

will be published elsewhere in due course.) The 4,6-dilithio derivative of dibenzofuran, obtained from the reaction of dibenzofuran with three equivalents of *sec*-butyllithium, was treated with dimethylformamide to afford dibenzofuran-4,6-dicarboxaldehyde. The Wittig-type reaction of this dialdehyde with diethylbenzylphosphonate and <sup>t</sup>BuOK in dry dimethylformamide gave 4,6-(2,2-diphenylethenyl)dibenzofuran in good yield. This stilbenoid was converted to the desired diphenanthro[1,2-*b*:2',1'-*d*]furan [m.p. 583–587 K (dec.)] by irradiation with UV light in the presence of air and iodine. The diphenanthro-furan was crystallized from solution in dimethoxyethane to provide the experimental sample.

The sample was mounted on a quartz pin with epoxy cement and a unit cell was determined at room temperature (295 K). The following non-idealized parameters were obtained from a least-squares fitting of the setting angles for 25 centered reflections:  $a = 6.825$  (2),  $b = 34.842$  (4),  $c = 7.749$  (1) Å,  $\alpha = 90.01$  (2),  $\beta = 90.01$  (2),  $\gamma = 90.01$  (2)°,  $V = 1842.8$  (6) Å<sup>3</sup>. The crystal was then cooled to 191 K utilizing a Molecular Structure Corporation low-temperature apparatus. The stated temperature was measured continuously during data collection in the cold gas flow just upstream of the crystal; the estimated uncertainty of the crystal temperature is  $\pm 2$  K. Unit-cell parameters for the low-temperature cell were obtained from a symmetry-constrained least-squares fit of the same reflections used to determine the room-temperature cell. The low-temperature unit-cell parameters are given in the *Experimental* section.

Data were collected utilizing graphite-monochromated radiation. Scan widths were  $(1.4 + 0.35\tan\theta)^\circ$  in  $\omega$ , with a background/scan time ratio of 1:2. No corrections were made for decay or absorption; the data were corrected for Lorentz and polarization effects. Systematic absences ( $0kl$ ,  $k+l = \text{odd}$ ;  $hk0$ ,  $h = \text{odd}$ ) were consistent with two space groups: *Pnma* and *Pna2*<sub>1</sub>. Since intensity statistics indicated a centrosymmetric space group, *Pnma* (No. 62) was given initial preference; refinement proceeded well and it was adopted.

The direct-methods program *SHELXS86* (Sheldrick, 1985) was used to generate an *E* map from which the initial positions of the non-H atoms were identified. Fourier difference methods were then used to locate the H atoms. The C and O atoms were refined anisotropically and the H atoms isotropically using full-matrix least squares (*TEXSAN*; Molecular Structure Corporation, 1989). The weighting scheme used was  $w = \sigma_F^{-2}$ , where  $\sigma_F = \sigma_{II}/2FLp$  and  $\sigma_I^2 = \sigma_{\text{cs}}^2(I) + (0.03I)^2$ . The maximum peak on the final electron density difference map was located at (−0.04, 0.25, 1.08), approximately at the midpoint of the C(2)—C(2<sup>1</sup>) bond; the minimum peak was located at (0.27, 0.36, 0.95) approximately at the center of the C(9)—C(14) ring.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, isotropic displacement parameters and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71246 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1052]

## References

- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.  
 Cioslowski, J., O'Connor, P. B. & Fleischmann, E. D. (1991). *J. Am. Chem. Soc.* **113**, 1086–1089.  
 Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 71, 148. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)  
 Fitzgerald, L. J., Gallucci, J. C. & Gerkin, R. E. (1993). *Acta Cryst.* **C49**, 398–400.  
 Gerkin, R. E., Lundstedt, A. P. & Reppart, W. J. (1984). *Acta Cryst.* **C40**, 1892–1894.  
 Gerkin, R. E. & Reppart, W. J. (1985). *Acta Cryst.* **C41**, 961–963.  
 Gerkin, R. E. & Reppart, W. J. (1986). *Acta Cryst.* **C42**, 480–482.  
 Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.  
 Kay, M. I., Okaya, Y. & Cox, D. E. (1971). *Acta Cryst.* **B27**, 26–33.  
 Molecular Structure Corporation (1989). *TEXSAN. TEXRAY Structure Analysis Package*. Version 5.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.  
 Reppart, W. J., Gallucci, J. C., Lundstedt, A. P. & Gerkin, R. E. (1984). *Acta Cryst.* **C40**, 1572–1576.  
 Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing 3*, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford Univ. Press.  
 Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

*Acta Cryst.* (1993). **C49**, 1952–1958

## Redetermination of the Structures of 1-Naphthoic Acid and 2-Naphthoic Acid

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### Abstract

The structures of 1-naphthoic acid and 2-naphthoic acid have been investigated in order to determine the degree of disorder of the carboxylic acid groups. 1-Naphthoic acid was found to be completely ordered with C—O bond lengths of 1.214 (3) and 1.312 (3) Å, and C—C—O bond angles of 124.8 (2) and 114.2 (2)°. 2-Naphthoic acid was found to possess a significant degree of disorder with C—O bond lengths of 1.256 (3) and 1.274 (3) Å, and C—C—O bond angles of 117.7 (2) and 119.1 (2)°. In 2-naphthoic acid, the acid H atom was refined at two sites with 0.5 occupancy at each. Analysis of the anisotropic displacement ellipsoids of the acid O atoms for each structure demonstrated that these

parameters are consistent with thermal motion of the O atoms. These results indicated that the proton, but not the O atoms, is disordered in the carboxylic acid group of 2-naphthoic acid. In each structure, the acid molecules form cyclic dimers about inversion centers, with an O...O(acceptor) distance of 2.653 (3) in 1-naphthoic acid and 2.618 (3) Å in 2-naphthoic acid. The cyclic dimers form layers in each of these structures wherein lateral closest intermolecular approaches to the acid O atoms are from ring H atoms. The intermolecular O...H close approaches, together with the intramolecular close approaches, are very uniform in distance and angle of approach for the two O atoms in the 2-naphthoic acid structure. In 1-naphthoic acid, the corresponding approaches are much less uniform due primarily to the presence of an H atom in a position *peri* to the carboxylic acid group. The layers are stacked in notably different arrangements which, however, conform closely to two categories of arrangement developed originally to describe the structures of benzoic acids.

### Comment

The structures of 1-naphthoic acid (Trotter, 1960) and 2-naphthoic acid (Trotter, 1961) have been reported based upon visual estimation of intensities of photographic data. The accuracy of the data did not permit refinement of the H atoms. Moreover, the reported configurations of the acid groups indicated that some disordering of the acid H atoms may be occurring. In our investigations of the structures of various dicarboxylic acids of naphthalene [1,8-naphthalenedicarboxylic acid (Fitzgerald, Gallucci & Gerkin, 1991), 1,2-naphthalenedicarboxylic acid (Fitzgerald, Gallucci & Gerkin, 1992) and 2,3-naphthalenedicarboxylic acid (Fitzgerald & Gerkin, 1992)], a wide range of carboxylic acid group disorder has been observed. It was therefore of interest to reinvestigate the structures of 1-naphthoic acid and 2-naphthoic acid in order to determine the extent of possible acid-H-atom disorder.

The unit cells determined for 1-naphthoic acid and 2-naphthoic acid in this study agree with those of Trotter within twice their combined uncertainties; the space-group assignments are also in agreement. The patterns of bond lengths and bond angles for the naphthalene cores of the two structures in the present study demonstrate values consistent with the dicarboxylic acids of naphthalene mentioned above, 1-naphthoic acid having a mean naphthalenic C—C bond length of 1.40 (3) Å and 2-naphthoic acid having a mean naphthalenic C—C bond length of 1.39 (3) Å. The C atoms of the naphthalene rings in 1-naphthoic acid have a mean deviation of 0.010 (5) Å from the best least-squares plane describ-

ing these atoms; the corresponding value for 2-naphthoic acid is 0.003 (2) Å.

The dihedral angle formed by the plane defined by C(11), O(1) and O(2) and the least-squares plane of the naphthalene rings was found to be 8.4 (3)° for 1-naphthoic acid and 1.4 (5)° for 2-naphthoic acid. The small deviation from planarity of the naphthalene rings and the nearly coplanar conformation of the carboxylic acid groups with respect to the naphthalene rings of these two structures occur despite significant intramolecular close approaches for O(1) and O(2) as shown in Figs. 1 and 2. For each of these structural results the present study is in general agreement with that of Trotter.

The configurations of the carboxylic acid groups in the present study are, however, significantly different from those of Trotter's study. The O—C—O angles reported by Trotter are 110° for 1-naphthoic acid and 112° for 2-naphthoic acid and thus considerably smaller than typical values (Borthwick, 1980). In the present study the O—C—O angles have values of 121.1 (2) and 123.2 (2)° for 1-naphthoic acid and 2-naphthoic acid, respectively. The values of the C—O bond lengths and C—C—O bond angles in 1-naphthoic acid in the present study indicate that

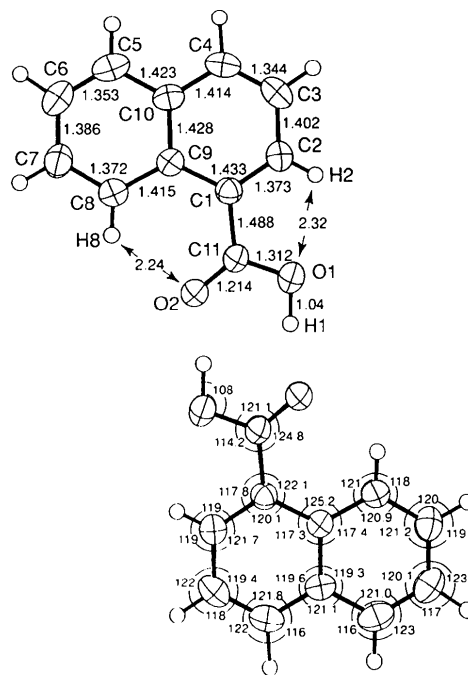


Fig. 1. An ORTEP (Johnson, 1976) drawing of two 1-naphthoic acid molecules in their cyclic-dimer arrangement. The molecules are related by an inversion center. One molecule shows the numbering scheme together with selected interatomic distances, the other shows bond angles. The maximum e.s.d.'s for distances and angles involving C and O atoms are 0.004 Å and 0.3°, respectively, and the maximum e.s.d.'s for distances and angles involving H atoms are 0.03 Å and 2°, respectively.

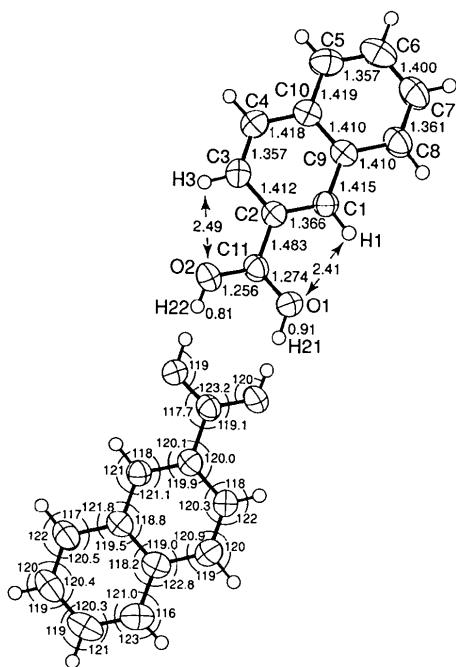


Fig. 2. An ORTEPII (Johnson, 1976) drawing of two 2-naphthoic acid molecules in their cyclic-dimer arrangement. The molecules are related by an inversion center. One molecule shows the numbering scheme together with selected interatomic distances and the other molecule shows bond angles. The maximum e.s.d.'s for distances and angles involving C and O atoms are 0.005 Å and 0.3°, respectively. The maximum e.s.d.'s for distances and angles involving ring H atoms are 0.03 Å and 2°, respectively, and for the 0.5 occupancy acid H atoms, 0.10 Å and 6°, respectively.

this carboxylic acid group is completely ordered. Consistent with this arrangement, only one acid-H-atom position was located on the difference map and refined in the least-squares process. For 2-naphthoic acid, the C—O bond lengths and C—C—O bond angles indicate a significant disordering of the acid H atom. The difference map in this case had two acid-H-atom positions which were refined with 0.5 occupation factors. The potential disorder indicated for 1-naphthoic acid in Trotter's report is clearly not present. For 2-naphthoic acid, the disorder indicated by Trotter's work is confirmed, but his C—O bond lengths [1.33 (2) and 1.37 (2) Å] and C—C—O bond angles (122 and 127°) are significantly larger than the present values.

The disordering of carboxylic acid groups has been described by Leiserowitz (1976) as a static process whereby the carboxylic acid groups are rotated 180° about the C—C bond, adopting alternate orientations throughout the crystal. Disorder such as this would not only produce two positions for the acid H atom, but two positions for each acid O atom, approximately 0.25 Å apart, resulting in an enlarged displacement parameter for the acid O atoms. Addi-

tionally, the principal component of the carboxylic O-atom displacement would be very nearly in the plane defined by the carboxyl C atom and the two carboxyl O atoms.† Analysis of the principal-axis components of selected anisotropic displacement ellipsoids for the present structures (Table 2) shows that the principal component for each of the carboxyl O atoms forms angles between 74 and 87° with the respective COO planes, and between 79 and 89° with the respective C—O bonds. This orientation of the principal component of the carboxyl O-atom displacement ellipsoids is much more consistent with thermal motion of the O atoms than with the static orientational disorder described by Leiserowitz (1976). It is also important to note that the displacement ellipsoids show no significant differences between the ordered 1-naphthoic acid and the disordered 2-naphthoic acid. In fact, 1-naphthoic acid has larger principal components for the carboxyl O atoms than does 2-naphthoic acid, evidence which again is inconsistent with static orientational disorder. Solid-state NMR studies (Meier, Graf & Ernst, 1982; Nagaoka, Terao, Imashiro, Saika, Hirota & Hayashi, 1983) have been interpreted as showing that the disorder in carboxylic acids is a dynamic process, with the acid proton oscillating rapidly between the two O atoms of the dimer. The orientation of, and the relative size of, the anisotropic displacement ellipsoids for the carboxyl O atoms of the present study are consistent with this dynamic proton-disordering model. Analysis of the anisotropic displacement ellipsoids in 1,8-naphthalenedicarboxylic acid (Fitzgerald *et al.*, 1991) led to the same conclusion, *i.e.* ordered O atoms, disordered H atoms.

Stereoviews of the unit cells of both 1-naphthoic acid and 2-naphthoic acid are shown in Fig. 3. In both cases, the molecules form cyclic dimers about inversion centers; the parameters describing the hydrogen bonds are listed in Table 3. These dimers are arranged in layers which in 1-naphthoic acid form a 23° angle with the *ac* cell face, and in 2-naphthoic acid a 46° angle with the *ac* cell face. Within a layer, lateral closest approaches occur between carboxyl O atoms and ring H atoms. These intermolecular O···H close approaches together with the intramolecular close approaches (excluding hydrogen-bonding approaches) are very uniform in distance and angle of approach for the two O atoms

† In the discussion of the disordered H atoms in 1,8-naphthalenedicarboxylic acid (Fitzgerald *et al.*, 1991) it was incorrectly stated that static orientational disorder would cause one of the principal axes of the carboxyl O atoms to lie along the C—O bond. A more accurate analysis shows that the principal axis would be near the COO plane and form a 65° angle with its own C—O bond as pointed out by Thompson, Lalancette & Vanderhoff (1992).

in the 2-naphthoic acid structure. The closest intermolecular approaches are: O(1)—H(4<sup>i</sup>) 2.59 (3) and O(2)—H(3<sup>ii</sup>) 2.72 (3) Å [Symmetry code: (i)  $x + 1, y - 1, z$ ; (ii)  $-x + 1, -y, -z$ ]. The closest non-bonded intramolecular approaches for O(1) and O(2) are shown in Fig. 2. The direction these atoms take in approaching the acid O atoms can be described by the hydrogen-bonded O...O...H angle. The O and H atoms described above for 2-naphthoic acid have the following angles of approach: O(2<sup>vi</sup>)...O(1)...H(4<sup>i</sup>) 87 (1), O(1<sup>vi</sup>)...O(2)...H(3<sup>ii</sup>) 87 (1), O(2<sup>vi</sup>)...O(1)—H(1) 160 (1) and O(1<sup>vi</sup>)...O(2)...H(3) 158 (1)° [symmetry code: (vi)  $-x + 2, -y - 1, -z$ .] The

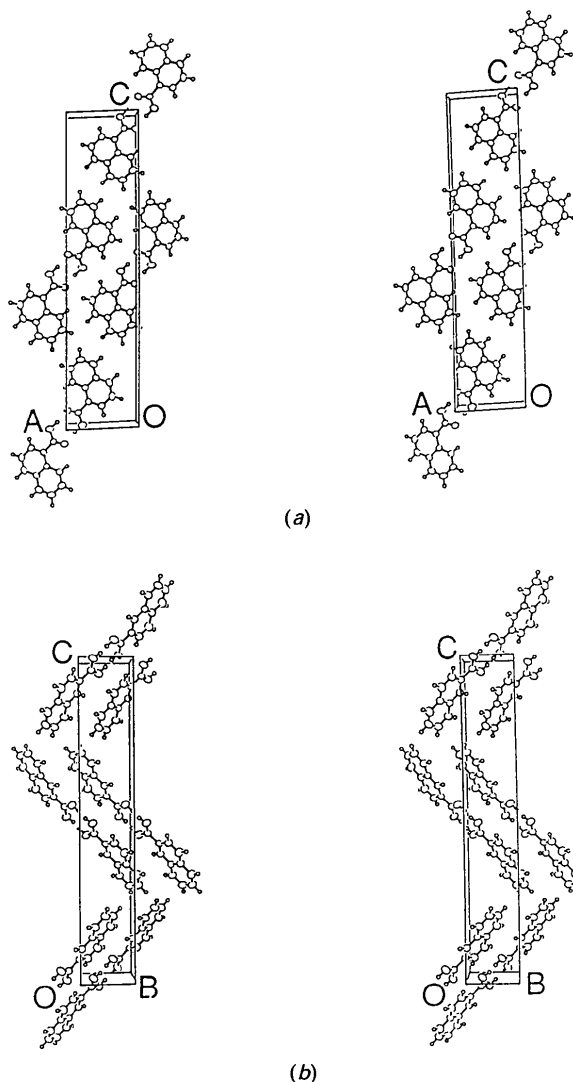


Fig. 3. Stereodiagrams showing (a) unit-cell packing of 1-naphthoic acid (ORTEPII; Johnson, 1976) viewed down the *b* axis (unit-cell contents plus four additional molecules are shown); (b) unit-cell packing of 2-naphthoic acid (ORTEPII; Johnson, 1976) viewed down the *a* axis (unit-cell contents plus seven additional molecules are shown).

corresponding intermolecular and intramolecular approaches in 1-naphthoic acid are much less uniform, due primarily to the presence of a *peri* H atom, H(8). The closest intermolecular approaches are: O(1)...H(2<sup>iv</sup>) 2.79 (3) and O(2)...H(3<sup>v</sup>) 2.76 (3) Å [symmetry code: (iv)  $-x + 1, -y + 1, -z + 1$ ; (v)  $x - 1, y - 1, z$ ]. The closest non-bonded intramolecular approaches are shown in Fig. 1. The angles of approach for these H atoms to the acid O atoms in 1-naphthoic acid are: O(2<sup>iii</sup>)...O(1)...H(2<sup>iv</sup>) 100 (1), O(1<sup>iii</sup>)...O(2)...H(3<sup>v</sup>) 73 (1), O(2<sup>iii</sup>)...O(1)...H(2) 161 (1) and O(1<sup>iii</sup>)...O(2)...H(8) 130 (1)° [symmetry code: (iii)  $-x, -y, -z + 1$ ]. The uniformity of the O-atom environment is suggested by Leiserowitz (1976) as the reason for disordering in benzoic acids and these structures are consistent with that view. The stacking arrangements for the two structures are shown in Fig. 4. These two stacking arrangements are notably different from each other, but conform closely to two of the categories developed by Miller, Curtin & Paul (1974) for benzoic acids. These two categories were described by Leiserowitz (1976) as 'stacking' and 'antiparallel'. The 1-naphthoic acid structure conforms to the former while the 2-naphthoic acid structure conforms to the latter.

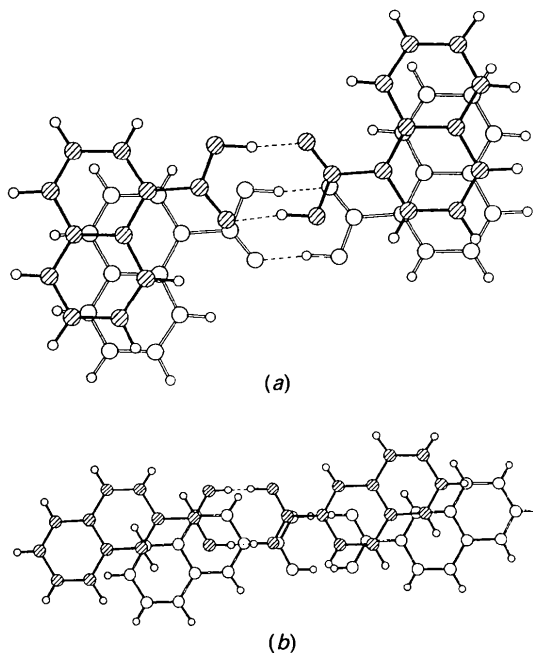


Fig. 4. PLUTO diagrams (Motherwell & Clegg, 1978) showing (a) the overlap of two cyclic dimers in 1-naphthoic acid. One layer is highlighted with filled bonds and crosshatched C and O atoms. The overlap, in agreement with Miller *et al.* (1974), places a carboxyl C atom over a carboxyl O atom. Part (b) shows the overlap of two cyclic dimers in 2-naphthoic acid. One layer is highlighted with filled bonds and crosshatched C and O atoms. The overlap, in agreement with Miller *et al.* (1974), places a carboxyl C atom over a *meta* ring C atom.

**Experimental****1-Naphthoic acid***Crystal data*

$C_{11}H_8O_2$   
 $M_r = 172.18$   
 Monoclinic  
 $P2_1/c$   
 $a = 6.906 (3) \text{ \AA}$   
 $b = 3.842 (5) \text{ \AA}$   
 $c = 30.958 (3) \text{ \AA}$   
 $\beta = 92.04 (2)^\circ$   
 $V = 821 (1) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.39 \text{ Mg m}^{-3}$

*Data collection*

Rigaku AFC-5S diffractometer  
 $\omega$  scans  
 Absorption correction: none  
 2316 measured reflections  
 2148 independent reflections  
 1050 observed reflections  
 $[I > 3\sigma(I)]$

*Refinement*

Refinement on  $F$   
 Final  $R = 0.046$   
 $wR = 0.055$   
 $S = 1.93$   
 1050 reflections  
 151 parameters  
 All H-atom parameters refined  
 $w = \sigma_F^{-2}$   
 $(\Delta/\sigma)_{\max} < 0.01$   
 $\Delta\rho_{\max} = 0.16 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.17 \text{ e \AA}^{-3}$

**2-Naphthoic acid***Crystal data*

$C_{11}H_8O_2$   
 $M_r = 172.18$   
 Monoclinic  
 $P2_1/n$   
 $a = 5.619 (2) \text{ \AA}$   
 $b = 4.957 (3) \text{ \AA}$   
 $c = 30.419 (3) \text{ \AA}$   
 $\beta = 92.38 (3)^\circ$   
 $V = 846.5 (5) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.35 \text{ Mg m}^{-3}$

*Data collection*

Rigaku AFC-5S diffractometer  
 $\omega$  scans  
 Absorption correction: none

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073 \text{ \AA}$   
 Cell parameters from 25 reflections  
 $\theta = 14-15^\circ$   
 $\mu = 0.089 \text{ mm}^{-1}$   
 $T = 296 \text{ K}$   
 Plate  
 $0.38 \times 0.38 \times 0.15 \text{ mm}$   
 Colorless

$R_{\text{int}} = 0.013$   
 $\theta_{\max} = 27.5^\circ$   
 $h = 0 \rightarrow 8$   
 $k = 0 \rightarrow 4$   
 $l = -40 \rightarrow 40$   
 6 standard reflections monitored every 150 reflections  
 intensity variation:  $\pm 2.0\%$

Extinction correction: Zachariasen (1963, 1968)  
 Extinction coefficient:  $1.66 (64) \times 10^{-6}$   
 Atomic scattering factors from Cromer & Waber (1974) for C and O atoms and from Stewart, Davidson & Simpson (1965) for H atoms

$R_{\text{int}} = 0.021$   
 $\theta_{\max} = 27.5^\circ$   
 $h = 0 \rightarrow 7$   
 $k = 0 \rightarrow 6$   
 $l = -39 \rightarrow 39$

2393 measured reflections  
 2178 independent reflections  
 1022 observed reflections  
 $[I > 3\sigma(I)]$

*Refinement*

Refinement on  $F$   
 Final  $R = 0.041$   
 $wR = 0.055$   
 $S = 1.99$   
 1022 reflections  
 155 parameters  
 All H-atom parameters refined  
 $w = \sigma_F^{-2}$   
 $(\Delta/\sigma)_{\max} < 0.01$   
 $\Delta\rho_{\max} = 0.16 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.17 \text{ e \AA}^{-3}$

6 standard reflections monitored every 150 reflections  
 intensity variation:  $\pm 2.5\%$

Extinction correction: Zachariasen (1963, 1968)  
 Extinction coefficient:  $1.05 (53) \times 10^{-6}$   
 Atomic scattering factors from Cromer & Waber (1974) for C and O atoms and from Stewart, Davidson & Simpson (1965) for H atoms

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ )

$B_{\text{eq}} = (8\pi^2/3)\sum_i\sum_j B_{ij}a_i^*a_j^*a_i \cdot a_j$				
	$x$	$y$	$z$	$B_{\text{eq}}$
1-Naphthoic acid				
O(1)	0.2289 (3)	0.2164 (7)	0.49220 (6)	5.7 (1)
O(2)	0.0233 (2)	-0.0576 (6)	0.44819 (5)	5.2 (1)
C(1)	0.3122 (3)	0.1814 (6)	0.41931 (7)	3.0 (1)
C(2)	0.4883 (4)	0.3222 (8)	0.43165 (8)	3.7 (1)
C(3)	0.6294 (4)	0.3971 (8)	0.40157 (10)	4.3 (1)
C(4)	0.5921 (4)	0.3300 (8)	0.35948 (9)	4.1 (1)
C(5)	0.3772 (4)	0.1144 (8)	0.29991 (8)	4.2 (1)
C(6)	0.2056 (4)	-0.0199 (8)	0.28563 (8)	4.4 (1)
C(7)	0.0613 (4)	-0.0868 (8)	0.31447 (8)	4.2 (1)
C(8)	0.0899 (4)	-0.0259 (7)	0.35791 (8)	3.6 (1)
C(9)	0.2675 (3)	0.1107 (6)	0.37461 (7)	2.9 (1)
C(10)	0.4140 (3)	0.1847 (6)	0.34454 (7)	3.2 (1)
C(11)	0.1739 (3)	0.1022 (7)	0.45374 (7)	3.3 (1)
H(1)	0.122 (4)	0.147 (9)	0.5135 (10)	7.1 (8) †
H(2)	0.515 (4)	0.363 (7)	0.4598 (8)	4.9 (7) †
H(3)	0.756 (4)	0.496 (7)	0.4101 (8)	4.7 (6) †
H(4)	0.697 (3)	0.381 (7)	0.3351 (8)	4.8 (6) †
H(5)	0.483 (3)	0.169 (6)	0.2804 (7)	3.2 (5) †
H(6)	0.192 (4)	-0.075 (7)	0.2540 (9)	5.1 (6) †
H(7)	-0.064 (4)	-0.182 (7)	0.3032 (8)	5.2 (7) †
H(8)	-0.011 (3)	-0.075 (7)	0.3760 (8)	3.8 (6) †
2-Naphthoic acid				
O(1)	1.1248 (3)	-0.3622 (5)	0.04817 (6)	4.8 (1)
O(2)	0.7946 (4)	-0.2572 (5)	0.00899 (6)	4.9 (1)
C(1)	1.0313 (5)	0.0236 (6)	0.11059 (8)	3.6 (1)
C(2)	0.8789 (4)	-0.0182 (5)	0.07509 (7)	3.5 (1)
C(3)	0.6681 (5)	0.1357 (6)	0.07011 (9)	4.3 (1)
C(4)	0.6151 (5)	0.3239 (6)	0.10059 (10)	4.6 (1)
C(5)	0.7201 (6)	0.5638 (7)	0.17069 (11)	5.0 (2)
C(6)	0.8729 (7)	0.6031 (7)	0.20584 (10)	5.4 (2)
C(7)	1.0829 (7)	0.4517 (7)	0.21048 (10)	5.3 (2)
C(8)	1.1362 (6)	0.2636 (7)	0.17980 (9)	4.7 (1)
C(9)	0.9809 (4)	0.2182 (5)	0.14294 (7)	3.6 (1)
C(10)	0.7691 (5)	0.3698 (6)	0.13795 (8)	3.8 (1)
C(11)	0.9345 (5)	-0.2255 (5)	0.04188 (8)	3.6 (1)
H(1)	1.170 (4)	-0.087 (5)	0.1132 (8)	4.3 (6) †
H(3)	0.567 (5)	0.096 (6)	0.0471 (9)	5.3 (7) †
H(4)	0.467 (5)	0.432 (6)	0.0970 (9)	5.8 (7) †
H(5)	0.581 (5)	0.662 (6)	0.1664 (9)	5.3 (8) †
H(6)	0.840 (5)	0.735 (7)	0.2276 (9)	6.7 (8) †
H(7)	1.186 (5)	0.484 (6)	0.2342 (9)	6.0 (7) †
H(8)	1.286 (5)	0.149 (7)	0.1825 (9)	6.5 (8) †
H(21)	1.16 (1)	-0.49 (2)	0.029 (3)	7 (2) †
H(22)	0.81 (2)	-0.39 (2)	-0.007 (3)	9 (3) †

† Refined isotropically.

Table 2. *Principal-axis components ( $\text{\AA}^2 \times 10^4$ ) of the anisotropic displacement ellipsoids of the carboxyl O atoms in the title structures with orientation angles ( $^\circ$ )*

The orientation angles specify the orientation of the ellipsoids with respect to the relevant C—O bond and the relevant C—O—O plane. Principal-axis components of the anisotropic ellipsoids for the carboxyl C atom and for the ring C atoms having the largest or smallest values of  $B_{\text{eq}}$  are given for comparison.

	$u_1$	$u_2$	$u_3$	Angle with C—O bond			Angle with C—O—O plane		
				$u_1$	$u_2$	$u_3$	$u_1$	$u_2$	$u_3$
1-Naphthoic acid									
O1	1347	477	344	89	79	2	87	1	1
O2	1205	385	367	87	46	64	86	10	6
C11	521	417	325	—	—	—	—	—	—
C6	765	558	363	—	—	—	—	—	—
C9	415	372	311	—	—	—	—	—	—
2-Naphthoic acid									
O1	908	467	436	86	37	23	81	2	0
O2	912	580	368	79	67	20	74	22	6
C11	541	469	373	—	—	—	—	—	—
C6	1042	575	416	—	—	—	—	—	—
C2	507	439	368	—	—	—	—	—	—

Table 3. *Hydrogen-bond parameters ( $\text{\AA}$ ,  $^\circ$ ) for the title structures with e.s.d.'s given in parentheses*

	O...O	H...O	O—H...O
1-Naphthoic acid			
O(1)—H(1)...O(2 <sup>iii</sup> )	2.653 (3)	1.62 (3)	172 (3)
2-Naphthoic acid			
O(1)—H(21)...O(2 <sup>iii</sup> )	2.618 (3)	1.71 (9)	177 (7)
O(2)—H(22)...O(1 <sup>vi</sup> )	2.618 (3)	1.82 (10)	169 (9)

Symmetry code: (–)  $x, y, z$ ; (iii)  $-x, -y, -z + 1$ ; (vi)  $-x + 2, -y - 1, -z$ .

Crystals of 2-naphthoic acid (Aldrich) were obtained by slow evaporation of an ethanol–water solution at room temperature. In order to produce non-twinned crystals of 1-naphthoic acid (Aldrich) it was necessary to evaporate solvent slowly from a xylene solution at 318 K. In each case, the experimental samples were mounted on pins with epoxy cement and data were collected using graphite-monochromated radiation.

Unit-cell parameters were obtained from symmetry-constrained least-squares fits of 25 centered reflections for each sample. Scan widths were  $(1.6 + 0.35 \tan \theta)^\circ$  in  $\omega$  for both 1-naphthoic acid and 2-naphthoic acid, and the background/scan time ratios were 0.5. The standard reflections were 1,0,22, 1,2,14, 2,0,20, 1,1,1, 0,1,2 and 2,2,3 for 1-naphthoic acid and 1,1,5, 0,1,6, 1,0,1, 3,1,12, 0,3,10 and 2,3,6 for 2-naphthoic acid. No corrections were made for decay or absorption. The data were corrected for Lorentz and polarization effects. Intensity data were found to have symmetry consistent with Laue group  $2/m$ . Systematic absences permitted unique assignments of 1-naphthoic acid to  $P2_1/c$  ( $h0l, l = 2n + 1; 0k0, k = 2n + 1$ ) and of 2-naphthoic acid to  $P2_1/n$  ( $h0l, h + l = 2n + 1; 0k0, k = 2n + 1$ ) (thus, both space groups are No. 14).

The direct-methods program *SHELXS86* (Sheldrick, 1985) produced an  $E$  map for each structure from which the initial positions of the C and O atoms were identified. Fourier difference methods were used to locate the initial positions of the H atoms. The C and O atoms were refined anisotropically, the H atoms isotropically, using full-matrix least squares (*TEXSAN*; Molecular Structure Corporation, 1989). For 2-naphthoic acid, the region between the carboxylic acid dimers was found to contain two possible sites for the acid H atom (see supplementary

material). Disordering of the acid H atom was consistent with the C—O bond lengths for this sample. The acid H atom for 2-naphthoic acid was therefore distributed at half occupancy between these two positions and refined isotropically. Significance testing (Hamilton, 1965) showed this model to be an improvement, at the 0.025 confidence level, over a model with one fully occupied acid H atom.

The weighting scheme used was  $w = \sigma_F^{-2}$ , where  $\sigma_F = \sigma_I/2FLp$  and  $\sigma_I^2 = \sigma_{\text{cs}}^2(I) + (0.03I)^2$ , for both structures. The maximum effect of extinction was 4.4% of  $F_o$  for 111 for 1-naphthoic acid and 4.2% of  $F_o$  for 101 for 2-naphthoic acid. The maximum peak on the electron density difference map for 1-naphthoic acid was located at (0.34, 0.25, 0.36), approximately at the midpoint of the C(9)—C(10) bond, and the minimum peak was located at (0.47, 0.18, 0.39), approximately at the center of the C(1)—C(4), C(9), C(10) ring. For 2-naphthoic acid, the maximum peak was located at (0.61, 0.14, 0.10), approximately 1  $\text{\AA}$  from C(3) and C(4), and the minimum peak was located at (0.32, 0.32, 0.60), approximately at the center of the C(1)—C(4), C(9), C(10) ring.

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Lists of structure factors, anisotropic thermal parameters, complete geometry, least-squares-planes data, a Fourier difference map for 2-naphthoic acid and *ORTEPII* drawings of the title compounds have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71168 (37 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1051]

## References

- Borthwick, P. W. (1980). *Acta Cryst.* **B36**, 628–632.  
 Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 71, 148. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)  
 Fitzgerald, L. J., Gallucci, J. C. & Gerkin, R. E. (1991). *Acta Cryst.* **B47**, 776–782.  
 Fitzgerald, L. J., Gallucci, J. C. & Gerkin, R. E. (1992). *Acta Cryst.* **B48**, 290–297.  
 Fitzgerald, L. J. & Gerkin, R. E. (1992). *Acta Cryst.* **C48**, 1971–1975.  
 Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502–510.  
 Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.  
 Leiserowitz, L. (1976). *Acta Cryst.* **B32**, 775–802.  
 Meier, B. H., Graf, F. & Ernst, R. R. (1982). *J. Chem. Phys.* **76**, 767–774.  
 Miller, R. S., Curtin, D. Y. & Paul, I. C. (1974). *J. Am. Chem. Soc.* **96**, 6340–6349.  
 Molecular Structure Corporation (1989). *TEXSAN*. *TEXRAY* Structure Analysis Package. Version 5.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.  
 Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO*. Program for Plotting Molecular and Crystal Structures. Univ. of Cambridge, England.  
 Nagaoka, S., Terao, T., Imashiro, F., Saika, A., Hirota, N. & Hayashi, S. (1983). *J. Chem. Phys.* **79**, 4694–4703.

- Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing 3*, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford Univ. Press.
- Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3174–3187.
- Thompson, H. W., Lalancette, R. A. & Vanderhoff, P. A. (1992). *Acta Cryst.* **C48**, 66–70.
- Trotter, J. (1960). *Acta Cryst.* **13**, 732–736.
- Trotter, J. (1961). *Acta Cryst.* **14**, 101–105.
- Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.
- Zachariasen, W. H. (1968). *Acta Cryst.* **A24**, 212–216.

*Acta Cryst.* (1993). **C49**, 1958–1961

### Structure and Absolute Configuration of (+)-6-[4-Chlorophenyl](1*H*-1,2,4-triazol-1-yl)methyl]-1-methyl-1*H*-benzotriazole (Vorozole) and its Hydrobromide Monohydrate†

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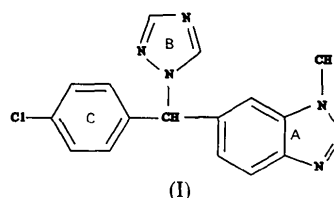
#### Abstract

The (+)-6-[4-chlorophenyl](1*H*-1,2,4-triazol-1-yl)methyl]-1-methyl-1*H*-benzotriazole base (I) and its hydrobromide salt (II) show similar bond angles except for the C—N—C angle of the 1,2,4-triazolyl moiety, which is smaller in (I) than in (II) because of the presence of the lone-pair electrons on the N atom of (I). The molecular conformation of both structures is different, the dihedral angles between the planar moieties are 105.3 (2), 84.6 (1) and 81.3 (1)° in (I) and 110.4 (2), 79.2 (2) and 108.8 (2)° in (II). The absolute configuration at the central chiral C atom of both molecules is *S*.

#### Comment

The cytochrome P450 (P450)-dependent aromatization of androgens into oestrogens is one of the most important reactions involved in steroid hormone biosynthesis (Van den Bossche *et al.*, 1990). So, an aromatase inhibitor might be of help in the treatment of oestrogen-dependent

disorders such as breast cancer, gynaecomastia and endometriosis. The title compound is a potent and selective inhibitor of the human placental aromatase by forming a stable complex with microsomal P450 from human placenta. For a better understanding of this complexation the crystal structure and the absolute configuration of the molecule were determined.



Perspective views showing the atomic numbering scheme for (I) and (II) are given in Figs. 1 and 2, respectively. Bond lengths and bond angles of the base and its salt are similar, except for the ring angle C14—N15—C16 which is smaller in the base because the lone-pair electrons on N15 occupy more space in the valence shell and thus decrease the C—N—C bond angle. In both structures the triazolyl ring *B* and the *p*-chlorophenyl ring *C* are planar within their respective experimental error. The benzotriazolyl ring *A* is also essentially planar. However, the molecular conformation of both structures is different. The dihedral angles between the rings *A* and *B*, *B* and *C*, and *A* and *C* are 84.6 (1), 105.3 (2) and 81.3 (1)° for (I) and 79.2 (2), 110.4 (2) and 108.8 (2)° for (II), respectively. As in previous reports (Nowell, Walker & Anderson, 1982; Branch & Nowell, 1985, 1986; Bruno, Foti, Grassi, Caruso & Risitano, 1988) the exocyclic angles around the N12 atom show considerable asymmetry with C11—N12—C16 being much larger than C11—N12—N13. This asymmetry is also usual in 1,2,3-triazoles (Nagawa, Goto, Honda & Nakanishi, 1987) and is visible in benzotriazole, where C10—N1—C9 is much larger than C10—N1—N2. As described previously (Brisse & Sygusch, 1974; Domenicano & Murray-Rust, 1979) the Cl atom of the *p*-chlorophenyl group causes an increase of the ring angle C19—C20—C21 and a decrease of the ring angles C18—C19—C20 and C20—C21—C22 from the  $sp^2$  value of 120.0°. The deviation of the Cl atom out of the mean ring plane *C* is in agreement with the mean deviation of 0.05 Å given by Brisse & Sygusch (1974).

In both crystals the molecules are held together by C—H...N hydrogen bonds (Taylor & Kennard, 1982). In the hydrobromide salt (II), which crystallizes as a monohydrate, Br is strongly hydrogen bonded to N15 but the water O atom is only weakly hydrogen bonded to C16. The contacts between the water H atoms and Br are all greater than the sum of the van der Waals radii.

For both structures the absolute configuration is *S* at C11 and was determined by calculating the Bijvoet coefficient according to the selection procedure of Beurskens, Noordik & Beurskens (1980).

† Internal codes of Janssen Research Foundation: R83842 and R86636.