

Structure of 1,8-Naphthalenedicarboxylic Acid (Naphthalic Acid), $C_{12}H_8O_4$: Ring Geometry and Hydrogen-Bonding Effects

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Abstract

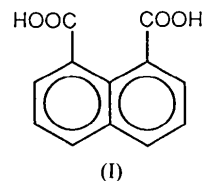
$C_{12}H_8O_4$, $M_r = 216.19$, orthorhombic, $Pbca$, $a = 15.308$ (2), $b = 17.926$ (2), $c = 7.093$ (2) Å, $V = 1946.4$ (5) Å³, $Z = 8$, $D_x = 1.48$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 1.05$ cm⁻¹, $F(000) = 896$, $T = 296$ K, $R = 0.043$ for 912 unique reflections having $I > 3\sigma(I)$. In this structure, 1,8-naphthalenedicarboxylic acid departs significantly from planarity. While the average deviation of carbons from the best least-squares plane for the naphthalene core is 0.055 (4) Å, the carboxyl carbons adopt positions +0.403 (4) and -0.350 (4) Å from that plane. The carboxyl groups are twisted in the same direction with respect to that plane and make an average dihedral angle of 42.6 (3)° with it. The nearly equal lengths of the C—O distances within the carboxyl groups [mean value 1.267 (5) Å] indicate almost complete disorder of the H atoms of these groups. Hydrogen bonding occurs in cyclic dimer fashion between two molecules related by a center of inversion. The carboxyl hydrogens appear to be subject to a symmetric double-minimum potential and to be disordered *via* tunneling; there is no evidence that the carboxyl oxygens are disordered. The mean carboxyl H—O acceptor distance is 1.90 (7) Å.

Introduction

In conjunction with continuing studies of positional disorder of the type displayed by dibenzofuran (Reppart, Gallucci, Lundstedt & Gerkin, 1984), the structures of naphthalenedicarboxylic acids have become of interest to us. This report presents an investigation of crystalline 1,8-naphthalenedicarboxylic acid, whose structure has not previously been described.

Experimental

1,8-Naphthalenedicarboxylic acid, (I), was obtained in an impure form by hydrolysis of technical grade 1,8-naphthalic anhydride from Aldrich Chemical Company. The impure acid was converted to its



disodium salt, which was treated in aqueous solution with Norit A decolorizing carbon. Following filtration of the carbon, nitric acid was added. The precipitate was recovered, dried and subsequently recrystallized from ethyl acetate by evaporation at room temperature. This preparation resulted in a notable profusion of each of three crystalline forms: columns, thin plates and tabular chunks. A tabular crystal with approximate principal dimensions 0.12 × 0.27 × 0.35 mm was selected and mounted with epoxy cement on a glass fiber. The sample was analyzed at room temperature with a Rigaku AFC5S diffractometer utilizing monochromated Mo $K\alpha$ radiation.

Unit-cell parameters were obtained from a symmetry-restricted least-squares fit of the setting angles for 25 centered reflections with $20 < 2\theta < 30^\circ$. Intensity data were measured for 2573 unique reflections (exclusive of standards) with $+h$, $+k$, $+l$ indices ($h_{\max} = 19$; $k_{\max} = 23$; $l_{\max} = 9$) and 2θ values in the range $4 < 2\theta < 55^\circ$. The ω - 2θ scan technique was employed with scan widths $(1.10 + 0.35\tan\theta)^\circ$ in ω , and a background/scan time ratio of 0.5. A variance was assigned to each reflection using the formula $\sigma_I^2 = \sigma_{cs}^2(I) + (0.03I)^2$ where σ_{cs} is based on counting statistics and I is the integrated intensity. Six standard reflections (230, 111, 122, 704, 622, 084) were measured after every 150 reflections; they showed, on average, a maximum non-systematic relative intensity variation of $\pm 2.7\%$. Accordingly, no decay correction was applied. The data were corrected for Lorentz and polarization effects. An absorption correction was not applied.

Among the primitive orthorhombic space groups allowed by the data, the observed systematic absences ($0kl$, $k = \text{odd}$; $h0l$, $l = \text{odd}$; $hk0$, $h = \text{odd}$) uniquely determined the space group as $Pbca$ (No. 61). The direct-methods program *MITHRIL*

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(Gilmore, 1984) in the *TEXSAN* structure analysis package (Molecular Structure Corporation, 1989) was used to generate an *E* map from which the initial positions of all the non-H atoms were identified. Fourier difference methods were used to locate the H-atom positions. Full-matrix least-squares refinement was performed to minimize the function $\sum \sigma_F^{-2} (|F_o| - |F_c|)^2$ in which $\sigma_F = \sigma_I / 2FLp$. Neutral-atom scattering factors and anomalous-dispersion factors were taken from Cromer & Waber (1974) for C and O; the scattering factor for H was taken from Stewart, Davidson and Simpson (1965). Using the data having $I > 3\sigma_I$, the non-H atoms were refined to the anisotropic stage and hydrogen positions were then identified. Owing to the somewhat limited size of the data set, the ring hydrogens were assigned canonical benzene hydrogen geometry (C—H distance = 0.95 Å; $B = 1.2 \times B_{eq}$ of the attached carbon atom) to reduce the number of independent variables. At this stage, the very nearly equal lengths of the two C—O distances in each carboxyl group indicated significant disorder of the carboxyl hydrogens. Consistent with this interpretation was the marked proximity of the O atoms of the inversion-related molecule, indicating strong hydrogen bonding. With no carboxyl hydrogens assigned, for 912 observations having $I > 3\sigma_I$ and 145 variables, $R = 0.052$ and $wR = 0.059$, $w = \sigma_F^{-2}$. The four carboxyl hydrogens of the hydrogen-bonded pair of molecules were first assigned to positions midway between hydrogen-bonded oxygens of the inversion-related pairs. Refinement for this model with 912 observations and 153 variables gave $R = 0.045$ and $wR = 0.047$. It was noted, however, that the isotropic displacement factors for the carboxyl hydrogens were approximately four times as large as expected. The four carboxyl hydrogens of the hydrogen-bonded pair of molecules were then assigned to eight sites (with 0.5 occupancy) each 1 Å from an O atom and on the line of centers of the O atom and its correspondent in the inversion-related mate. These coordinates and isotropic displacement factors were then refined by least-squares methods, converging to the values given below. Evaluating these three models: (a) no carboxyl hydrogens; (b) four carboxyl hydrogens at the midpoint of the O—O distance; and (c) four carboxyl hydrogens at half-occupancy disordered over eight sites, using Hamilton's ratio test (Hamilton, 1965), showed that the model adopted for this report (c) was a significant improvement over the others at the 0.5% level of confidence.

The results of the final refinement cycle were: 912 observations having $I > 3\sigma_I$; 161 variables; $R = 0.043$; $wR = 0.045$; $w = \sigma_F^{-2}$; $S = 1.35$; $(\Delta/\sigma)_{\max} < 0.02$. Maximum and minimum peaks on the final electron density difference map had values +0.17 and -0.20 e Å⁻³ respectively. The maximum peak

Table 1. Final positional parameters and equivalent isotropic and isotropic displacement parameters, B_{eq}/B (Å²), for 1,8-naphthalenedicarboxylic acid, with their estimated standard deviations

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}/B
O(1)	0.8325 (2)	0.0545 (1)	0.0371 (4)	4.7 (1)
O(2)	0.9125 (2)	-0.0339 (1)	0.1752 (4)	3.7 (1)
O(3)	0.9531 (2)	-0.0636 (1)	-0.2034 (4)	3.8 (1)
O(4)	1.0359 (2)	-0.1474 (2)	-0.0550 (5)	5.1 (2)
C(1)	0.7801 (2)	-0.0690 (2)	0.0250 (5)	3.1 (2)
C(2)	0.6952 (3)	-0.0478 (2)	0.0542 (5)	4.3 (2)
C(3)	0.6259 (2)	-0.0986 (3)	0.0354 (6)	5.0 (2)
C(4)	0.6437 (3)	0.1705 (2)	-0.0077 (6)	5.0 (2)
C(5)	0.7470 (3)	-0.2719 (2)	-0.0676 (6)	4.8 (2)
C(6)	0.8292 (3)	0.2977 (2)	-0.0922 (6)	4.9 (2)
C(7)	0.8982 (2)	-0.2470 (2)	-0.1004 (5)	4.0 (2)
C(8)	0.8855 (2)	-0.1721 (2)	-0.0761 (5)	3.1 (2)
C(9)	0.8011 (2)	0.1438 (2)	-0.0312 (5)	3.2 (2)
C(10)	0.7301 (2)	-0.1955 (2)	-0.0390 (5)	3.8 (2)
C(11)	0.8469 (2)	-0.0131 (2)	0.0810 (5)	3.3 (2)
C(12)	0.9627 (2)	-0.1239 (2)	-0.1105 (5)	3.4 (2)
H(7)	0.879 (5)	0.081 (4)	0.041 (11)	4 (2)†
H(8)	0.950 (5)	-0.015 (4)	0.200 (11)	3 (2)†
H(9)	0.998 (4)	0.034 (3)	-0.198 (8)	1 (1)†
H(10)	1.071 (5)	-0.123 (4)	-0.055 (13)	4 (2)†

† Refined isotropically.

was located at $x = 0.88$, $y = -0.04$, $z = -0.32$, approximately 1.44 Å from O(3); the minimum peak was located at $x = -0.20$, $y = 0.01$, $z = 0.05$, on average approximately 1.35 Å from C(1), C(2), C(11) and O(1). [For the final refinement cycle for 1121 independent observations having $I > 3\sigma_I$: $R = 0.060$; $wR = 0.054$; $S = 1.41$; $(\Delta/\sigma)_{\max} < 0.01$. Similarly, for the final refinement cycle for 1704 independent observations having $I > 0$: $R = 0.110$; $wR = 0.060$; $S = 1.24$; $(\Delta/\sigma)_{\max} < 0.01$. These latter results are for comparison purposes only.]

Final atomic coordinates, equivalent isotropic and isotropic displacement parameters and their uncertainties are given in Table 1.* The molecule is shown in Fig. 1.

Since in this structure the asymmetric unit is an entire molecule, there are no symmetry constraints among any sets of distances or angles in the molecule. Selected interatomic distances and angles within the molecule are given with their uncertainties in Table 2. Data regarding hydrogen bonding are given in Table 3.

Subsequent to data collection using the tabular chunk, FT/IR spectra were obtained for each of the crystalline forms present in the sample growth using a Perkin-Elmer infrared microscope. These IR

* Lists of structure factors, anisotropic displacement parameters, positional parameters of ring hydrogens and data pertaining to least-squares best-fit planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54083 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

results permitted identification of the columns as 1,8-naphthalic anhydride, while the tabular chunks and thin plates were identified as 1,8-naphthalenedicarboxylic acid. Further, the unit-cell parameters obtained from a least-squares fit of the setting angles for 25 reflections with $6 < 2\theta < 30^\circ$ from a columnar crystal agreed with those found by Grigor'eva & Chetkina (1975) for naphthalic anhydride. Finally, unit-cell parameters obtained for a thin plate agreed very well with those for the tabular chunk of 1,8-naphthalenedicarboxylic acid.*

Discussion

The molecular structure of 1,8-naphthalenedicarboxylic acid, apart from the basic naphthalene core, is dominated by the strain of accommodating the two carboxyl groups and the hydrogen bonding in which these groups participate.

Bond lengths and angles, given in Table 2, manifest pseudo- C_2 symmetry with the twofold axis lying along the C(9)—C(10) bond. In Fig. 2 results of structural studies of three related molecules are presented: 1,8-bis(dimethylamino)naphthalene (Einspahr, Robert, Marsh & Roberts, 1973), 1,8-dimethoxynaphthalene (Cosmo, Hambley & Sternhell, 1990) and 1,8-naphthalenedicarboxylic

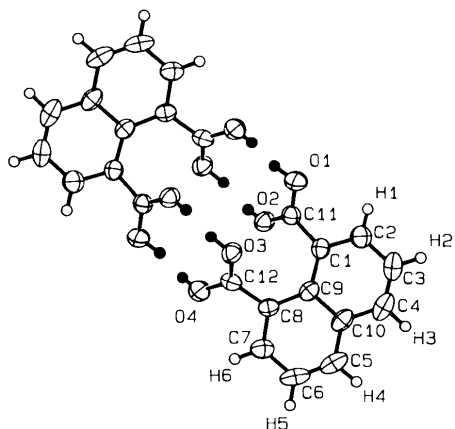


Fig. 1. A view of the 1,8-naphthalenedicarboxylic acid molecule and its inversion-related partner drawn using ORTEPII (Johnson, 1976) and showing the numbering scheme adopted for this report. Thermal ellipsoids are drawn at 50% probability for all atoms except H, for which they have been set artificially small. The filled symbols represent half-occupancy H atoms at the eight least-squares optimized sites of this hydrogen-bonded dimer.

Table 2. Bond lengths (Å) and angles ($^\circ$) for 1,8-naphthalenedicarboxylic acid, with their estimated standard deviations

Naphthalene core			
C(1)—C(2)	1.371 (5)	C(9)—C(1)—C(2)	120.9 (3)
C(2)—C(3)	1.404 (5)	C(1)—C(2)—C(3)	121.5 (3)
C(3)—C(4)	1.353 (5)	C(2)—C(3)—C(4)	119.2 (4)
C(4)—C(10)	1.414 (5)	C(3)—C(4)—C(10)	121.7 (4)
C(5)—C(10)	1.408 (5)	C(4)—C(10)—C(9)	120.0 (3)
C(5)—C(6)	1.352 (6)	C(10)—C(9)—C(1)	116.5 (3)
C(6)—C(7)	1.394 (5)	C(7)—C(8)—C(9)	120.5 (3)
C(7)—C(8)	1.367 (4)	C(8)—C(9)—C(10)	116.7 (3)
C(8)—C(9)	1.424 (5)	C(9)—C(10)—C(5)	119.8 (3)
C(9)—C(10)	1.429 (4)	C(10)—C(5)—C(6)	121.4 (4)
C(9)—C(1)	1.436 (4)	C(5)—C(6)—C(7)	119.2 (4)
		C(6)—C(7)—C(8)	121.8 (4)
Mean C—C	1.396 (30)	Mean interior C—C—C	119.9 (1.8)
		C(8)—C(9)—C(1)	126.7 (3)
		C(5)—C(10)—C(4)	120.1 (4)
Carboxyl groups			
C(1)—C(11)	1.485 (4)	O(1)—C(11)—O(2)	123.3 (3)
C(8)—C(12)	1.485 (5)	O(1)—C(11)—C(1)	117.3 (3)
		O(2)—C(11)—C(1)	119.3 (3)
C(11)—O(1)	1.270 (4)	O(3)—C(12)—O(4)	123.2 (3)
C(11)—O(2)	1.263 (4)	O(3)—C(12)—C(8)	119.2 (3)
C(12)—O(3)	1.273 (4)	O(4)—C(12)—C(8)	117.5 (3)
C(12)—O(4)	1.260 (4)		
O(1)—H(7)	0.85 (8)	C(11)—O(1)—H(7)	112 (5)
O(2)—H(8)	0.69 (7)	C(11)—O(2)—H(8)	130 (7)
O(3)—H(9)	0.87 (6)	C(12)—O(3)—H(9)	113 (4)
O(4)—H(10)	0.69 (8)	C(12)—O(4)—H(10)	120 (7)

* Shok & Gol'der (1970) have reported unit-cell parameters determined from data collected from a thin plate crystallized from a solution of naphthalic anhydride in chlorobenzene: $a = 15.27$, $b = 18.13$, $c = 7.11$ Å, space group $Pbca$. On the basis of the data reported above, it appears that these thin plates were 1,8-naphthalenedicarboxylic acid rather than naphthalic anhydride as reported.

acid (this study). Similarly to the present structure, the 1,8-bis(dimethylamino)naphthalene structure manifests a pseudo-twofold axis lying along the C(9)—C(10) bond (our numbering) while the 1,8-dimethoxynaphthalene structure possesses rigorously twofold axes along the C(9)—(10) bonds (our numbering) of each of the two crystallographically inequivalent molecules in that structure. The bond lengths and angles given in Fig. 2 are values averaged consistent with such C_2 symmetry.*

The bond-length patterns of these three molecules are remarkably similar: C(9)—C(1) \approx C(9)—C(10) > C(4)—C(10) > C(2)—C(3) > C(1)—C(2) > C(3)—C(4), the largest discrepancy (0.019 Å) arising between C(3)—C(4) of the diamino compound and the other two compounds; all other values agree to within less than 0.010 Å.

Comparison of appropriate distances and angles in these three molecules shows the effects of crowding of the 1,8 substituents. In each instance, $\angle C(8)—C(9)—C(10)$ [and $\angle C(1)—C(9)—C(10)$] are $117.1 (3)^\circ$ or less while $\angle C(8)—C(9)—C(1)$ — the exterior angle

* In our calculations we have amended published values from Cosmo, Hambley & Sternhell (1990) for 1,8-dimethoxynaphthalene on the basis of internal consistency of bond lengths and angles as follows: b from 18.849 to 14.849 Å and the y coordinate of C(1) from 0.0005 (1) to -0.0005 (1). Consistent with the b -axis change, D_v changes from 1.044 to 1.33 g cm^{-3} .

Table 3. *Hydrogen-bond parameters for 1,8-naphthalenedicarboxylic acid and related dicarboxylic acids*

1,8-Naphthalenedicarboxylic acid			H—acceptor oxygen distance, neutron adjusted (Å)		Oxygen—H—acceptor oxygen angle, neutron adjusted (°)	
Oxygen—acceptor oxygen	Distance (Å)					
O(1)—O(4) ^y	2.618 (4)	H(7)—O(4) ^y	1.61 (7)	O(1)—H(7)—O(4) ^y	170 (7)	
O(2)—O(3) ^y	2.707 (4)	H(8)—O(3) ^y	1.75 (7)	O(2)—H(8)—O(3) ^y	158 (7)	
O(3)—O(2) ^y	2.707 (4)	H(9)—O(2) ^y	1.69 (6)	O(3)—H(9)—O(2) ^y	173 (5)	
O(4)—O(1) ^y	2.618 (4)	H(10)—O(1) ^y	1.60 (8)	O(4)—H(10)—O(1) ^y	174 (8)	

Related dicarboxylic acids			
	Oxygen—acceptor oxygen distance (Å)	H—acceptor oxygen distance (Å)	Oxygen—H—acceptor oxygen angle (°)
1,4-Naphthalenedicarboxylic acid (Derissen, Timmermans & Schoone, 1979)	2.64 (3)	1.54 (3)	137
Terephthalic acid (Bailey & Brown, 1967)	2.608 (3)	1.53 (1)	168
Phthalic acid (Küppers, 1981)	2.680 (3)	1.70 (2)	177
Isophthalic acid (Alcala & Martinez-Carrera, 1972)	2.594 (6)	1.77 (6)	176
	2.697 (6)	1.98 (6)	162

Symmetry code: none x, y, z ; (i) $2 - x, -y, -z$.

at the upper ring juncture — is $125.7(3)^\circ$ or greater. Coincident with that, the C(1)—C(8) distances range from 2.548 to 2.562 (8) Å while the C(4)—C(5) distances (on the side of the rings opposite the substituents) range from 2.440 to 2.446 (8) Å. Thus the former are considerably longer and the latter are somewhat shorter than the corresponding distance for naphthalene itself: 2.478 (6) Å (Cruickshank, 1957). This geometry allows the 1,8 substituents to be farther apart than would the strict naphthalene geometry. For the diamino compound and the diacid the deviation of angles from 120° continues at C(1) and C(8), the 'inner' exterior angles at these carbons [$\angle C(9)—C(1)—C(11)$ and $\angle C(9)—C(8)—C(12)$] being $121.1(3)^\circ$ or greater and thus providing additional space between the 1,8 substituents. For the

dimethoxy compound, however, the corresponding angles are $117.0(3)^\circ$ and the O atoms are separated by virtually the same distance [2.545 (4) Å] as C(1) and C(8) [2.548 (4) Å].

This rather striking difference also involves differences in the planarity of the three molecules, also illustrated in Fig. 2. The diacid is decidedly non-planar, the C atoms of the naphthalene core having a mean deviation of 0.055 (4) Å from the best least-squares ring plane and the carboxyl carbons C(11) and C(12) being substantially removed from the ring plane, and in opposite directions. The diamino compound is similarly non-planar in the core (mean deviation from the best ring plane is 0.071 Å), with the N atoms, again in opposite directions, even further removed from this plane than the

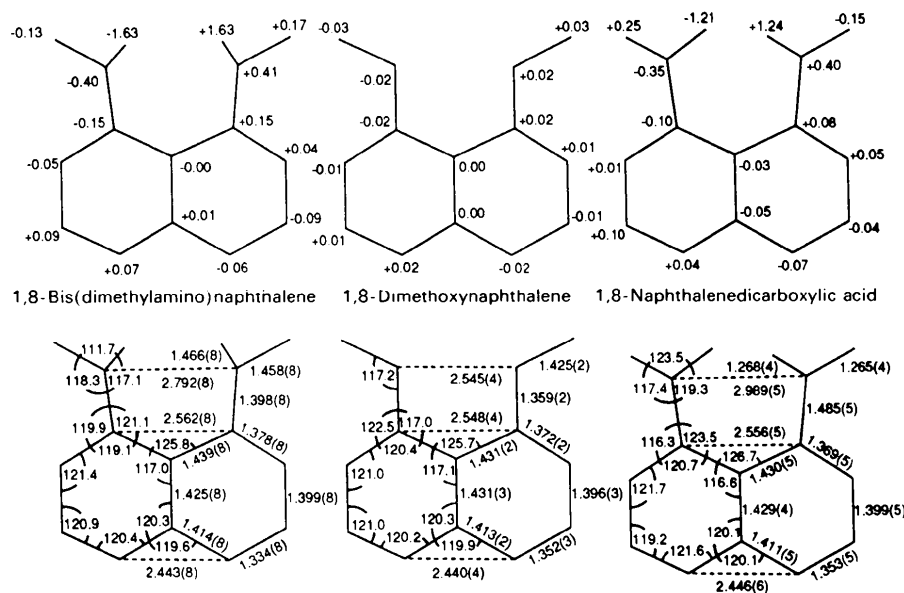


Fig. 2. Geometrical parameters (Å, °) for three well characterized crowded 1,8-disubstituted naphthalene molecules, drawn closely to scale. The angles and distances cited are from corresponding individual values averaged on the assumption that a twofold axis lies along the C(9)—C(10) bond direction (see text). The 1,8-bis(dimethylamino)naphthalene data are based on Einspahr, Robert, Marsh & Roberts (1973); the 1,8-dimethoxynaphthalene data are based on Cosmo, Hambley & Sternhell (1990) (with corrections); the 1,8-naphthalenedicarboxylic acid data are from the present study.

carboxyl carbons of the diacid. The net result is that the C(11)—C(12) distance for the diacid is 2.989 (5) Å and the N—N distance for the diamino compound is 2.792 (8) Å, both of which are substantially greater than the corresponding C(1)—C(8) distances. In contrast, as shown in Fig. 2, the dimethoxynaphthalene is virtually planar – not only in the core, but for the 1,8-methoxy O and C atoms as well. This degree of planarity results in significant nonbonded interactions between the methoxy groups and C(2) and C(7) and their H atoms which tend to force the methoxy groups together, as evidenced by the 122.5 (2)° outer exterior angles [\angle C(2)—C(1)—O and \angle C(7)—C(8)—O] and the 2.545 (4) Å O—O distance cited above. The non-planar ring geometry of both the diamino compound and this diacid call into question the possibility suggested by Cosmo, Hambley & Sternhell (1990) that “the naphthalene nucleus is extraordinarily difficult to deform in the direction perpendicular to the aromatic rings.”

Fig. 3 presents a view of 1,8-naphthalenedicarboxylic acid from a direction in the mean plane of the rings a few degrees from the C(9)—C(10) bond direction. The nonplanarity of the naphthalene core is evident as is the rotation of the carboxyl groups with respect to the naphthalene core which is documented in Fig. 2. The plane defined by carboxyl-group atoms C(11), O(1) and O(2) makes a dihedral angle 42.0 (2)° with the core plane; the plane defined by the carboxyl group atoms C(12), O(3) and O(4) makes a dihedral angle 43.2 (2)° with the core plane. This configuration is similar to that for 1,8-bis(dimethylamino)naphthalene as shown by Einspahr, Robert, Marsh & Roberts (1973) and also to that of 1,8-dinitronaphthalene (Akopyan, Kitai-gorodskii & Struchkov, 1965). The effect of steric interaction can also be seen for atoms C(1) and C(8) whose distances from their respective COO planes are: C(1), 0.067 (4) and C(8), –0.099 (4) Å. This displacement results in pyramidal geometry at the carboxyl carbons.

Distances and angles involving the carboxyl groups of the 1,8-diacid are listed in Table 2. The four distinct C—O bond lengths are notably similar, ranging only from 1.260 (4) to 1.273 (4) Å, and are intermediate in value between the mean lengths for aromatic acid C—O double bonds, 1.226 Å, and aromatic acid C—O single bonds, 1.305 Å (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). Further, as listed in Table 3, the oxygen—oxygen distances between the refined molecule and its inversion-related partner are quite short, averaging 2.663 (44) Å. These facts indicate that the two 1,8-naphthalenedicarboxylic acid molecules form hydrogen bonds of the cyclic dimer type, two cyclic dimers per inversion-related pair. The four hydrogens involved in the inversion-related pairs were success-

fully refined distributed at half occupancy over eight sites, approximately 0.8 Å from each oxygen, as shown in Fig. 1. The similarity of the carbonyl groups and the fact that the hydrogens are not centrally located between the oxygens indicates that the hydrogens reside in a symmetric double-minimum potential. Additional evidence regarding the potential experienced by the carboxyl hydrogens can be found in the frequency of the O—H stretch, 3200–2600 cm⁻¹, in the IR spectrum of 1,8-naphthalenedicarboxylic acid (Davies, 1974; confirmed in this research). This value corresponds to the region given by Blinc, Hadzi & Novak (1960) as typical of carboxylic acids with symmetric double-minimum potentials. The hydrogens achieve this disordering by tunneling through the potential energy barrier of the symmetric double minimum on a time scale several orders of magnitude shorter (Brickman & Zimmerman, 1969) than the time required to scan a reflection. That an averaging of alternate orientations of the carboxyl groups within the crystal does not explain the hydrogen disorder nor the equal lengths of the C—O bonds can be seen by examination of the displacement parameters of the oxygens. If the carboxyl groups were orientationally disordered, the difference in bond lengths of the single- and double-bonded oxygens should cause one of the larger principal axes of the displacement ellipsoids for these oxygens to lie nearly along the C—O bonds. However, for 1,8-naphthalenedicarboxylic acid, as shown in Table 4, the largest principal axes of the displacement ellipsoids for these oxygens make angles of 84, 86, 88 and 82°, respectively, with the corresponding C—O bonds, while for O(1) and O(4) even the intermediate principal axes make angles of 86 and 68°, respectively. These results are indeed normal, being consistent with the expectation that displacement occurs more readily normal to a bond (bending) than along it (stretching). Moreover, the principal values of the displacement factors, particu-

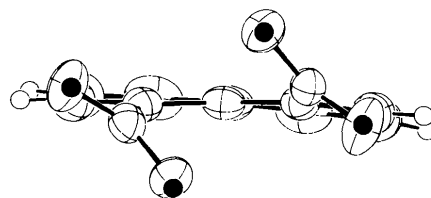


Fig. 3. A view of a 1,8-naphthalenedicarboxylic acid molecule from a direction lying in the mean plane of the rings a few degrees from the C(9)—C(10) bond direction drawn using ORTEP II (Johnson, 1976). Thermal ellipsoids are drawn at 50% probability for all atoms except H, for which they have been set artificially small. The filled symbols represent the four half-hydrogens of the two carboxyl groups of this molecule. The rotation of the carboxyl groups out of the mean plane of the rings is apparent, as are tilting and skewing of various portions of the molecule with respect to each other.

Table 4. Principal axis components of the anisotropic displacement ellipsoids ($\text{\AA}^2 \times 10^4$) of carboxyl O atoms in 1,8-naphthalenedicarboxylic acid and angles ($^\circ$) specifying the orientation of these ellipsoids with respect to the relevant C—O bond direction

Principal axis components of the anisotropic ellipsoids for selected C atoms are given for comparison.

	U_1	U_2	U_3	Angle between axis 1 and C—O bond ($^\circ$)	Angle between axis 2 and C—O bond ($^\circ$)	Angle between axis 3 and C—O bond ($^\circ$)
O(1)	856	558	358	84	86	7
O(2)	589	449	362	86	50	40
O(3)	600	467	364	88	57	33
O(4)	1043	501	378	82	68	24
C(6)	1037	527	314			
C(12)	549	395	331			

larly for O(2) and O(3), are not larger than is normal for well-ordered atoms at this temperature. Thirdly, O(1) and O(4) appear to have a pattern of principal axes values which is similar to that shown by C(6), while O(2) and O(3) have a different pattern of values, similar to that shown by C(12). Such similarities and differences appear inconsistent with hypothetical oxygen disordering resulting from alternate orientations of these carboxyl groups. In conclusion, several types of evidence support the assignment of an ordered oxygen-disordered hydrogen structure.

Additional distances and angles characterizing the hydrogen bonds are given in Table 3, along with corresponding values for four related dicarboxylic acids for comparison. Because of the arrangement of the carboxyl groups with respect to the inversion center, there are in the present case only two unique oxygen-acceptor oxygen distances. As would be expected, the values for distances and angles involving the positions occupied by half-hydrogens show larger uncertainties than the remaining data for this structure. Accordingly, hydrogen positions based on a neutron-adjusted bond length of 1.015 Å (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1986) were used to calculate the values listed in Table 3.

The hydrogen-bond parameters for this 1,8-diacid are comparable to those listed for other aromatic dicarboxylic acids. In the 1,8-diacid the carboxyl groups do not form the cyclic hydrogen bonds around a symmetry element. In fact, the carboxyl groups are splayed apart in order to relieve their crowding (*cf.* Figs. 1 and 3). Consequently, the dihedral angle between the plane defined by C(11), O(1) and O(2) and that defined by C(12)ⁱ, O(3)ⁱ and O(4)ⁱ is 32.4 (6)°; moreover, the second cyclic dimer

Table 5. Intermolecular closest approaches in the 1,8-naphthalenedicarboxylic acid structure, with their estimated standard deviations

Hydrogen-bonding approaches are not included in this tabulation.

	Observed distance (Å)	Observed distance — van der Waals radius sum (Å)
H(3)—H(6) ⁱⁱ	2.44 (1)	0.04
H(6)—H(3) ⁱⁱ	2.44 (1)	0.04
O(1)—H(4) ⁱⁱ	2.66 (1)	0.06
H(4)—O(1) ⁱ	2.66 (1)	0.06
H(4)—H(7) ⁱ	2.48 (7)	0.08
H(7)—H(4) ⁱⁱ	2.48 (7)	0.08
H(4)—H(10) ⁱⁱ	2.49 (8)	0.09
H(10)—H(4) ⁱⁱ	2.49 (8)	0.09
O(3)—H(1) ⁱⁱ	2.78 (1)	0.18
H(1)—O(3) ⁱⁱ	2.78 (1)	0.18
O(4)—H(4) ⁱⁱⁱ	2.78 (1)	0.18
H(4)—O(4) ⁱⁱ	2.78 (1)	0.18
O(2)—H(5) ⁱⁱⁱ	2.84 (1)	0.24
H(5)—O(2) ⁱⁱⁱ	2.84 (1)	0.24
O(4)—H(3) ⁱⁱⁱ	2.85 (1)	0.25
H(3)—O(4) ⁱⁱ	2.85 (1)	0.25

Symmetry code: none x, y, z ; (i) $2-x, -y, -z$; (ii) $-\frac{1}{2}+x, \frac{1}{2}-y, -z$; (iii) $\frac{1}{2}+x, -\frac{1}{2}-y, -z$; (iv) $\frac{1}{2}-x, \frac{1}{2}+y, z$; (v) $\frac{1}{2}-x, -\frac{1}{2}+y, z$; (vi) $\frac{1}{2}-x, -y, \frac{1}{2}+z$; (vii) $x, -\frac{1}{2}-y, \frac{1}{2}+z$; (viii) $x, \frac{1}{2}-y, -\frac{1}{2}+z$.

has the same value of the corresponding dihedral angle owing to the positioning of the molecules with respect to the inversion center.

The close approaches, excluding hydrogen bonds, for this 1,8-diacid structure are listed in Table 5. These close approaches involve H or O atoms on the perimeter of the molecule, as expected. The molecular packing is shown in Fig. 4, in which the eight molecules whose major portions lie interior to the unit cell are drawn together with their hydrogen-bonded partners.

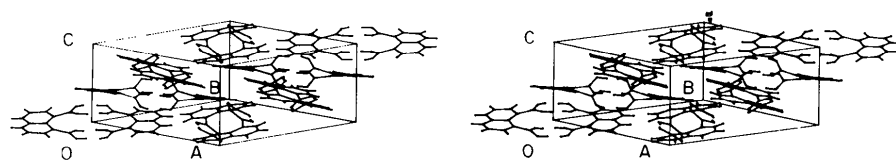


Fig. 4. Stereoview stick diagram of a unit cell of 1,8-naphthalenedicarboxylic acid showing the packing of the hydrogen-bonded dimeric units. Drawn using ORTEPII (Johnson, 1976).

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The Ordered and Disordered Phases of Three Unsymmetrical Cyclic Nitramines: (I), 1,3-Dinitro-1,3-diazacyclohexane; (II), 1,3-Dinitro-1,3-diazacycloheptane; (III), 1,5-Dinitro-3-nitroso-1,3,5-triazacycloheptane

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Abstract

(I): $C_4H_8N_4O_4$, $M_r = 176.13$, monoclinic, $P2_1/c$, $a = 6.63$ (1), $b = 21.39$ (2), $c = 6.06$ (1) Å, $\beta = 120.0$ (1)°, $V = 744.26$ Å³, $Z = 4$, $D_x = 1.572$, $D_m = 1.570$ g cm⁻³ by flotation in benzene/bromoform, $F(000) = 368.0$, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 1.31$ cm⁻¹, $T = 290$ K, $R = 0.056$ for 811 unique observed reflexions. (II): $C_5H_{10}N_4O_4$, $M_r = 190.16$, monoclinic, $P2_1/n$, $a = 8.738$ (8), $b = 11.20$ (1), $c = 8.383$ (7) Å, $\beta = 90.1$ (1)°, $V = 820.41$ Å³, $Z = 4$, $D_x = 1.539$, $D_m = 1.528$ g cm⁻³ by flotation in benzene/carbon tetrachloride, $F(000) = 400.0$, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 1.24$ cm⁻¹, $T = 290$ K, $R = 0.056$ for 829 unique observed reflexions. (III): $C_4H_8N_6O_5$, $M_r = 220.15$, monoclinic, Pc , $a = 11.30$ (1), $b = 6.34$ (1), $c = 12.23$ (1) Å, $\beta = 102.4$ (1)°, $V = 855.74$ Å³, $Z = 4$, $D_x = 1.709$, $D_m = 1.707$ g cm⁻³ by flotation in carbon tetrachloride/bromoform, $F(000) = 456.0$,

$\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 1.45$ cm⁻¹, $T = 290$ K, $R = 0.037$ for 1985 unique observed reflexions. NNO_2 groups are planar to within 0.025 Å in all three structures, C atoms deviate up to 0.478 Å from these planes. Molecules of (I) and (II) are dish shaped (both NO_2 groups on same side of ring), both molecules in (III) are overall chairlike (NO_2 groups on opposite sides of ring). Plastically crystalline above transition temperatures, sparse data consistent with body-centred-cubic structures with $a = 7.5$ (1), 7.7 (1), 7.8 (1) Å for (I), (II) and (III) respectively. Thermodynamic data, ΔH , ΔS , ΔV for the transitions are reported. The ordered to plastic transformations are discussed in relation to the crystal structures reported for the ordered phases.

Introduction

The three related compounds (I), (II) and (III) (1,3-dinitro-1,3-diazacyclohexane, 1,3-dinitro-1,3-diaza-

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