C13—C14—C15	119.2 (3)	C7—C15—C10	105.3 (2)
C7—C15—C14	135.9 (3)	C10—C15—C14	118.7 (2)
C1—C16—C17	123.3 (2)	C1—C16—C21	117.9 (2)
C17—C16—C21	118.8 (2)	C16—C17—C18	120.5 (2)
C17—C18—C19	120.3 (3)	C18—C19—C20	119.8 (3)
C19—C20—C21	120.4 (3)	C16—C21—C20	120.2 (3)
C1—C22—C23	118.1 (2)	C1—C22—C27	122.4 (2)
C23—C22—C27	119.4 (2)	C22—C23—C24	119.9 (3)
C23—C24—C25	120.3 (3)	C24—C25—C26	119.7 (3)
C25—C26—C27	120.9 (3)	C22—C27—C26	119.9 (3)

Table 5. *A comparison of the main characteristic geometrical parameters (Å, °) of chromenes (I)–(IV)*

	(I)[a]	(II)	(III)	(IV)
O1—C1	1.458 (4)	1.458 (2)	1.458 (6)	1.441 (3)
O1—C5	1.364 (4)	1.372 (2)	1.367 (6)	1.390 (3)
Bending angle along O1···C2	23.2 (2)	22.8 (2)	31.0 (3)	27.0 (3)
Bending angle along O1···C3	12.2 (2)	9.6 (2)	19.7 (3)	15.8 (3)

Reference: (a) Aldoshin *et al.* (1995).

Table 6. *Photochemical data and calculated steric strain energy (E_s) values of the pyran rings in compounds (I)–(IV)*

	λ_{max} (nm)	A_0	E_s (kcal mol^{-1})†
(I)‡	436	0.77	9.92
(II)	432	0.84	10.19
(III)	Non-photochromic		15.2
(IV)	427/452	1.43/1.39	13.14

† 1 cal = 4.184 J.   ‡ Aldoshin *et al.* (1995).

For all compounds, program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993) for (II) and (III); *SHELX*76 (Sheldrick, 1976) for (IV). For all compounds, molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited for all three title compounds with the IUCr (Reference: PA1201). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Anthracene-1,8-dicarboxylic Acid

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Abstract

Anthracene-1,8-dicarboxylic acid, $C_{16}H_{10}O_4$, crystallized in the noncentrosymmetric space group $P2_12_12_1$. The carboxyl H and O atoms are ordered. The carboxyl groups make angles of 13.9 (2) and 21.6 (2)° with the best-fit core plane and the average distance of the core atoms from this plane is 0.018 (12) Å. The anthracene core displays near twofold symmetry. Each molecule is involved in cyclic-dimer hydrogen bonding with two other molecules so as to form zigzag chains of hydrogen-bonded molecules which are not cross-linked with one another. These discrete chains are separated from each other by C···C, C···H and H···H closest approaches.

Comment

The present study of anthracene-1,8-dicarboxylic acid, (I), was undertaken as part of a continuing investigation of hydrogen bonding in aromatic carboxylic acids. The assignment of this structure in the noncentrosymmetric space group $P2_12_12_1$ makes it of interest for its potential utility in nonlinear optics (Prasad & Williams, 1991).

(I)
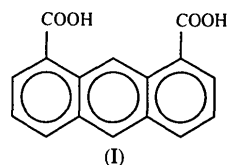
The carboxyl H atoms in (I) (Fig. 1) are ordered. In the C15 carboxyl group, the C—O distances are 1.318 (8) and 1.202 (7) Å, while in the C16 carboxyl group they are 1.324 (6) and 1.209 (6) Å, consistent with single and double bonds, respectively. Moreover, the carboxyl O atoms are ordered; the principal displacement tensor axes of the O atoms are nearly perpendicular to the carboxyl group planes, as observed previously for ordered carboxyl O atoms in 1- and 2-naphthoic acid (Fitzgerald & Gerkin, 1993).

For the two carboxyl groups, the differences of the pairs of C_{ring}—C—O angle values ($\Delta\theta$) and carboxyl C—O distances (Δr) within each group are such that the two pairs of $|\Delta\theta|$ and $100|\Delta r|$ values bracket closely
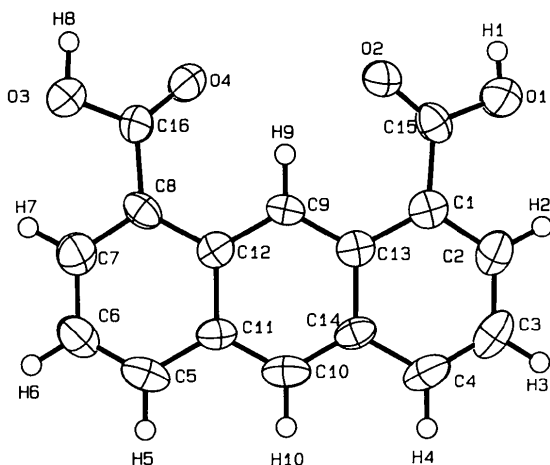
Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of anthracene-1,8-di-carboxylic acid showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for all atoms except H atoms, for which they have been set artificially small.

the best line relating the corresponding quantities for various naphthalene dicarboxylic acids [Fitzgerald & Gerkin (1992) after Dieterich, Paul & Curtin (1974)].

The anthracene core displays near twofold symmetry (Table 2); the average difference between core distances which would be strictly equal under twofold symmetry is 0.005 (16) Å, while the corresponding average angular difference is 0.2 (12)°.

The planes of the C15 and C16 carboxyl groups make angles of 13.9 (2) and 21.6 (2)°, respectively, with the least-squares best-fit core plane and an angle of 9.2 (2)° with one another. The orientations of the carboxyl group planes are responsible for the largest differences within the molecule with respect to pseudo-twofold symmetry. The average distance of the core atoms from the best-fit core plane is 0.018 (12) Å.

Each molecule (Fig. 2) is involved in cyclic-dimer hydrogen bonding with two other molecules (but not, of course, across centers of inversion) so as to form discrete zigzag chains of hydrogen-bonded molecules not cross-linked with one another. Each carboxyl O atom is involved in a single strong hydrogen bond either as a

donor (O1 and O3) or as an acceptor (O2 and O4). With atom O1 as donor, the $O_d \cdots O_a$ distance is 2.698 (7), $H1 \cdots O_a$ is 1.94 (7) Å and the O_d—$H1 \cdots O_a$ angle is 148 (7)°, while with atom O3 as donor, the $O_d \cdots O_a$ distance is 2.645 (6), $H8 \cdots O_a$ is 1.67 (7) Å and the O_d—$H8 \cdots O_a$ angle is 174 (6)°.

The closest approaches of atoms from discrete hydrogen-bonded chains involve $C \cdots C$, $C \cdots H$ and $H \cdots H$ pairs (1 pair, 3 pairs and 1 pair, respectively), with separation distances ranging from 0.07 Å larger to 0.02 Å smaller than the sums of the appropriate van der Waals radii (Bondi, 1964). This pattern of close approaches is apparent in Fig. 2.

It is of interest that this anthracene-1,8-dicarboxylic acid structure is quite different from that determined for its molecular analog naphthalene-1,8-dicarboxylic acid (Fitzgerald, Gallucci & Gerkin, 1991). In the latter compound, pairs of molecules related by an inversion center form two sets of cyclic hydrogen bonds with one another to produce closed cycles rather than extended chains as in the present structure. Since there appears to be no compelling explanation for the structural difference, it may be possible to obtain the title diacid in a form similar to the naphthalene-1,8-dicarboxylic acid structure and *vice versa*.

Experimental

Crystal data

$C_{16}H_{10}O_4$	Mo $K\alpha$ radiation
$M_r = 266.25$	$\lambda = 0.71073$ Å
Orthorhombic	Cell parameters from 25
$P2_12_12_1$	reflections
$a = 10.646$ (3) Å	$\theta = 10.7–12.2°$
$b = 16.547$ (2) Å	$\mu = 0.098$ mm^{-1}
$c = 6.899$ (3) Å	$T = 298$ K
$V = 1215.4$ (6) Å^3	Column
$Z = 4$	$0.38 \times 0.19 \times 0.12$ mm
$D_x = 1.455$ Mg m^{-3}	Yellow
D_m not measured	

Data collection

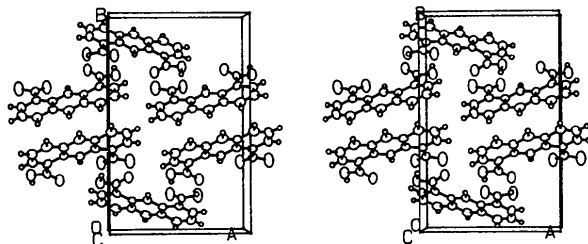|	
Rigaku AFC-5S diffractometer	$\theta_{max} = 27.5°$
	$h = 0 \rightarrow 13$
ω–2θ scans	$k = 0 \rightarrow 21$
Absorption correction:	$l = 0 \rightarrow 8$
none	6 standard reflections
1639 measured reflections	monitored every 150
1639 independent reflections	reflections
796 observed reflections	intensity variation: $\pm 1.8\%$
[$I > 1\sigma(I)$]	

Fig. 2. A stereoview (*ORTEP*II; Johnson, 1976) of a portion of the title structure including a unit cell. Displacement ellipsoids are drawn at the 50% probability level for all atoms except H atoms, for which they have been set artificially small.

Refinement

Refinement on F	Extinction correction:
$R = 0.051$	Zachariasen (1963, 1968)
$wR = 0.050$	Extinction coefficient:
$S = 1.39$	$3(3) \times 10^{-7}$
796 reflections	Atomic scattering factors
190 parameters	from Stewart, Davidson
$w = \sigma_F^{-2}$	& Simpson (1965) for
$(\Delta/\sigma)_{max} = <0.01$	H atoms and Cromer &
$\Delta\rho_{max} = 0.21$ e $\AA^{-3}$	Waber (1974) for C and O
$\Delta\rho_{min} = -0.25$ e $\AA^{-3}$	atoms

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\AA^2$)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O1	0.3510 (5)	0.6680 (4)	0.1483 (9)	0.081 (2)
O2	0.5552 (4)	0.6748 (3)	0.1018 (6)	0.064 (2)
O3	1.0589 (4)	0.7290 (3)	0.2043 (7)	0.061 (2)
O4	0.8541 (4)	0.7541 (3)	0.1951 (7)	0.063 (1)
C1	0.4803 (6)	0.6138 (3)	0.3932 (9)	0.041 (2)
C2	0.3744 (6)	0.5810 (4)	0.4775 (11)	0.054 (2)
C3	0.3796 (6)	0.5416 (4)	0.6568 (11)	0.061 (2)
C4	0.4894 (7)	0.5347 (4)	0.7516 (10)	0.056 (2)
C5	0.9390 (7)	0.5978 (4)	0.8179 (10)	0.055 (2)
C6	1.0450 (7)	0.6302 (4)	0.7475 (10)	0.057 (2)
C7	1.0447 (6)	0.6684 (4)	0.5642 (10)	0.051 (2)
C8	0.9378 (5)	0.6756 (3)	0.4567 (8)	0.040 (2)
C9	0.7100 (5)	0.6432 (3)	0.4226 (8)	0.038 (2)
C10	0.7142 (6)	0.5668 (4)	0.7803 (9)	0.052 (2)
C11	0.8240 (6)	0.6007 (3)	0.7116 (9)	0.041 (2)
C12	0.8226 (5)	0.6405 (3)	0.5261 (9)	0.037 (2)
C13	0.5988 (5)	0.6095 (3)	0.4932 (9)	0.039 (2)
C14	0.6020 (6)	0.5701 (3)	0.6796 (8)	0.040 (2)
C15	0.4680 (6)	0.6547 (4)	0.2018 (10)	0.044 (2)
C16	0.9433 (6)	0.7228 (3)	0.2737 (9)	0.043 (2)

Table 2. *Selected geometric parameters ($\AA$, °)*

C1—C2	1.380 (8)	C10—C11	1.380 (8)
C1—C13	1.440 (8)	C10—C14	1.383 (8)
C2—C3	1.399 (9)	C11—C12	1.440 (8)
C3—C4	1.344 (9)	C13—C14	1.442 (8)
C4—C14	1.424 (8)	C1—C15	1.490 (8)
C5—C6	1.341 (9)	C15—O1	1.318 (8)
C5—C11	1.427 (8)	C15—O2	1.202 (7)
C6—C7	1.413 (9)	O1—H1	0.85 (7)
C7—C8	1.364 (8)	C8—C16	1.486 (8)
C8—C12	1.439 (7)	C16—O3	1.324 (6)
C9—C12	1.397 (7)	C16—O4	1.209 (7)
C9—C13	1.396 (7)	O3—H8	0.98 (7)
C2—C1—C13	119.7 (6)	C1—C13—C14	118.0 (5)
C1—C2—C3	121.6 (6)	C9—C13—C14	118.2 (5)
C2—C3—C4	120.2 (6)	C4—C14—C10	122.4 (5)
C3—C4—C14	121.9 (6)	C4—C14—C13	118.5 (6)
C6—C5—C11	121.5 (6)	C10—C14—C13	119.1 (5)
C5—C6—C7	120.1 (6)	C2—C1—C15	118.7 (6)
C6—C7—C8	121.9 (6)	C13—C1—C15	121.6 (6)
C7—C8—C12	119.6 (6)	C1—C15—O1	114.0 (6)
C12—C9—C13	122.4 (5)	C1—C15—O2	124.5 (6)
C11—C10—C14	122.9 (5)	O1—C15—O2	121.5 (6)
C5—C11—C10	122.4 (6)	C15—O1—H1	98 (5)
C5—C11—C12	118.7 (6)	C7—C8—C16	118.4 (5)
C10—C11—C12	118.8 (5)	C12—C8—C16	121.9 (6)
C8—C12—C9	123.2 (5)	C8—C16—O3	112.6 (5)
C8—C12—C11	118.2 (5)	C8—C16—O4	125.1 (6)
C9—C12—C11	118.6 (5)	O3—C16—O4	122.3 (6)
C1—C13—C9	123.8 (5)	C16—O3—H8	105 (3)

The unit-cell parameters were obtained from a symmetry-constrained least-squares fit. The scan width was (1.40 + 0.35tanθ)° in ω and the ratio of background to scan time

was 0.5. No correction was made for decay or absorption, but the data were corrected for Lorentz and polarization effects. The intensities were consistent with Laue group *mmm*. The systematic absences determined the space group uniquely as $P2_12_12_1$ (No. 19), which is noncentrosymmetric. Because the data afforded few tests of the 00*l* extinction condition (*l* = odd), the alternative possibility (00*l*, no condition) consistent with only $P2_12_12$ (No. 18, also noncentrosymmetric) was tested; no solution was obtained, however, thus confirming $P2_12_12_1$. The direct-methods program *SHELXS86* (Sheldrick, 1985) produced an E map 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 carboxyl H atoms, while the ring H atoms were defined canonically (C—H 0.95 $\AA$ and $B_{eq} = 1.2B_{eq}$ of the attached C atom). The C and O atoms were refined anisotropically and the carboxyl H atoms isotropically, using full-matrix least-squares methods (*TEXSAN*; Molecular Structure Corporation, 1989). An extinction coefficient was refined in the later stages; the maximum effect of extinction was 1.2% of F_o for 200. The maximum positive residual electron density (0.21 e $\AA^{-3}$) occurred $\sim$1.6 $\AA$ from atoms C8 and C12, and the maximum negative peak (-0.25 e $\AA^{-3}$) occurred $\sim$1.3 $\AA$ from atoms C5 and C6.

Data collection: *MSCAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

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An Orthorhombic Phase of 3,6-Di(2-pyridyl)-1,4-dihydro-1,2,4,5-tetrazine

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Abstract

The title compound, $C_{12}H_{10}N_6$, crystallized in the orthorhombic system with space group $P2_12_12_1$. The N atoms of the two terminal pyridine rings are *trans* with respect to one another and the dihedral angle between the two least-squares planes of the pyridine rings is 22.6 (2)°. The central tetrazine ring has a boat conformation. Both intra- and intermolecular hydrogen bonds are observed.

Comment

The triclinic form of the title compound, (I), has been reported by Caira, Giles, Nassimbeni, Sheldrick & Hazell (1976). We report here on an orthorhombic form of this compound. The N atoms of the two pyridine rings were clearly identified by analyzing the displacement parameters of the possible positions. These two N atoms are *trans* with respect to one another, similar to the case in the previously reported triclinic structure. The central tetrazine ring has a boat conformation, with atoms N22 and N25 sitting at the bow and stern, respectively. Two short bond distances, C21—N26 of 1.284 (2) and N23—C24 of 1.276 (2) Å, and four long bond distances ranging from 1.385 (2) to 1.431 (2) Å were observed in this ring. The two short distances indicate that the double-bond character is localized between the C21/N26 and N23/C24 atom pairs.

(I)
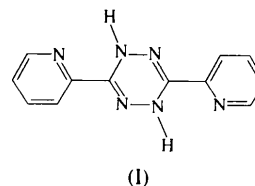
Only intramolecular hydrogen bonds were reported for the triclinic structure, whereas in the present orthorhombic structure, both intramolecular and weaker intermolecular hydrogen bonds are observed. Two intramolecular hydrogen-bonding distances are present between atoms N16 and H22, and atoms N36 and H25 [2.33 (2) and 2.32 (2) Å, respectively]. Two intermolecular hydrogen bonds occur between one molecule and a second molecule (*A*) related by the symmetry operation $(-x, \frac{1}{2} + y, \frac{1}{2} - z)$ (Fig. 1). The distances are 2.55 (2) for H22···N26*A* and 2.50 (2) Å for H12···N23*A*. There are no significant short intermolecular contacts between non-H atoms. The closest intermolecular distance observed is 3.262 (2) Å between atoms N22 and N26*A*. The dihedral angle between the two pyridine-ring planes is 22.6 (2)°, which is significantly smaller than that found in the triclinic structure (41.2°). This smaller angle is attributed to the combination effects of both intra- and intermolecular hydrogen bonds. Least-squares-planes data has been deposited as supplementary material.
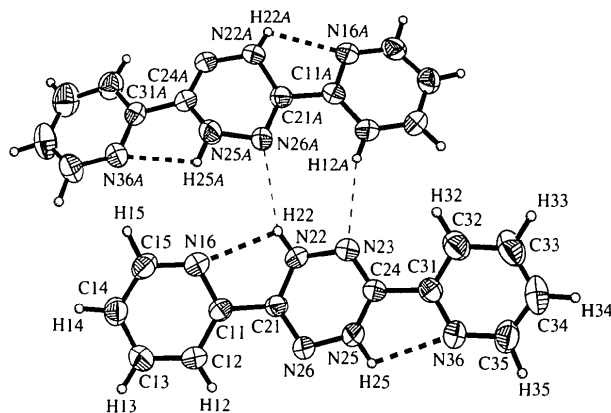

Fig. 1. An *ORTEP* drawing (Johnson, 1965) of the title compound showing 50% probability ellipsoids for non-H atoms and H atoms as spheres of arbitrary radii. Intramolecular hydrogen bonds are shown by broken lines and intermolecular hydrogen bonds by dashed lines. Molecule *A* is generated by the symmetry operation $(-x, \frac{1}{2} + y, \frac{1}{2} - z)$.

Experimental

The title compound was synthesized according to the literature method of Geldard & Lions (1965). It was dissolved in a mixture of *n*-hexane and ethyl acetate (1:1 *v/v*). The orthorhombic crystals were grown by slow evaporation of the solvent mixture at room temperature.