varphi_k + \varphi_{h-k})$  to a particular  $\varphi_h$  were sometimes different. Relationships between the symbols were derived from these differences. The most frequently occurring relationships were  $a = \pi$ , and  $b = \pi$ , but there were also a few indications that  $b = 0$ . There appeared to be no preferred value of  $c$ . Symbol  $a$  was replaced by  $\pi$ , but at this stage, no substitution was made for  $b$ . The tangent formula was then used (Karle & Hauptman, 1956)

$$\tan(\varphi_h) = A/B, \quad (2)$$

where

$$A = \sum_k |E_k E_{h-k}| \sin(\varphi_k + \varphi_{h-k}),$$

$$B = \sum_k |E_k E_{h-k}| \cos(\varphi_k + \varphi_{h-k}).$$

In the application of this formula, eight different values for  $b$  were used: 0,  $\pm \pi/4$ ,  $\pm \pi/2$ ,  $\pm 3\pi/4$ ,  $\pi$  and five for  $c$ : 0,  $\pi/4$ ,  $\pi/2$ ,  $3\pi/4$ ,  $\pi$ . The restriction of the possible values of  $c$  between 0 and  $\pi$  fixed the enantiomorph. There were 40 different combinations of the possible values for the two symbols  $b$  and  $c$  and the tangent formula was applied to each of them.

For each combination, the 73 reflections whose phases were determined from equation (1) in terms of  $b$  and  $c$  were given the appropriate numerical values. The tangent formula was then used to obtain the values of all 135 phases from this starting set of 73 reflections. The complete set of phases was then refined with the tangent formula for 10 cycles. The consistency of a set of phases can be measured by the  $Q$  value (Drew, Templeton & Zalkin, 1969) where:

$$Q = \sum_h |E_h - t_h E_h| / \sum_h |E_h|,$$

and  $t_h$ , the consistency of an individual  $\varphi_h$  is

$$t_h = (A^2 + B^2)^{1/2} / \sum_k |E_{h-k} E_k|.$$

The  $Q$  values for the 40 different combinations are shown in Table 2. The most consistent sets of phases have the lowest  $Q$  values.

Table 2.  $Q$  values ( $\times 100$ ) for the 40 combinations of values of  $b$  and  $c$

| Values of $c$ | Values of $b$ |         |         |          |       |          |          |          |
|---------------|---------------|---------|---------|----------|-------|----------|----------|----------|
|               | 0             | $\pi/4$ | $\pi/2$ | $3\pi/4$ | $\pi$ | $5\pi/4$ | $3\pi/2$ | $7\pi/4$ |
| 0             | 23            | 30      | 28      | 17       | 17    | 17       | 28       | 30       |
| $\pi/4$       | 25            | 30      | 28      | 22       | 17    | 17       | 29       | 33       |
| $\pi/2$       | 27            | 23      | 19      | 19       | 17    | 18       | 30       | 23       |
| $3\pi/4$      | 25            | 30      | 28      | 18       | 20    | 20       | 29       | 30       |
| $\pi$         | 23            | 30      | 29      | 17       | 16    | 17       | 29       | 30       |

This Table confirmed the results obtained from the symbolic-addition approach, that  $b$  was close to  $\pi$ . In this Table, the solutions with  $b = 0$  or  $\pi$  and  $c = 0$  or  $\pi$  all have centric phases. The complete procedure described above using equations (1) and (2) was carried out using a computer program written for the CDC 6600.

$E$  maps were calculated using the refined phases for several of the solutions with  $Q = 0.17$ , but none showed the complete structure. Distances and angles between the highest peaks in the  $E$  maps were then calculated in an attempt to find fragments of the molecule. The  $E$  map with  $b = \pi$  and  $c = \pi/2$  appeared to be the most promising\* and the 20 strongest peaks, numbered in

\* In retrospect, it was found that no other  $E$  map contained so much of the molecule.

order of electron density, are shown in Fig. 1. This is the *c* projection, and superimposed on the peaks is the skeleton of the correct structure. Several peaks, such as *X*4 and *X*5, which were approximately equidistant from each other and from *X*1 were rejected as making no chemical sense. Peaks *X*12–*X*7–*X*1–*X*2 and *X*14–*X*3–*X*11–*X*10 were connected by distances and angles which were consistent with the geometry of the molecule. The parameters of these atoms were refined by least squares along with those of peaks *X*6, *X*8, *X*9, *X*13, *X*19 whose positions could not be ruled out on chemical grounds. The *R* value ( $R = \Sigma |\Delta F| / \Sigma |F_o|$ ) after 3 cycles of least-squares refinement using isotropic thermal parameters was 0.41. An observed Fourier synthesis was calculated and several new peaks, connected by appropriate distances and angles to the original peaks were found. 22 atoms were then refined by least squares: after three cycles, the temperature factors of several atoms were much higher than the remainder. These atoms were rejected. Among them were peaks *X*6, *X*12, *X*14, *X*19 in the original *E* map. It was later discovered that the positions of peaks *X*6, *X*14, *X*19 in the original *E* map differed by about 0.5 Å from positions of atoms after refinement.

A difference-Fourier calculated from the parameters of the remaining atoms, showed the rest of the structure. The 25 heavy atoms were refined anisotropically to an *R* of 0.092. A difference-Fourier clearly showed all 23 hydrogen atoms. Two cycles of full-matrix least-squares refinement on the heavy atoms, keeping the hydrogen contribution to the structure factors con-

stant, reduced *R* to 0.066. Then the hydrogen parameters were refined for two cycles keeping the heavy-atom contributions fixed. Refinement was concluded with three cycles of full-matrix refinement of all 308 parameters (heavy atoms anisotropic, and hydrogen atoms isotropic). The final *R* value for the non-zero data was 0.045 (0.048 for all data). The maximum shift-deviation ratio over all parameters was 0.4. The final parameters for the heavy atoms are given in Table 3, together with their standard deviations, and for the hydrogen atoms are listed in Table 4. The bond distances and angles in the molecule are shown in Table 5. Table 6 lists the observed and calculated structure factors.

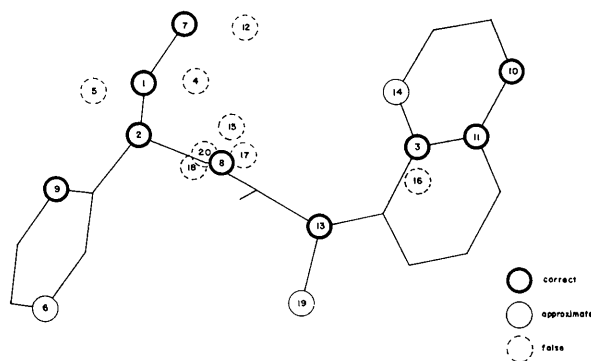


Fig. 1. *c* projection of the molecule showing the peaks found in the *E* map ( $b = \pi$ ,  $c = \pi/2$ ). Peaks are numbered in decreasing order of electron density.

Table 3. Final fractional coordinates ( $\times 10^4$ ) and thermal parameters ( $\times 10^2$ ) for the non-hydrogen atoms in (+)-(R)-N-methyl-1-[(1-naphthyl)ethyl]-(R)-O-methylmandelamide\*

|       | <i>x</i>  | <i>y</i>  | <i>z</i> | <i>B</i> <sub>11</sub> | <i>B</i> <sub>22</sub> | <i>B</i> <sub>33</sub> | <i>B</i> <sub>12</sub> | <i>B</i> <sub>13</sub> | <i>B</i> <sub>23</sub> |
|-------|-----------|-----------|----------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| O(1)  | 4490 (2)  | -1983†    | 6714 (2) | 614 (9)                | 521 (9)                | 353 (6)                | 36 (7)                 | 47 (6)                 | -22 (6)                |
| O(2)  | 5706 (1)  | -0061 (4) | 9791 (1) | 552 (8)                | 708 (10)               | 271 (5)                | -60 (8)                | 63 (5)                 | 34 (6)                 |
| C(1)  | 3052 (2)  | 0528 (5)  | 5610 (2) | 412 (8)                | 688 (16)               | 382 (9)                | 03 (10)                | 38 (7)                 | -37 (10)               |
| C(2)  | 2390 (2)  | 1824 (6)  | 4992 (3) | 468 (11)               | 789 (18)               | 461 (10)               | 46 (12)                | 31 (9)                 | -39 (12)               |
| C(3)  | 2275 (2)  | 3257 (5)  | 5733 (3) | 431 (12)               | 665 (17)               | 631 (14)               | 38 (12)                | 88 (9)                 | 128 (13)               |
| C(4)  | 2822 (2)  | 3365 (5)  | 7156 (3) | 473 (12)               | 634 (17)               | 657 (14)               | 36 (12)                | 56 (10)                | -80 (13)               |
| C(5)  | 3484 (2)  | 2050 (5)  | 7750 (3) | 472 (11)               | 666 (16)               | 446 (10)               | 07 (11)                | 52 (8)                 | -85 (10)               |
| C(6)  | 3612 (2)  | 0627 (4)  | 7006 (2) | 328 (8)                | 576 (12)               | 349 (7)                | -40 (8)                | 68 (6)                 | -20 (8)                |
| C(7)  | 4382 (2)  | -0749 (4) | 7701 (2) | 444 (9)                | 533 (12)               | 325 (8)                | -20 (9)                | -95 (7)                | -05 (8)                |
| C(8)  | 5520 (2)  | -0040 (4) | 8510 (2) | 410 (9)                | 486 (11)               | 305 (7)                | 15 (9)                 | -64 (6)                | 33 (8)                 |
| N(9)  | 6257 (1)  | 0603 (4)  | 7802 (2) | 381 (7)                | 552 (10)               | 305 (6)                | 09 (7)                 | 59 (5)                 | 59 (7)                 |
| C(10) | 7259 (2)  | 1498 (5)  | 8629 (2) | 426 (9)                | 541 (14)               | 443 (9)                | -63 (10)               | 60 (8)                 | 10 (10)                |
| C(11) | 8286 (2)  | 1203 (4)  | 8002 (3) | 386 (9)                | 475 (12)               | 457 (12)               | -57 (9)                | 22 (7)                 | 52 (9)                 |
| C(12) | 8683 (2)  | 2425 (5)  | 7271 (3) | 462 (11)               | 554 (15)               | 671 (13)               | -31 (11)               | 100 (10)               | 152 (12)               |
| C(13) | 9628 (3)  | 2168 (6)  | 6673 (4) | 529 (13)               | 709 (19)               | 754 (16)               | -104 (14)              | 187 (12)               | 160 (15)               |
| C(14) | 10169 (2) | 0705 (6)  | 6813 (4) | 440 (11)               | 769 (20)               | 703 (15)               | -74 (14)               | 136 (11)               | -09 (15)               |
| C(15) | 9812 (2)  | -0614 (5) | 7575 (3) | 380 (9)                | 606 (15)               | 572 (11)               | 01 (10)                | -36 (8)                | -68 (11)               |
| C(16) | 10386 (3) | -2152 (6) | 7753 (4) | 531 (14)               | 686 (10)               | 725 (15)               | 88 (13)                | -62 (12)               | -70 (15)               |
| C(17) | 10059 (3) | -3394 (5) | 8507 (4) | 661 (19)               | 653 (19)               | 790 (18)               | 117 (16)               | -202 (15)              | -55 (17)               |
| C(18) | 9141 (3)  | -3163 (5) | 9129 (3) | 744 (18)               | 546 (16)               | 629 (14)               | -119 (14)              | -194 (13)              | 122 (13)               |
| C(19) | 8534 (3)  | -1691 (5) | 8962 (3) | 516 (13)               | 496 (14)               | 508 (11)               | -58 (12)               | -71 (10)               | 88 (10)                |
| C(20) | 8851 (2)  | -0369 (4) | 8080 (2) | 380 (9)                | 462 (12)               | 429 (9)                | -65 (8)                | -50 (7)                | 30 (9)                 |
| C(21) | 5144 (3)  | -3373 (5) | 7327 (3) | 748 (17)               | 531 (15)               | 491 (11)               | -36 (14)               | 86 (11)                | 29 (12)                |
| C(22) | 6002 (2)  | 0817 (6)  | 6289 (2) | 446 (11)               | 916 (21)               | 325 (8)                | -54 (13)               | 85 (8)                 | 128 (11)               |
| C(23) | 6961 (3)  | 3307 (6)  | 8804 (5) | 702 (18)               | 601 (18)               | 917 (23)               | -13 (15)               | 276 (17)               | -172 (17)              |

\* Standard deviations (estimated by least squares for the least significant digit) are given in parentheses.

† Parameter fixed during refinement.

Table 4. Final coordinates ( $\times 10^3$ ) and thermal parameters ( $\times 10$ ) for the hydrogen atoms

| Also given are the C-H distances in Å*. |          |          |          |          |          | Table 4 (cont.) |          |          |          |         |          |
|---|----------|----------|----------|----------|----------|-----------------|----------|----------|----------|---------|----------|
|   | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> | C-H (Å)  | <i>x</i>        | <i>y</i> | <i>z</i> | <i>B</i> | C-H (Å) |          |
| H(1)                                    | 315 (2)  | -058 (4) | 508 (3)  | 28 (4)   | 1.05 (3) | H(18)           | 882 (3)  | -406 (6) | 972 (4)  | 56 (9)  | 1.05 (4) |
| H(2)                                    | 199 (3)  | 172 (5)  | 391 (4)  | 51 (8)   | 1.07 (4) | H(19)           | 789 (3)  | -151 (4) | 932 (3)  | 26 (5)  | 0.94 (3) |
| H(3)                                    | 185 (3)  | 431 (5)  | 526 (4)  | 51 (8)   | 1.05 (4) | H(21a)          | 479 (4)  | -366 (7) | 803 (5)  | 77 (12) | 0.92 (5) |
| H(4)                                    | 276 (3)  | 432 (5)  | 771 (4)  | 47 (7)   | 0.98 (4) | H(21b)          | 605 (5)  | -286 (8) | 780 (5)  | 95 (14) | 1.17 (6) |
| H(5)                                    | 394 (3)  | 212 (5)  | 872 (4)  | 44 (7)   | 0.95 (3) | H(21c)          | 516 (5)  | -438 (9) | 662 (6)  | 93 (14) | 1.07 (6) |
| H(7)                                    | 406 (2)  | -121 (3) | 847 (3)  | 18 (5)   | 0.99 (3) | H(22a)          | 534 (3)  | 014 (5)  | 586 (4)  | 49 (8)  | 0.98 (4) |
| H(10)                                   | 741 (2)  | 101 (3)  | 955 (3)  | 18 (5)   | 0.96 (3) | H(22b)          | 571 (4)  | 206 (7)  | 593 (4)  | 74 (11) | 1.09 (5) |
| H(12)                                   | 829 (3)  | 348 (5)  | 716 (3)  | 37 (7)   | 1.04 (4) | H(22c)          | 664 (3)  | 095 (5)  | 595 (4)  | 49 (8)  | 0.91 (4) |
| H(13)                                   | 987 (3)  | 312 (6)  | 620 (4)  | 47 (8)   | 0.97 (3) | H(23a)          | 671 (3)  | 372 (6)  | 776 (5)  | 60 (10) | 1.06 (5) |
| H(14)                                   | 1085 (3) | 054 (4)  | 640 (3)  | 36 (6)   | 1.01 (3) | H(23b)          | 761 (4)  | 391 (5)  | 956 (4)  | 58 (9)  | 1.07 (4) |
| H(16)                                   | 1116 (4) | -226 (4) | 733 (4)  | 60 (9)   | 1.10 (4) | H(23c)          | 627 (4)  | 341 (6)  | 936 (4)  | 66 (10) | 1.10 (4) |
| H(17)                                   | 1054 (4) | -452 (9) | 855 (4)  | 94 (14)  | 1.07 (7) |                 |          |          |          |         |          |

\* Standard deviations in parentheses refer to the least significant digit.

Table 5. Bond distances and angles\*

| Distances, Å |           | Angles, degrees   |           |
|--------------|-----------|-------------------|-----------|
| C(1)-C(2)    | 1.380 (5) | C(7)-C(8)         | 1.539 (3) |
| C(2)-C(3)    | 1.371 (6) | C(8)-O(2)         | 1.228 (2) |
| C(3)-C(4)    | 1.384 (4) | C(8)-N(9)         | 1.347 (3) |
| C(4)-C(5)    | 1.384 (5) | N(9)-C(10)        | 1.488 (3) |
| C(5)-C(6)    | 1.382 (5) | N(9)-C(22)        | 1.459 (3) |
| C(6)-C(1)    | 1.391 (3) | C(10)-C(23)       | 1.514 (6) |
| C(6)-C(7)    | 1.508 (4) | C(10)-C(11)       | 1.520 (3) |
| C(7)-O(1)    | 1.411 (4) | C(11)-C(12)       | 1.363 (5) |
| O(1)-C(21)   | 1.422 (5) | C(11)-C(20)       | 1.427 (5) |
|              |           | C(12)-C(13)       | 1.410 (4) |
|              |           | C(13)-C(14)       | 1.336 (5) |
|              |           | C(14)-C(15)       | 1.416 (5) |
|              |           | C(15)-C(16)       | 1.408 (6) |
|              |           | C(15)-C(20)       | 1.429 (3) |
|              |           | C(16)-C(17)       | 1.350 (6) |
|              |           | C(17)-C(18)       | 1.391 (5) |
|              |           | C(18)-C(19)       | 1.381 (6) |
|              |           | C(19)-C(20)       | 1.411 (5) |
|              |           | C(11)-C(10)-C(23) | 115.5 (3) |
|              |           | C(10)-C(11)-C(20) | 120.1 (3) |
|              |           | C(10)-C(11)-C(20) | 121.0 (3) |
|              |           | C(12)-C(11)-C(20) | 119.0 (2) |
|              |           | C(11)-C(12)-C(13) | 121.7 (4) |
|              |           | C(12)-C(13)-C(14) | 120.6 (4) |
|              |           | C(13)-C(14)-C(15) | 120.8 (3) |
|              |           | C(14)-C(15)-C(16) | 121.4 (3) |
|              |           | C(16)-C(15)-C(20) | 119.5 (3) |
|              |           | C(14)-C(15)-C(20) | 119.1 (3) |
|              |           | C(15)-C(16)-C(17) | 121.3 (3) |
|              |           | C(16)-C(17)-C(18) | 120.4 (4) |
|              |           | C(17)-C(18)-C(19) | 121.4 (4) |
|              |           | C(18)-C(19)-C(20) | 120.4 (3) |
|              |           | C(19)-C(20)-C(15) | 117.7 (3) |
|              |           | C(19)-C(20)-C(11) | 123.4 (2) |
|              |           | C(11)-C(20)-C(15) | 118.9 (3) |
|              |           | C(6)-C(1)-C(2)    | 120.0 (3) |
|              |           | C(1)-C(2)-C(3)    | 121.0 (3) |
|              |           | C(2)-C(3)-C(4)    | 119.5 (3) |
|              |           | C(3)-C(4)-C(5)    | 119.6 (4) |
|              |           | C(4)-C(5)-C(6)    | 121.1 (3) |
|              |           | C(5)-C(6)-C(1)    | 118.7 (3) |
|              |           | C(7)-C(6)-C(1)    | 121.6 (4) |
|              |           | C(5)-C(6)-C(7)    | 119.7 (2) |
|              |           | C(6)-C(7)-C(8)    | 110.9 (3) |
|              |           | C(6)-C(7)-O(1)    | 114.0 (2) |
|              |           | C(8)-C(7)-O(1)    | 110.2 (2) |
|              |           | C(7)-O(1)-C(21)   | 112.7 (2) |
|              |           | N(9)-C(8)-O(2)    | 122.6 (2) |
|              |           | N(9)-C(8)-C(7)    | 119.6 (2) |
|              |           | C(7)-C(8)-O(2)    | 117.8 (2) |
|              |           | C(8)-N(9)-C(22)   | 123.6 (2) |
|              |           | C(8)-N(9)-C(10)   | 117.1 (2) |
|              |           | C(10)-N(9)-C(22)  | 117.6 (2) |
|              |           | N(9)-C(10)-C(11)  | 110.2 (2) |
|              |           | N(9)-C(10)-C(23)  | 109.8 (2) |

\* Standard deviations for the least significant digit given in parentheses.

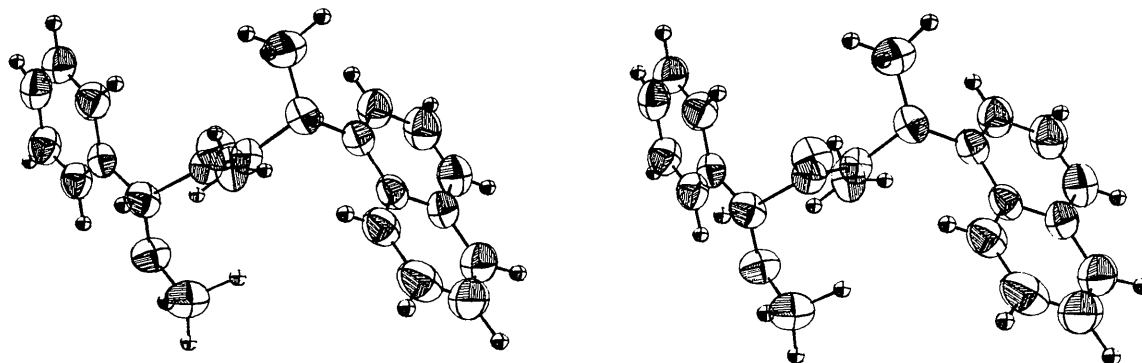


Fig. 2. A stereopair of the molecule of (+)-(R)-N-methyl-1-[(1-naphthyl)ethyl]-(R)-O-methylmandelamide.

At this stage, the method of phase determination described above was re-examined. The phases for the 153 reflections with highest |E| were taken from the final least-squares refinement (R=0.045) and refined by use of the tangent formula. The final consistency index Q was 0.18 and an E map calculated using these

phases showed the complete structure. However, this set of phases did not correspond to any of the sets summarized in Table 2. On examining the symbolic addition approach with equation (1), the reasons for this were apparent. It had been necessary to assign the phase phi\_h of several reflections from one phase pair

Table 6. Observed and calculated structure factors (x 10)\*

\* Reflections marked with an asterisk were assigned zero weight in the least-squares refinement. F\_000 (x 10)=1760.0.

Table with multiple columns containing reflection indices (h, k, l), observed structure factors (F\_o), and calculated structure factors (F\_c). The table is organized into several sections based on reflection indices, such as 110, 111, 112, etc. Each section contains a list of reflections and their corresponding F\_o and F\_c values. Some reflections are marked with an asterisk (\*).

$(\varphi_k + \varphi_{h-k})$ . The value of  $|(\varphi_h - \varphi_k - \varphi_{h-k})|$ , calculated from phases taken from least-squares refinement, was as high as  $\pi/4$  for a few of the most crucial phase relationships. This difference had been compounded to  $\pi/2$  and  $\pi$  for some of the reflections. An example of this is given in Table 7.

Table 7. Deviations in the symbolic addition approach

| $h$            | $k$            | $h-k$         | $(\varphi_h - \varphi_k - \varphi_{h-k})^*$ | $E_h E_k E_{h-k}$ |
|----------------|----------------|---------------|---|-------------------|
| 11 4 $\bar{3}$ | 6 2 5          | 5 2 $\bar{8}$ | 54°   | 12.6              |
| 2 1 1          | 11 4 $\bar{3}$ | 9 $\bar{3}$ 4 | 31  | 9.7               |

\* Phases taken from least-squares refinement.

When the symbolic-addition approach was used, the phase of the 211 reflection was calculated as  $b + \pi$  from the relationships shown in Table 7. Such an assignment had introduced an error of  $\pi/2$  in the phase of the reflection. Often, several such assignments will cancel each other out, but in this particular phase determination, they did not. Such an error can be guarded against by using more symbols, both in the first stage with the symbolic addition equation and in the second stage with the tangent-formula refinement. In the present structure determination, such a procedure would have been of limited value, as the  $Q$  value for the correct set of phases was 0.18: not significantly different from many other solutions.

### Discussion of the structure

A stereopair of the complete molecule, showing the refined positions of all 48 atoms is shown in Fig. 2. The enantiomorph with both asymmetric carbon atoms

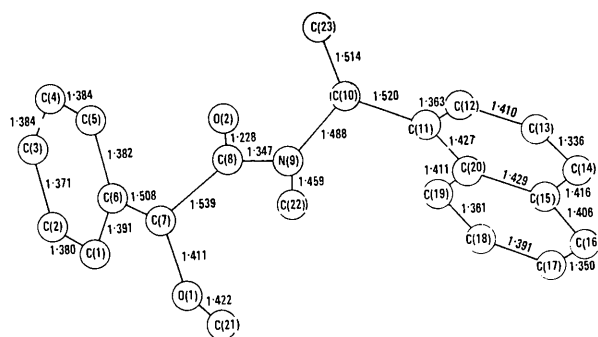


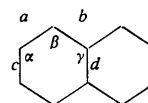
Fig. 3. Bond distances between the heavy atoms in the molecule.

in the ( $R$ ) configuration is drawn. Fig. 3 shows the numbering of the atoms and the bond distances between the heavy atoms in the molecule.

The benzene ring is planar to within experimental error (maximum deviation of an atom from the plane = 0.004 Å). The average bond distance over the six atoms in the benzene ring is 1.382 Å. When allowance is made for thermal motion, the average becomes 1.390 Å, a value which is close to the expected value. The internal ring angles are all within 1.3° of 120°. The carbon atom C(7) is 0.067 Å away from the plane of the benzene ring.

The dimensions of the chain connecting the benzene and naphthalene rings are unexceptional. The average bond distances are: C-C single bonds 1.520 Å, C-O single bonds 1.416 Å, C-O double bonds 1.228 Å, N-C single bond (adjacent to =O) 1.347 Å, N-C single bond (not adjacent to =O) 1.474 Å. All these bond lengths agree well with previously found values (*Tables of Interatomic Distances*, 1965). The angles between atoms in this chain are also as expected.

Although in the present molecule the naphthalene group is monosubstituted, some comparison can be made with the dimensions found by Cruickshank (1957) in naphthalene. In that determination, the molecule was located about a centre of symmetry: the average bond distances and angles are shown below.



$$a = 1.361, b = 1.425, c = 1.421, d = 1.410 \text{ \AA} .$$

$$\alpha = 120.51^\circ, \beta = 120.25^\circ, \gamma = 119.23^\circ .$$

Within the accuracy of that determination ( $R=0.12$ , hydrogen parameters not refined), the differences between the lengths observed for  $b$ ,  $c$  and  $d$  are not too significant. In the present molecule, the four bonds comparable to  $a$  in naphthalene are the shortest: the distances being 1.363, 1.335, 1.350 and 1.381 Å. The four angles comparable to  $\gamma$  are the smallest; all being less than 120°. The angles comparable to  $\alpha$  and  $\beta$  are greater than 120°, except for the internal angle at C(11). The internal variations between the remaining bond distances in the naphthalene group are considerable, but appear to follow no regular pattern. In most cases, those bonds closest to the substituted carbon C(11) are longer than their counterparts; but the considerable

Table 8. Least-squares planes calculations for the naphthalene grouping\*

|         | C(11)   | C(12)   | C(13)   | C(14)   | C(15)  | C(20)  | C(16)   | C(17)   | C(18)   | C(19)   | C(10)    |
|---------|---------|---------|---------|---------|--------|--------|---------|---------|---------|---------|----------|
| Plane 1 | -0.004  | 0.004   | 0.000   | -0.005  | 0.004  | 0.000  | (0.023) | (0.062) | (0.089) | (0.044) | (-0.014) |
| Plane 2 | (0.023) | (0.072) | (0.080) | (0.043) | 0.009  | -0.004 | -0.006  | 0.010   | -0.004  | -0.005  | (0.003)  |
| Plane 3 | -0.013  | 0.016   | 0.019   | -0.012  | -0.015 | -0.024 | -0.002  | 0.006   | 0.028   | -0.003  | (-0.028) |

\* Distances from the planes are given in Å. Distances given in parentheses are for atoms given zero weight in the calculation of the particular plane.

difference between C(18)–C(19) and C(13)–C(14) is an exception to this.

Unlike the benzene ring discussed above, the naphthalene grouping is significantly non-planar. Least-squares planes calculations are shown in Table 8.

Both the six-membered rings (planes 1,2) making up the naphthalene group are planar to within experimental error. However, the deviations from the least-squares plane for the 10 atoms making up the naphthalene group appear to be significant but the results are not as conclusive as they would be if the thermal motion of the molecule were less. Calculations show that the planes of the two six-membered rings intersect at an angle of  $1.8^\circ$ .

The non-planarity of the naphthalene group does not appear to be the consequence of packing or of molecular configuration. The methyl group C(23) bonded to C(10) is directed away from the plane of the naphthalene group. The *c* projection of the unit cell is shown in Fig. 4. There are no significantly short intramolecular contacts; there are only two distances between non-hydrogen atoms under  $3.0 \text{ \AA}$ . These are C(8)–C(21) at  $2.91 \text{ \AA}$  and C(22)–O(1) at  $2.98 \text{ \AA}$ . None of the intermolecular distances are significantly short; the minimum distances between the naphthalene and benzene groups involve hydrogen atoms: C(2)–H(14) ( $x-1, y, z$ ) at  $2.75 \text{ \AA}$  and C(18)–H(2) ( $1-x, y-\frac{1}{2}, 1-z$ ) at  $3.00 \text{ \AA}$ .

The hydrogen atoms, as can be seen in Fig. 2, have all refined to acceptable positions and the C–H distances are listed in Table 4. The average C–H bond length is  $1.025 \text{ \AA}$ , a value which is somewhat shorter than the standard C–H bond length but is typical of X-ray diffraction work. The three methyl groups all have approximately staggered configurations.

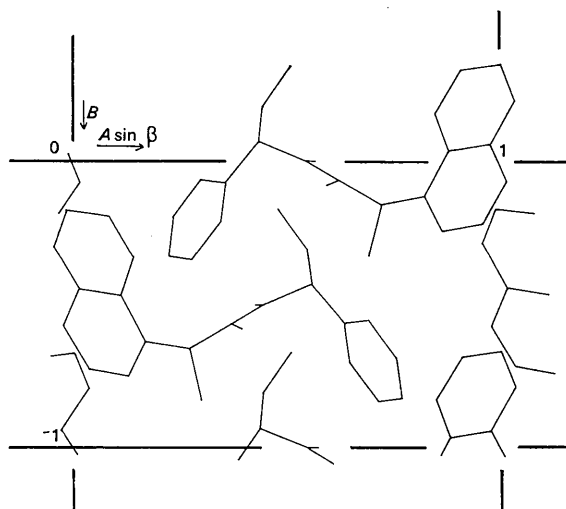


Fig. 4. The *c* projection of the unit cell.

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## The Use of a 'Connectivity' or 'Bonding' Array in Molecular Geometry Calculations

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A symmetric array can be formed in computer store from a connectivity or bonding scheme for the crystallographic asymmetric unit. Its application to the systematic evaluation of bond lengths, direction cosines, valence angles and dihedral (torsion) angles is discussed.

### Introduction

The calculation of the various geometrical characteristics of a molecule or crystal structure is lengthy, but

mathematically trivial. Computer programs for this task require either the calculation of all possible interatomic distances less than a specified limit (*e.g.* Rollett, 1965), a process easy to use but wasteful of computer time (and requiring the user to sift a large volume of output), or the calculation of specified distances, a process wasteful of the user's time and prone to mis-

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