Table 2. *Hydrogen-bonding and C—H···O contact geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O1^{i}	0.75 (4)	2.00 (4)	2.713 (3)	158 (4)
C4—H4A···O2^{ii}	0.97	2.70	3.661 (3)	173
C8—H8F···O2^{iii}	0.96	2.56	3.451 (3)	154

Symmetry codes: (i) $1 - x, \frac{1}{2} + y, -z$; (ii) $1 - x, y - \frac{1}{2}, -z$; (iii) $2 - x, y - \frac{1}{2}, 1 - z$.

All H atoms were found in electron-density difference maps but were replaced in calculated positions and allowed to refine as riding models, except for the hydroxyl H3 atom whose coordinates and isotropic temperature factor were allowed to refine individually. The occupancy for the disordered methyl group (C8) was refined. Isotropic displacement parameters for methylene and carboxyl H atoms were allowed to refine individually, whilst isotropic displacement parameters for the methyl protons on C5, C6 and C8 were refined as individual groups.

Data collection: *XSCANS* (Siemens, 1996). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1455). Services for accessing these data are described at the back of the journal.

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N,*N*′-Bis(3-methoxyphenyl)-1,8:4,5-naphthalenetetracarboximide–trifluoroacetic acid–phenol (1/2.5/0.5)

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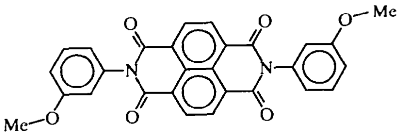
Abstract

In the title compound, $C_{28}H_{18}N_2O_6 \cdot 2.5C_2HF_3O_2 \cdot 0.5C_6H_6O$, the naphthalenetetracarboxylic diimide moiety lies about an inversion centre and is planar, but conjugation between the phenyl substituent and the tetracyclic fragment is disrupted due to rotation around C—N bonds.

Comment

Derivatives of 1,8:4,5-naphthalenetetracarboxylic diimide (NTCDI) have been known for a long time (Patai, 1970). Their electronic and spectral properties and the ability to co-polymerize with different amines to give rigid-chain heterocyclic polyimides have been widely studied and used (Khiefets *et al.*, 1977; Zhong *et al.*, 1992; Cammarata *et al.*, 1992; Orzeszko & Sikorski, 1993; Gajiwala & Zand, 1993, 1995; Zhou & Lu, 1995; Adachi *et al.*, 1995; Lokey *et al.*, 1997; Borsenberger *et al.*, 1996). Knowledge of the molecular structure of NTCDI derivatives is essential for explaining and understanding their unusual properties. However, only a few structures of intercalative complexes of NTCDI have been studied (Jazwinski *et al.*, 1987; Shimizu *et al.*, 1994; Houghton *et al.*, 1997; Staab *et al.*, 1997). Here we report the results of an investigation of the *N*,*N*′-bis[(3-methoxyphenyl)imide] of 1,8:4,5-naphthalenetetracarboxylic acid, (I).



$\cdot 2.5C_2HF_3O_2 \cdot 0.5C_6H_6O$

(I)

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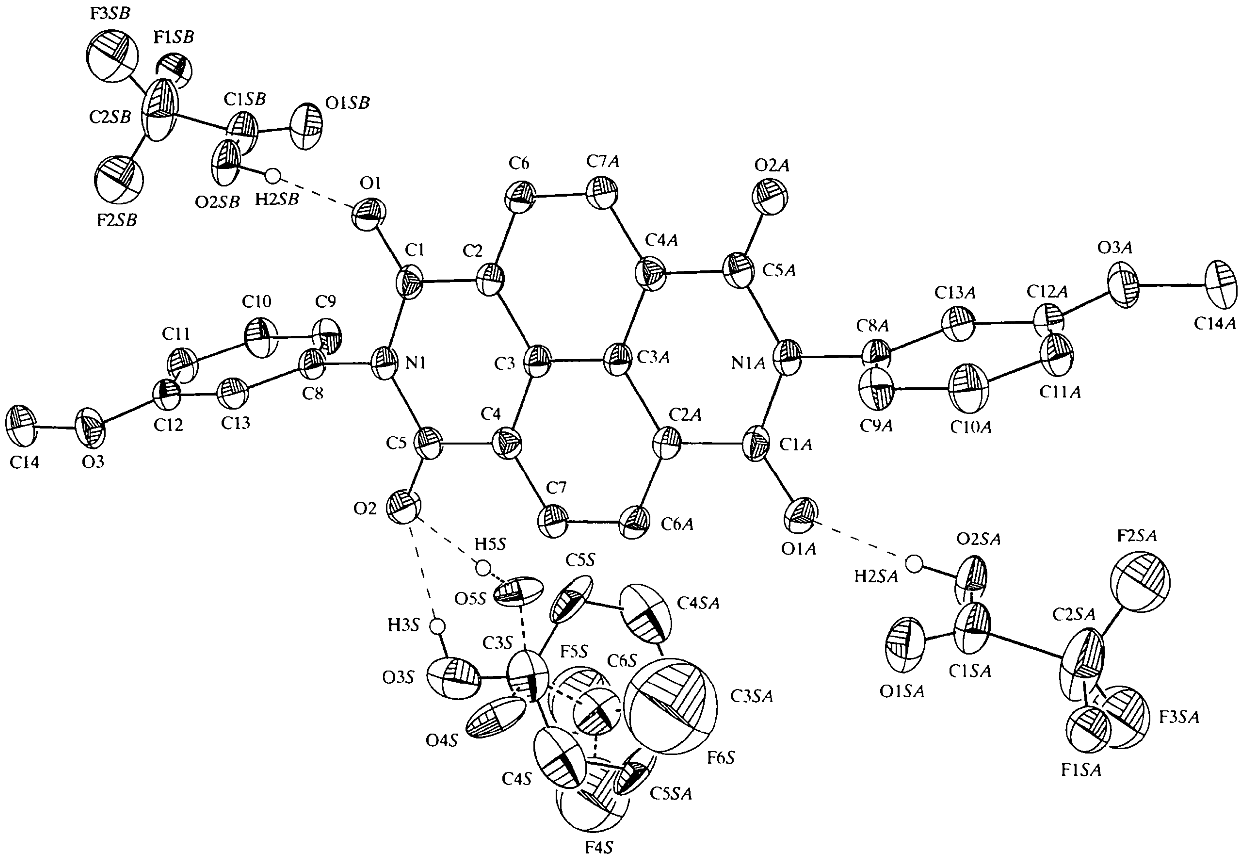

Fig. 1. A view of (I) with displacement ellipsoids drawn at the 50% probability level. Apart from those in TFAA molecules, H atoms have been omitted for clarity. Atoms carrying the suffixes *A* and *B* are related to unsuffixed atoms by the symmetry operations $1-x$, $2-y$, $3-z$ and $x-1$, $y-1$, $z-1$, respectively. Only one component of the disorder is shown for each CF_3 group. For a further description of the disorder in this structure see the text over.

In the crystal phase compound (I) forms a solvate with stoichiometry NTDCI·2.5TFAA·0.5phenol. Molecule (I) is situated on a centre of inversion which coincides with the midpoint of the C3—C3*A* bond (Fig. 1). A non-disordered TFAA molecule forms an intermolecular hydrogen bond H2*S*···O1^{i} [symmetry code: (i) $x+1$, $y+1$, $z+1$ (Table 2)] with one of the carbonyl groups of the imide moiety. The disordered TFAA and phenol molecules also form hydrogen bonds by their OH groups with the carbonyl O2 atom, O5*S*···O2 and O3*S*···O2 [O···O distances of 2.68 (1) and 2.78 (2) Å, respectively], but positions of relevant H atoms were not located due to disorder.

Molecule (I) is planar, in agreement with experimental data for *N*-ethyl-1,8-naphthalenedicarboxylimide (Easton *et al.*, 1992). Conjugation between the π-systems of the phenyl group and naphthalenediimide fragment is disrupted due to rotation around the N—C_{ar} bond [the C1—N1—C8—C9 torsion angle is 75.2 (4)°]. This is confirmed also by values of the N1—C8 bond [1.463 (4) Å] which is typical for non-conjugated Nsp^2—C_{ar} bonds (Allen *et al.*, 1987). The methoxy group is almost coplanar with the benzene ring, the C11—C12—O3—C14 torsion angle being −4.5 (5)°.

Experimental

Compound (I) was synthesized by condensation of 1,8:4,5-naphthalenetetracarboxylic dianhydride (20 mmol) with *m*-methoxyaniline (40 mmol) at elevated temperatures of 453 K in the presence of benzoic acid (10 mmol) as a catalyst. Crystals appropriate for X-ray structural analysis were grown from a mixture of trifluoroacetic acid (TFAA) with phenol (5:1).

Crystal data

$C_{28}H_{18}N_2O_6{\cdot}2.5C_2HF_3O_2{\cdot}$-
0.5C_6H_6O
$M_r = 810.58$
Triclinic
$P\overline{1}$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 10$–11°

$a = 8.905$ (4) Å
$b = 9.497$ (3) Å
$c = 10.321$ (5) Å
$\alpha = 93.83$ (3)°
$\beta = 99.90$ (3)°
$\gamma = 90.42$ (3)°
$V = 857.8$ (6) Å^3
$Z = 1$
$D_x = 1.568$ Mg m^{-3}
D_m not measured

$\mu = 0.143$ mm^{-1}
$T = 153$ (2) K
Parallelepiped
0.50 × 0.30 × 0.20 mm
Dark yellow

Data collection

Siemens *P*3/PC diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4291 measured reflections
4026 independent reflections
2886 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.030$
$\theta_{\rm max} = 28.06°$
$h = -7 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -13 \rightarrow 13$
2 standard reflections every 98 reflections intensity decay: 10%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.089$
$wR(F^2) = 0.236$
$S = 1.13$
3984 reflections
350 parameters
H atoms: see text

$w = 1/[\sigma^2(F_o^2) + (0.14P)^2 + 1.64P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{\rm max} = 0.67$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.80$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1—C1	1.388 (4)	C1—C2	1.483 (4)
N1—C5	1.408 (4)	C4—C5	1.483 (4)
N1—C8	1.463 (4)		
C12—O3—C14	116.9 (3)	O1—C1—C2	121.3 (3)
C1—N1—C5	125.5 (2)	N1—C1—C2	117.2 (3)
C1—N1—C8	117.7 (2)	O2—C5—N1	120.1 (3)
C5—N1—C8	116.5 (3)	O2—C5—C4	123.3 (3)
O1—C1—N1	121.5 (3)	N1—C5—C4	116.6 (3)
C5—N1—C1—O1	177.8 (3)	C8—N1—C5—C4	178.1 (3)
C8—N1—C1—O1	3.2 (5)	C1—N1—C8—C13	−104.5 (3)
C5—N1—C1—C2	−1.7 (5)	C5—N1—C8—C13	80.4 (4)
C8—N1—C1—C2	−176.3 (3)	C1—N1—C8—C9	75.2 (4)
C1—N1—C5—O2	−175.9 (3)	C5—N1—C8—C9	−99.9 (4)
C8—N1—C5—O2	−1.2 (5)	C14—O3—C12—C11	−4.5 (5)
C1—N1—C5—C4	3.5 (5)	C14—O3—C12—C13	176.7 (3)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2*S*—H2*S*···O1$^{\rm i}$	0.82	1.83	2.647 (3)	173

Symmetry code: (i) $1 + x, 1 + y, 1 + z$.

The asymmetric unit of (I) contains half of a solvate phenol molecule lying across an inversion centre, resulting in disorder of its OH group. One TFAA molecule occupies the same space as the phenol, and is also disordered across the inversion centre. The deepest trough in the final ΔF synthesis is located within the disorder region and limitations in the disorder model are thought to account for the high value of R_1.

All TFAA F atoms were refined isotropically. All C—F bond lengths of TFAA molecules, except C2*S*—F3*B*, were constrained to literature values of 1.32 Å (Allen *et al.*, 1987). In the phenol molecule, the C3*S*—C4*S* bond length was similarly constrained to 1.40 Å.

The H atoms of the naphthalenediimide and non-disordered TFAA were found by difference Fourier synthesis, whereas H atoms of the disordered solvent molecules were calculated geometrically. The H atoms of the diimide were refined freely with isotropic displacement parameters. The other H atoms were refined using a riding model with $U_{\rm iso} = 1.2U_{\rm eq}$ of the parent atom.

Data collection: *P*3 (Siemens, 1989*a*). Cell refinement: *P*3. Data reduction: *XDISK* (Siemens, 1989*b*). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1349). Services for accessing these data are described at the back of the journal.

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