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Naphthalene-1,8-dicarboxylic anhydride: a monoclinic polymorph

Dan Zhao,* FeiFei Li and AiYun Zhang

Department of Physics and Chemistry, Henan Polytechnic University, Jiaozuo, Henan 454000, People's Republic of China
Correspondence e-mail: iamzd@hpu.edu.cn

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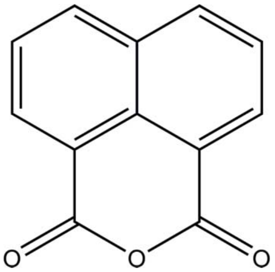
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.002 Å; R factor = 0.045; wR factor = 0.131; data-to-parameter ratio = 14.4.

A new type of naphthalene-1,8-dicarboxylic anhydride, $C_{12}H_6O_3$, was synthesized hydrothermally. Unlike the two previously reported polymorphs, which crystallize in the orthorhombic space groups $P2_12_12_1$ [Shok *et al.* (1971). *Kristallografiya*, **16**, 500–502; Grigor'eva & Chetkina (1975). *Kristallografiya*, **20**, 1289–1290] and *Pbca* [Shok & Gol'der (1970). *Zh. Strukt. Khim.* **11**, 939–940], this present structure crystallizes in the monoclinic space group $P2_1/c$. In this structure, the planar [total puckering amplitude Q = 0.0362 (15)] molecules lie parallel to each other along the a axis.

Related literature

The previously reported polymorphs crystallize in $P2_12_12_1$ (Shok *et al.*, 1971; Grigor'eva & Chetkina, 1975) and *Pbca* (Shok & Gol'der, 1970). For puckering parameters, see: Evans & Boeyens (1989).



Experimental

Crystal data

$C_{12}H_6O_3$	V = 862.49 (3) Å^3
M_r = 198.17	Z = 4
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
a = 3.7687 (1) Å	μ = 0.11 mm^{-1}
b = 14.5269 (3) Å	T = 296 K
c = 15.8083 (3) Å	0.20 × 0.10 × 0.10 mm
β = 94.752 (2)°	

Data collection

Bruker APEXII CCD diffractometer	7560 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	1964 independent reflections
T_{min} = 0.875, T_{max} = 0.982	1201 reflections with $I > 2\sigma(I)$
	R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045	136 parameters
$wR(F^2)$ = 0.131	H-atom parameters constrained
S = 1.00	$\Delta\rho_{max}$ = 0.18 e Å^{-3}
1964 reflections	$\Delta\rho_{min}$ = −0.17 e Å^{-3}

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2709).

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supplementary materials

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Naphthalene-1,8-dicarboxylic anhydride: a monoclinic polymorph

D. Zhao, F. F. Li and **A. Y. Zhang**

Comment

1,8-Naphthalenedicarboxylate (1,8-NDC), can be used as a rigid building blocks to design multiple metal-organic coordination polymers, as its multiple coordination sites, high symmetry and large conjugated structure. The single-crystal structure of naphthalene-1,8-dicarboxylic anhydride was firstly determined by Shok and Gol'der to be a orthorhombic space group *Pbca* (Shok, *et al.*, 1970). Later a β-phase was discovered with the space group $P2_12_12_1$ (Shok *et al.*, 1971; Grigor'eva & Chetkina, 1975). In this paper, a new type of naphthalene-1,8-dicarboxylic acid anhydride was hydrothermally synthesized and characterized by single-crystal X-ray diffraction with the monoclinic space group $P2_1/c$.

The asymmetric unit contains only one independent molecule with the planar [total puckering amplitude Q = 0.0362 (15) (Evans & Boeyens, 1989)] molecules parallel to each other along the *a*-axis (Fig. 2).

Experimental

Yellow prism-shaped single crystals of Naphthalene-1,8-dicarboxylic acid anhydride were initially obtained in our attempt to prepare metal-organic coordination polymers of 1,8-NDC associated with molybdate. A mixture of 3 mmol of MoO_3, 2 mmol of $Mn(Ac)_2$, 2.0 mmol KOH and 1.5 mmol of Naphthalene-1,8-dicarboxylic anhydride, was sealed in a 25 ml Teflonlined bomb at 160°C for 5 days and then cooled to room temperature. A few single crystals suitable for X-ray diffraction analysis were obtained.

Refinement

All of the H atoms were treated as riding atoms with distances C—H = 0.93 Å (CH), and $U_{iso}(H) = 1.2 U_{eq}(C)$. The final refinement show that the highest peak in the difference electron density map equals to 0.18 e/Å^3 at the distance of 0.65 Å from C5 while the deepest hole equals to -0.17 e/Å^3 at the distance of 0.61 Å from C1.

Figures

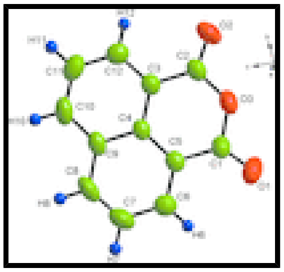

Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity. [Symmetry code: *x*, *y*, *z*]

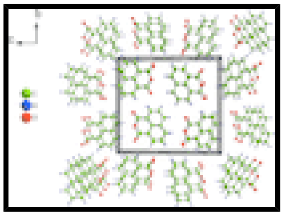

Fig. 2. A packing diagram of the title compound viewed down the *a*–axis.

Naphthalene-1,8-dicarboxylic anhydride

Crystal data

$C_{12}H_6O_3$

$M_r = 198.17$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 3.7687$ (1) Å

$b = 14.5269$ (3) Å

$c = 15.8083$ (3) Å

$\beta = 94.752$ (2)°

$V = 862.49$ (3) Å^3

$Z = 4$

$F(000) = 408$

$D_x = 1.526$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1938 reflections

$\theta = 2.6$–27.9°

$\mu = 0.11$ mm^{-1}

$T = 296$ K

Prism, yellow

0.20 × 0.10 × 0.10 mm

Data collection

Bruker APEXII CCD diffractometer

Radiation source: fine-focus sealed tube

graphite

ω scans

Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)

$T_{min} = 0.875$, $T_{max} = 0.982$

7560 measured reflections

1964 independent reflections

1201 reflections with $I > 2\sigma(I)$

$R_{int} = 0.027$

$\theta_{max} = 27.5$°, $\theta_{min} = 1.9$°

$h = -4 \rightarrow 4$

$k = -17 \rightarrow 18$

$l = -20 \rightarrow 20$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.131$

$S = 1.00$

1964 reflections

136 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0732P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.18$ e Å^{-3}

$\Delta\rho_{min} = -0.17$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
C5	0.3898 (4)	0.64036 (9)	0.28567 (8)	0.0399 (4)
C1	0.2469 (4)	0.64100 (10)	0.19687 (9)	0.0486 (4)
C6	0.5444 (4)	0.56205 (10)	0.32018 (9)	0.0503 (4)
H6	0.5618	0.5098	0.2868	0.060*
C11	0.3060 (5)	0.87580 (12)	0.43612 (10)	0.0588 (5)
H11	0.2878	0.9279	0.4696	0.071*
C4	0.3603 (3)	0.72008 (9)	0.33538 (8)	0.0356 (4)
C3	0.1982 (4)	0.80075 (10)	0.30145 (8)	0.0397 (4)
C2	0.0514 (4)	0.80154 (11)	0.21286 (9)	0.0478 (4)
C8	0.6540 (4)	0.63636 (11)	0.45452 (10)	0.0544 (5)
H8	0.7441	0.6341	0.5111	0.065*
C7	0.6755 (4)	0.56069 (12)	0.40523 (10)	0.0571 (5)
H7	0.7788	0.5072	0.4284	0.068*
C9	0.4972 (4)	0.71882 (10)	0.42179 (8)	0.0429 (4)
O3	0.0835 (3)	0.72159 (7)	0.16646 (6)	0.0557 (3)
C12	0.1693 (4)	0.87738 (11)	0.35104 (9)	0.0504 (4)
H12	0.0594	0.9302	0.3283	0.061*
C10	0.4642 (4)	0.79925 (12)	0.47005 (9)	0.0555 (4)
H10	0.5534	0.7998	0.5267	0.067*
O2	−0.1003 (4)	0.86395 (8)	0.17671 (7)	0.0747 (4)
O1	0.2558 (4)	0.57887 (8)	0.14772 (7)	0.0766 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C5	0.0368 (8)	0.0459 (9)	0.0377 (8)	−0.0059 (7)	0.0073 (6)	0.0044 (6)
C1	0.0597 (10)	0.0486 (9)	0.0376 (8)	−0.0111 (8)	0.0043 (7)	0.0002 (7)
C6	0.0511 (10)	0.0467 (9)	0.0544 (10)	−0.0002 (7)	0.0116 (8)	0.0037 (7)
C11	0.0618 (11)	0.0624 (11)	0.0531 (10)	−0.0070 (9)	0.0104 (8)	−0.0178 (9)
C4	0.0306 (7)	0.0447 (8)	0.0321 (7)	−0.0061 (6)	0.0063 (6)	0.0035 (6)
C3	0.0357 (8)	0.0463 (8)	0.0376 (8)	−0.0043 (7)	0.0053 (6)	0.0023 (7)
C2	0.0499 (9)	0.0539 (9)	0.0391 (8)	0.0002 (8)	0.0008 (7)	0.0061 (7)

C8	0.0447 (10)	0.0789 (12)	0.0387 (8)	−0.0011 (8)	−0.0020 (7)	0.0195 (9)
C7	0.0506 (11)	0.0605 (11)	0.0600 (10)	0.0071 (8)	0.0043 (8)	0.0210 (9)
C9	0.0345 (8)	0.0618 (10)	0.0325 (7)	−0.0063 (7)	0.0033 (6)	0.0027 (7)
O3	0.0705 (8)	0.0593 (7)	0.0354 (6)	−0.0055 (6)	−0.0075 (5)	0.0030 (5)
C12	0.0495 (10)	0.0483 (9)	0.0545 (10)	0.0006 (7)	0.0103 (8)	0.0005 (7)
C10	0.0524 (10)	0.0797 (12)	0.0339 (8)	−0.0086 (9)	0.0014 (7)	−0.0075 (8)
O2	0.0918 (10)	0.0725 (8)	0.0572 (7)	0.0227 (7)	−0.0100 (7)	0.0185 (6)
O1	0.1232 (12)	0.0586 (8)	0.0480 (7)	−0.0138 (7)	0.0075 (7)	−0.0131 (6)

Geometric parameters (Å, °)

C5—C6	1.3706 (19)	C3—C12	1.3710 (19)
C5—C4	1.4090 (18)	C3—C2	1.463 (2)
C5—C1	1.4613 (19)	C2—O2	1.1922 (17)
C1—O1	1.1931 (16)	C2—O3	1.3844 (17)
C1—O3	1.3900 (17)	C8—C7	1.354 (2)
C6—C7	1.394 (2)	C8—C9	1.4146 (19)
C6—H6	0.9300	C8—H8	0.9300
C11—C10	1.351 (2)	C7—H7	0.9300
C11—C12	1.400 (2)	C9—C10	1.407 (2)
C11—H11	0.9300	C12—H12	0.9300
C4—C3	1.4072 (18)	C10—H10	0.9300
C4—C9	1.4197 (19)		

C6—C5—C4	120.72 (13)	O2—C2—C3	126.39 (15)
C6—C5—C1	119.88 (13)	O3—C2—C3	117.26 (13)
C4—C5—C1	119.39 (12)	C7—C8—C9	121.35 (14)
O1—C1—O3	116.57 (13)	C7—C8—H8	119.3
O1—C1—C5	126.36 (15)	C9—C8—H8	119.3
O3—C1—C5	117.07 (12)	C8—C7—C6	120.70 (14)
C5—C6—C7	120.05 (14)	C8—C7—H7	119.7
C5—C6—H6	120.0	C6—C7—H7	119.7
C7—C6—H6	120.0	C10—C9—C8	123.93 (13)
C10—C11—C12	120.65 (14)	C10—C9—C4	118.02 (13)
C10—C11—H11	119.7	C8—C9—C4	118.05 (13)
C12—C11—H11	119.7	C2—O3—C1	125.38 (11)
C3—C4—C5	121.58 (12)	C3—C12—C11	119.71 (14)
C3—C4—C9	119.28 (12)	C3—C12—H12	120.1
C5—C4—C9	119.13 (12)	C11—C12—H12	120.1
C12—C3—C4	120.72 (12)	C11—C10—C9	121.62 (14)
C12—C3—C2	119.96 (13)	C11—C10—H10	119.2
C4—C3—C2	119.30 (13)	C9—C10—H10	119.2
O2—C2—O3	116.33 (13)		

Fig. 1

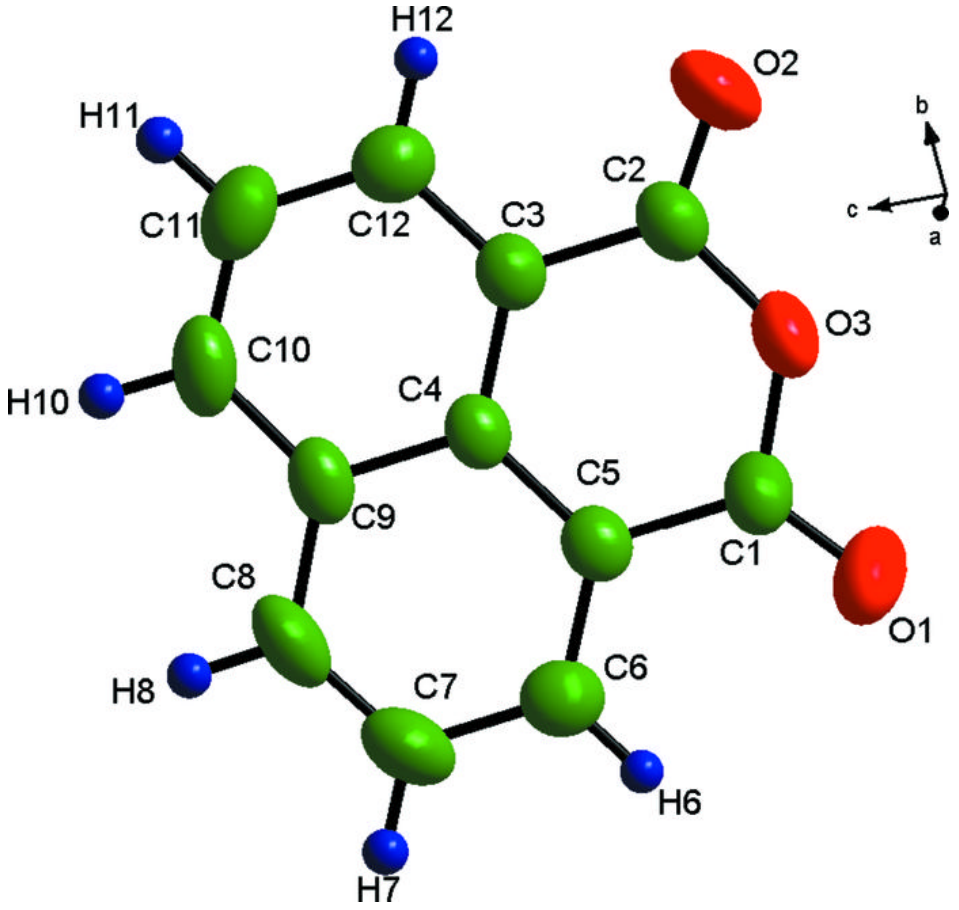
H12
O2
H11
b
C2
c
a
C11
C12
C3
O3
C10
H10
C4
C5
C9
C1
C8
O1
C6
H8
C7
H6
H7

Fig. 2