Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Two polymorphs of *N*,*N*′-diphenethylterephthalamide

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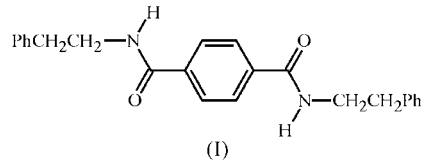
Received 9 March 2006
Accepted 11 May 2006
Online 15 June 2006

The title compound, $C_{24}H_{24}N_2O_2$, crystallizes as a triclinic polymorph from dimethylformamide and a monoclinic polymorph from ethanol. In both forms, the molecule displays crystallographic inversion symmetry, and the packing involves translationally related 'ladders' of molecules connected by N—H···O═C hydrogen bonds. Differences between the structures can be rationalized in terms of weak C—H···O contacts. Powder and differential scanning calorimetry investigations of new samples gave no evidence for the triclinic form, and it seems to represent a disappearing polymorph.

Comment

We are interested in the amides of terephthalic acid, and have synthesized several such compounds from dimethyl terephthalate and published their crystal structures (Jones *et al.*, 2002). In six of the seven structures, the molecules crystallized with crystallographic inversion symmetry. Compounds with free NH functional groups formed ladder-like chains of molecules by intermolecular N—H···O═C hydrogen bonding of the expected form (two donors and two acceptors per molecule), and a related single chain was observed in *N*-cyclohexyl-4-(methoxycarbonyl)benzamide, with only one O═C-NH group per molecule (Jones & Kuś, 2004). We present here the structures of two polymorphs of *N*,*N*′-diphenethylterephthalamide, (I). The crystals were obtained from dimethylformamide (DMF) (thick tablets, triclinic form, henceforth '*T*') and ethanol (laths, monoclinic form, henceforth '*M*'). Measurements for *T* were conducted at 133 K and for *M* at 203 K; below this temperature, crystals of *M* disintegrate.

Both molecules (Figs. 1 and 2) show the expected inversion symmetry; the origins were chosen such that the molecular centres lie at ($\frac{1}{2}$, $\frac{1}{2}$, 0) (*T*) and (0, $\frac{1}{2}$, 0) (*M*). The molecules are closely similar, although the bond lengths in *M* are consistently slightly shorter; this difference is presumably attributable to libration effects at the higher measurement temperature. Corresponding torsion angles also show only minor differences, *e.g.* the rotation of the carbonyl group by *ca*



(I)

30° out of the central ring plane, the extended side-chain conformation and the perpendicular position of the terminal ring relative to the chain (Tables 1 and 3). The molecular dimensions may be regarded as normal. A search of the Cambridge Structural Database (Allen, 2002; Version 5.27) for the structural subunit Ph—C(═O)—NH—CH_2 showed a mean C—C—C═O torsion angle of 24.1 (6)°; the C—C—C angle corresponding to C2—C1—C4 of the current structures (*syn* to the NH function) was consistently greater than 120°, whereas that corresponding to C3—C1—C4 was narrower [122.46 (8) and 118.34 (8)°, respectively].

Both compounds show only one symmetry-independent classical hydrogen bond (Tables 2 and 4), but this suffices to

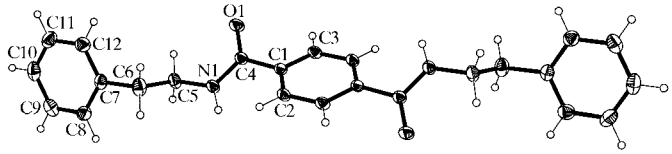


Figure 1
The molecule of the triclinic polymorph of the title compound. Ellipsoids represent 50% probability levels.

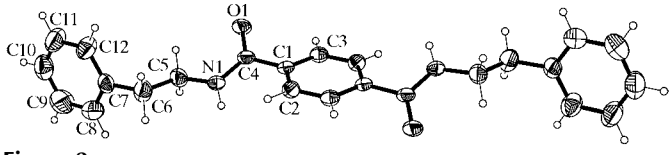


Figure 2
The molecule of the monoclinic polymorph of the title compound. Ellipsoids represent 50% probability levels.

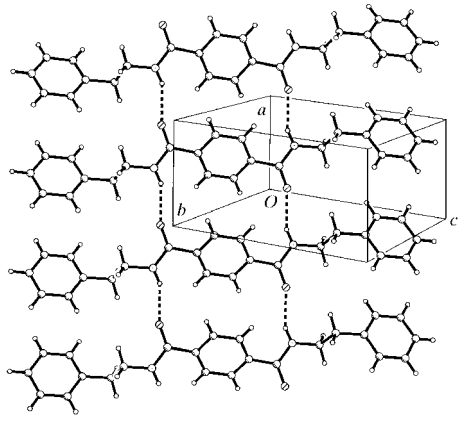


Figure 3
The packing of the triclinic polymorph, viewed perpendicular to (021).

 DOI: 10.1107/S0108270106017422

form the usual ladder motif (Figs. 3 and 4) involving rings of graph set $R_2^2(18)$ (Etter, 1990). Neighbouring molecules in the ladder are related by translation. In *T*, the repeat distance of the chain, *ca* 5 Å, corresponds to the short *a* axis; in *M*, it corresponds to the short *b* axis, whereby the adjacent ladders in Fig. 4 are related by 2_1 and *c*-glide operators. The same repeat distance was observed in two of our earlier structures, namely *N*,*N*′-di-*n*-butyl- and *N*,*N*′-di-*n*-hexylterephthalamide (Jones *et al.*, 2002). In the related benzamide (Jones & Kuś, 2004), the crystal repeat distance was *ca* 10 Å, but there were two symmetry-independent molecules in the chain.

In the hope of explaining or at least rationalizing the existence of the two polymorphs, an analysis of the packing differences needs to be conducted. The projection of *T* along the short axis (Fig. 5) shows that the molecules lie parallel to the (021) planes. Neighbouring 'ladders' are connected across inversion centres ($\frac{1}{2}$, 0, $\frac{1}{2}$) by a borderline 'weak' C—H···O interaction (Desiraju & Steiner, 1999) involving a *meta* H atom of the terminal ring (Table 2). The horizontal rows of molecules in Fig. 5 are appreciably offset. There is a consistent

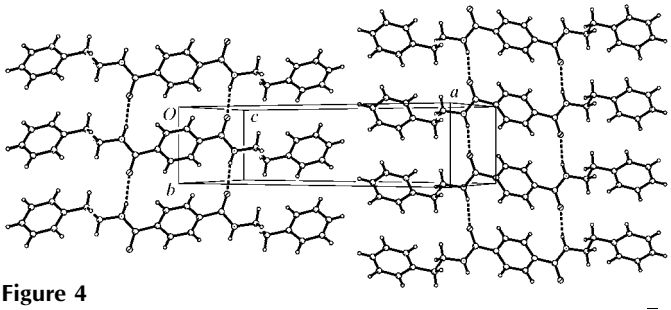


Figure 4
The packing of the monoclinic polymorph, viewed perpendicular to $(10\bar{1})$.

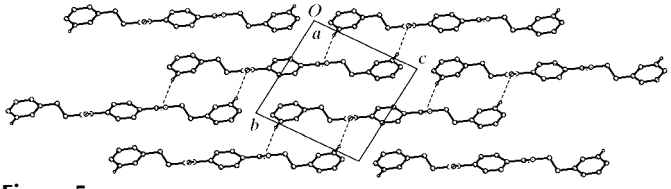


Figure 5
The packing of the triclinic polymorph, projected parallel to the *a* axis. Weak C—H···O interactions are shown as dashed lines; H atoms not involved in these interactions have been omitted for clarity.

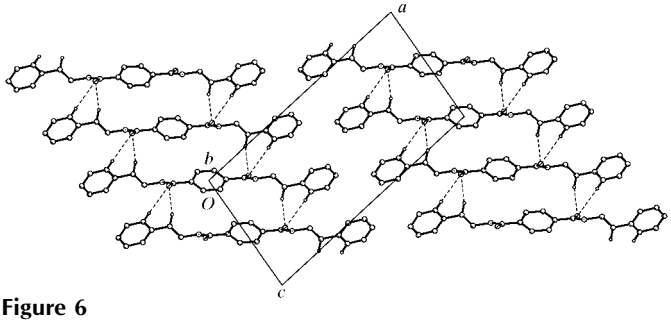


Figure 6
The packing of the monoclinic polymorph, projected parallel to the *b* axis. Weak C—H···O interactions are shown as dashed lines; H atoms not involved in these interactions have been omitted for clarity.

directionality of the C═O groups, whereby the groups at the left of each molecule point out of the paper.

The projection of *M* along the short axis (Fig. 6) shows that the molecules lie in planes parallel to $(30\bar{2})$. Neighbouring ladders are connected *via* a bifurcated $(C—H)_2\cdots O$ interaction (Table 4), involving a methylene H atom and an *ortho* H atom of the terminal ring, *via* a *c*-glide operator and align parallel to the *z* axis; the offset is much less than in *T*. The C═O groups alternate in direction, in and out of the paper, in contrast to *T*.

There are no significant C—H···π or stacking interactions in either form. It could be surmised that the different packing patterns, although distinguishable in terms of C—H···O contacts, might be more subtly determined by the sum of many much weaker van der Waals-type interactions. It might be instructive to predict the packing of this compound (Day *et al.*, 2005), although such methods are still in their infancy.

After determining the structures, it seemed worthwhile to investigate more closely the relative stability of the two phases and any possible phase changes. Unfortunately, the samples used for the single-crystal measurements were no longer available. A new synthesis and new recrystallizations were undertaken. Although the same conditions were used, the new samples seemed optically to contain only the *M* phase (poorly formed and intergrown laths, in contrast to the well formed and generally larger and thicker tablets of form *T*). Powder investigations based on the new samples confirmed that only the *M* phase was present. The powder pattern was not changed by either (i) heating to temperatures slightly below the melting point and recooling, (ii) melting and recooling, (iii) stirring a suspension for one week and re-isolating, or (iv) rapid (kinetically controlled) crystallization from ethanol or DMF. Cooling the samples to liquid nitrogen temperature gave inconclusive results; two new reflections at low angle arose in the powder pattern, but the overall pattern did not correspond to form *T*. Differential scanning calorimetry measurements gave no indication of any phase change up to the melting point. We are therefore unable to form any conclusions as to possible phase interchanges between forms *T* and *M*. Form *T* seems to represent a 'disappearing polymorph' (Dunitz & Bernstein, 1995) and may thus be metastable, whereas form *M*, now found exclusively, is presumably the stable form.

Experimental

The title compound was prepared according to the method described by Jones *et al.* (2002). The resulting white solid was washed several times with toluene and methanol and dried in air [yield 80%, m.p. 543–545 K for form *M* (form *T* is no longer available)]. Analysis calculated: C 77.39, H 6.49, N 7.52%; found C 77.43, H 6.54, N 7.55%. ^{1}H NMR (DMSO-d_6/TMS): δ 8.66 (*bs*, 2H), 7.87 (*s*, 4H), 7.32–7.18 (*m*, 10H), 3.49 (*q*, 4H), 2.85 (*t*, 4H). IR (cm^{-1}, KBr pellets): 3301, 3085, 3064, 3030, 2969, 2933, 2868, 1630, 1544, 1497, 1465, 1455, 1372, 1323, 1290, 1194, 1161, 1120, 1088, 1053, 1032, 1022, 910, 857, 749, 700. ESI MS (*m*/*z*, intensity): 170 (24) $[M + 2H]^{2+}$, 339 (100) $[M + H]^+$, 677 (30) $[2M + H]^+$. Single crystals were obtained from the relevant solvent (see *Comment*) by slow evaporation.

Polymorph *T*

Crystal data

$C_{24}H_{24}N_2O_2$
M_r = 372.45
Triclinic, $P\overline{1}$
a = 5.1845 (12) Å
b = 9.719 (2) Å
c = 10.041 (2) Å
α = 95.305 (5)°
β = 98.541 (5)°
γ = 101.663 (5)°
V = 486.08 (18) Å^3
Z = 1
D_x = 1.272 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 133 (2) K
Tablet, colourless
0.4 × 0.2 × 0.1 mm

Data collection

Bruker SMART 1000 CCD area detector diffractometer
ω scan
5728 measured reflections
2899 independent reflections
2271 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 30.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.127
S = 1.03
2899 reflections
131 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0648P)^2 + 0.1016P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

O1—C4	1.2395 (13)	C5—C6	1.5235 (17)
N1—C4	1.3449 (14)	C6—C7	1.5137 (16)
N1—C5	1.4568 (14)		
C3—C1—C4	118.12 (9)	C2—C1—C4	122.36 (9)
C5—N1—C4—C1	−179.32 (11)	N1—C5—C6—C7	−178.62 (10)
C3—C1—C4—O1	−31.21 (16)	C5—C6—C7—C8	87.46 (14)

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^{i}	0.864 (16)	2.155 (16)	2.9606 (14)	155.1 (14)
C6—H6A···O1^{i}	0.99	2.79	3.5395 (17)	133
C9—H9···O1^{ii}	0.95	2.73	3.3351 (18)	122

Symmetry codes: (i) $x+1, y, z$; (ii) $-x+1, -y, -z+1$.

Polymorph *M*

Crystal data

$C_{24}H_{24}N_2O_2$
M_r = 372.45
Monoclinic, $P2_1/c$
a = 19.688 (2) Å
b = 5.0178 (6) Å
c = 10.1344 (11) Å
β = 97.762 (2)°
V = 992.03 (19) Å^3
Z = 2
D_x = 1.247 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 203 (2) K
Lath, colourless
0.50 × 0.20 × 0.08 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
ω scans
11272 measured reflections
2029 independent reflections
1091 reflections with $I > 2\sigma(I)$
R_{int} = 0.078
θ_{max} = 26.4°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.134
S = 1.01
2029 reflections
131 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0622P)^2 + 0.0804P]$ 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}

Table 3
Selected geometric parameters (Å, °) for (II).

O1—C4	1.241 (2)	C5—C6	1.493 (3)
N1—C4	1.336 (3)	C6—C7	1.508 (3)
N1—C5	1.448 (3)		
C3—C1—C4	118.26 (18)	C2—C1—C4	122.94 (19)
C5—N1—C4—C1	−174.68 (19)	N1—C5—C6—C7	179.0 (2)
C3—C1—C4—O1	−30.5 (3)	C5—C6—C7—C8	88.3 (3)

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^{i}	0.84 (2)	2.08 (2)	2.908 (2)	165.7 (19)
C6—H6A···O1^{ii}	0.98	2.77	3.664 (3)	151
C12—H12···O1^{ii}	0.94	2.70	3.537 (3)	149

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

Amide H atoms were refined freely. Other H atoms were included at calculated positions and refined using a riding model, with fixed C—H bond lengths of 0.95 (CH) and 0.99 Å (CH_2) for the triclinic form, and 0.94 (CH) and 0.98 Å (CH_2) for the monoclinic form; U_{iso}(H) values were fixed at 1.2U_{eq}(C).

For both compounds, data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3008). Services for accessing these data are described at the back of the journal.

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