# Two concomitant polymorphs of N,N′-bis[4-(diethylamino)phenyl]-terephthaldiamide

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The title compound, $C_{28}H_{34}N_4O_2$, crystallizes simultaneously as a monoclinic, (I$m$), and a (twinned) triclinic polymorph, (I$t$), from $d_6$-dimethyl sulfoxide. Polymorph (I$t$) ($P\bar{1}$, $Z = 1$) displays the standard 'ladder' packing for this group of compounds, with neighbouring inversion-symmetric molecules related by translation and connected by hydrogen bonds of the form N—H···O=C. Polymorph (I$m$) ($Cc$, $Z = 4$) has no imposed symmetry; there are three independent hydrogen bonds, one classical N—H···O=C and a bifurcated system with N—H···O=C augmented by a short C—H···O=C interaction. Each molecule is thereby linked to four neighbouring molecules, two lower and two higher, so that a crosslinked three-dimensional pattern is formed rather than the standard ladder.

## Comment

We are interested in the amides of terephthalic acid and have synthesized several such compounds from dimethyl terephthalate and published their structures (Jones *et al.*, 2002). In six of the seven structures, the molecules crystallized with imposed inversion symmetry. Compounds with free NH functional groups formed ladder-like chains of molecules by translation *via* hydrogen bonding of the expected form N—H···O=C (two donors and two acceptors per molecule, but generally only one set per asymmetric unit), and a similar example, N,N′-bis(methoxycarbonylmethyl)terephthalamide, was presented by Armelin *et al.* (2001). A related single chain was observed in N-cyclohexyl-4-(methoxycarbonyl)benzamide, with only one O=CNH moiety per molecule (Jones & Kuś, 2004). We have also reported (Ossowski *et al.*, 2006) the structures of two polymorphs of N,N′-diphenethylterephthalamide, one triclinic and one monoclinic, each of which crystallized with imposed inversion symmetry and the standard 'ladder' structure, but with different C—H···O interactions; subsequently, all attempts to obtain the triclinic form actions; subsequently, all attempts to obtain the triclinic form

failed and we thus regard it as a 'disappearing polymorph' (Dunitz & Bernstein, 1995). Differential scanning calorimetry (DSC) measurements of this compound gave no indication of any phase change up to the melting point. We have now found two polymorphs of another related derivative, N,N′-bis[4-(diethylamino)phenyl]terephthaldiamide, (I), and report their structures here. For some of our other recent reports on polymorphism, see Jones & Mangalagiu (2009, and references therein), Lozano *et al.* (2004), Henschel *et al.* (2005) and Zerbe *et al.* (2007).



(I)
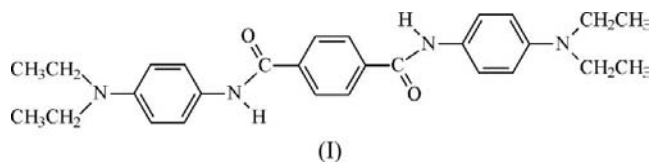
Small amounts of crystalline material were available from an NMR tube containing a solution of (I) in $d_6$-DMSO (dimethyl sulfoxide). Most of the sample consisted of poorly formed yellow prisms and plates, which were generally cracked and somewhat opaque. However, a usable single crystal was found and proved to be monoclinic [henceforth referred to as (I$m$)]. A few rather clearer plate-shaped crystals were identified optically and seemed to have a different unit cell, although they were invariably twinned. Eventually, an apparently untwinned triclinic crystal [form (I$t$)] was found
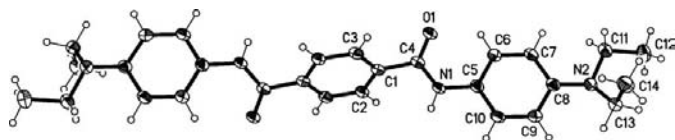


**Figure 1**
The molecular structure of polymorph (I$t$). Ellipsoids represent 50% probability levels.
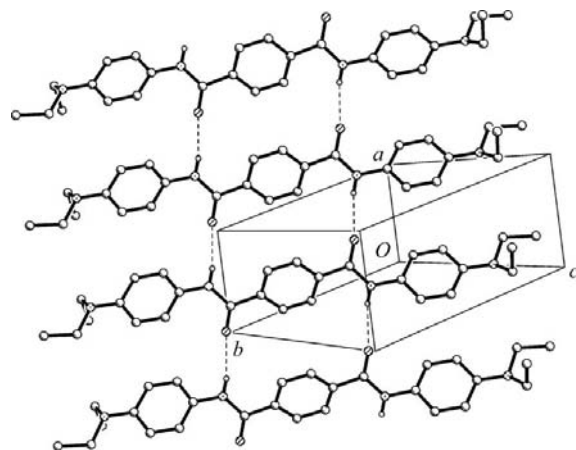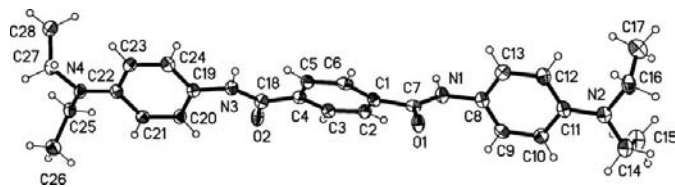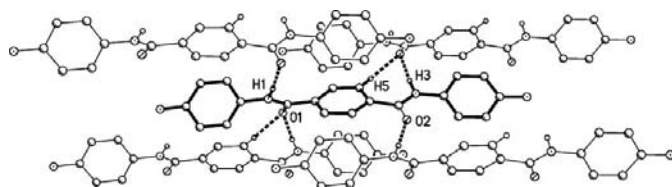


**Figure 2**
The packing of (I$t$) viewed perpendicular to (013).

**Figure 3**
The molecular structure of polymorph (I*m*). Ellipsoids represent 50% probability levels.



**Figure 4**
The hydrogen-bonding environment of polymorph (I*m*). The neighbouring molecules top left and bottom right are displaced out of the paper towards the viewer, whereas the molecules top right and bottom left lie below the central molecule.

and measured, although this too proved to be twinned to a small extent.

The molecule of polymorph (I*t*) is shown in Fig. 1; it displays inversion symmetry, so that there is one molecule per unit cell. The C1—C4(=O1)—N1—C5 fragment is planar and subtends an interplanar angle of 42.56 (5)° to the central ring and 27.63 (7)° to the outer ring; the rings themselves subtend an angle of 70.07 (5)°. The packing (Fig. 2) is of the established 'ladder' type, with classical hydrogen bonds of the form N—H···O=C linking the molecules by translation parallel to the *a* axis. A precondition for this type of packing is that the N—H vectors should be antiparallel, and this is fulfilled exactly (angle between vectors = 180°) for inversion-symmetric molecules.

The molecule of polymorph (I*m*) is shown in Fig. 3; there is, unusually for this type of molecule, no imposed molecular symmetry and indeed the molecule departs totally even from approximate inversion symmetry. The two central moieties C1—C7(=O1)—N1—C8 and C4—C18(=O2)—N3—C19 [chemically identical to the fragment discussed above for (I*t*)] subtend different interplanar angles to their neighbouring rings; the former makes an angle of 85.9 (2)° to the outer ring and 60.0 (1)° to the central ring, whereas the latter makes corresponding angles of 23.0 (3) and 7.7 (3)° (for corresponding torsion angles, see Tables 1 and 3). The angle between the N—H vectors is 79°, and the 'ladder' packing is thus rendered impossible.

Fig. 4 shows the principal hydrogen bonds between the molecule and its four neighbouring molecules (two as acceptors and two as donors). N1—H1···O2 is a classical isolated hydrogen bond, whereas the hydrogen bond N3—H3···O1 is augmented by C5—H5···O1, forming a bifurcated system; we observed a similar system in *N*,*N'*-di-*tert*-butylterephthaldi-amide (Jones *et al.*, 2002). At first sight, the 'ladder' pattern
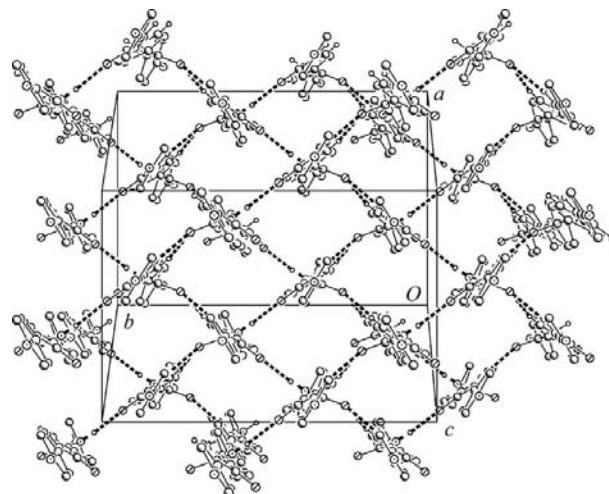


**Figure 5**
The crosslinked packing of polymorph (I*m*).

seems to be upheld, but this is an artefact of projection in the view direction; in fact, all hydrogen-bonded neighbour molecules are displaced in height with respect to the central molecule. The crosslinking leads to a three-dimensional pattern (Fig. 5).

Difficulties in recrystallizing the title compound (especially with regard to reproducibility) make it difficult to establish relationships between the phases. Powder investigations of the title compound were unsuccessful because of the very limited amount of compound available. Furthermore, the powder sample had been crystallized from methanol and was very probably a methanol solvate, although no single crystals could be obtained to confirm this. Nevertheless, it is reasonable to surmise that the monoclinic form is less stable; its density is 1.278 Mg m$^{-3}$ compared to 1.303 Mg m$^{-3}$ for the triclinic form (for a brief discussion of the 'density rule', see, for example, Bernstein, 2002). The crosslinked packing pattern of the monoclinic form thus probably represents a kinetically stable island on the way to the simpler and presumably more efficient ladder pattern of the triclinic form. DSC measurements of (I) show a phase change at 407 K with $\Delta H = 21$ J g$^{-1}$. Thermogravimetric analysis at this point gave no indication of any mass change. The melting point determined by DSC for (I) is 547 K (3 K higher than measured by standard methods).

It is not clear if terephthaldiamides, in view of their potentially different hydrogen-bonding patterns, have a generally high tendency to form polymorphs, and indeed this tendency can scarcely be quantified. However, our investigations at least show the value of a careful optical investigation of crystalline samples for revealing different crystal forms.

## Experimental

The title compound was synthesized from terephthaloyl chloride and *N*,*N*-diethylbenzene-1,4-diamine in benzene solution (standard procedure). The resulting golden yellow solid was washed with toluene and methanol and dried in air [yield *ca* 40%; m.p. 544 K (uncorrected)]. Analysis calculated for $C_{28}H_{34}N_4O_2$: C 73.33, H 7.47, N 12.22; found C 73.29, H 7.76, N 12.45. $^1$H NMR (DMSO-$d_6$/TMS,

400 MHz): $\delta$ 10.07 (s, 2H, NH), 8.04 (s, 4H, ArH), 7.54, 6.66 (dd, 4H, $J$ = 9.1 Hz, ArH), 3.30 (q, 4H, –CH$_2$CH$_3$), 1.07 (t, 6H, –CH$_2$CH$_3$). $^{13}$C NMR (DMSO-$d_6$/TMS, 100 MHz): $\delta$ 164.07, 144.57, 137.46, 127.55, 127.50, 122.49, 111.80, 43.85, 12.48. IR (cm$^{-1}$, KBr pellets): 3435, 3325, 3049, 2968, 2930, 2867, 2829, 1639, 1593, 1517, 1414, 1387, 1372, 1346, 1325, 1286, 1263, 1246, 1188, 1144, 1117, 1074, 1057, 1017, 1007, 930, 896, 866, 830, 811, 782, 686, 643. ESI MS ($m/z$, intensity): 230 (5) $[M + 2H]^{2+}$, 459.5 (100) $[M + H]^+$, 916.8 (52) $[2M]^+$; 457.3 (100) $[M - H]^-$. Single crystals were obtained from DMSO-$d_6$ solution (after NMR measurement). Both forms crystallized together in the NMR tube.

## Polymorph (I$t$)

### Crystal data

| | |
|---|---|
| C$_{28}$H$_{34}$N$_4$O$_2$ | $\gamma$ = 103.53 (2)° |
| $M_r$ = 458.59 | $V$ = 584.2 (3) Å$^3$ |
| Triclinic, $P\bar{1}$ | $Z$ = 1 |
| $a$ = 5.1100 (9) Å | Cu $K\alpha$ radiation |
| $b$ = 9.946 (3) Å | $\mu$ = 0.66 mm$^{-1}$ |
| $c$ = 12.107 (3) Å | $T$ = 100 K |
| $\alpha$ = 100.54 (2)° | 0.35 × 0.30 × 0.08 mm |
| $\beta$ = 93.90 (2)° | |

### Data collection

| | |
|---|---|
| Oxford Diffraction Xcalibur Nova O diffractometer | 4870 measured reflections |
| | 4870 independent reflections |
| Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2008) | 4407 reflections with $I > 2\sigma(I)$ |
| $T_{min}$ = 0.647, $T_{max}$ = 1.000 | $R_{int}$ = 0.000 |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$ = 0.053 | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2)$ = 0.162 | |
| $S$ = 1.12 | |
| 4870 reflections | $\Delta\rho_{max}$ = 0.24 e Å$^{-3}$ |
| 164 parameters | $\Delta\rho_{min}$ = −0.19 e Å$^{-3}$ |

## Polymorph (I$m$)

### Crystal data

| | |
|---|---|
| C$_{28}$H$_{34}$N$_4$O$_2$ | $V$ = 2383.5 (2) Å$^3$ |
| $M_r$ = 458.59 | $Z$ = 4 |
| Monoclinic, $Cc$ | Cu $K\alpha$ radiation |
| $a$ = 11.5899 (6) Å | $\mu$ = 0.64 mm$^{-1}$ |
| $b$ = 16.7899 (8) Å | $T$ = 100 K |
| $c$ = 13.4785 (8) Å | 0.30 × 0.20 × 0.08 mm |
| $\beta$ = 114.667 (6)° | |

**Table 1**
Selected torsion angles (°) for (I$t$).

| | | | |
|---|---|---|---|
| C2—C1—C4—N1 | −28.03 (16) | C6—C5—N1—C4 | −44.32 (18) |
| C1—C4—N1—C5 | −177.78 (10) | | |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1···O1$^i$ | 0.832 (18) | 2.161 (18) | 2.9773 (14) | 166.8 (14) |

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

**Table 3**
Selected torsion angles (°) for (I$m$).

| | | | |
|---|---|---|---|
| C2—C1—C7—N1 | 51.4 (6) | C13—C8—N1—C7 | −87.1 (6) |
| C5—C4—C18—N3 | 3.9 (7) | C4—C18—N3—C19 | −178.0 (4) |
| C1—C7—N1—C8 | −177.8 (4) | C20—C19—N3—C18 | 24.4 (8) |

**Table 4**
Hydrogen-bond geometry (Å, °) for (I$m$).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1···O2$^i$ | 0.93 (4) | 2.03 (4) | 2.960 (5) | 175 (6) |
| N3—H3···O1$^{ii}$ | 0.92 (4) | 2.24 (4) | 3.149 (5) | 168 (4) |
| C5—H5···O1$^{ii}$ | 0.95 | 2.32 | 3.262 (6) | 171 |
| C14—H14$A$···O1$^{iii}$ | 0.99 | 2.55 | 3.223 (7) | 126 |

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

### Data collection

| | |
|---|---|
| Oxford Diffraction Xcalibur Nova O diffractometer | 12374 measured reflections |
| | 2182 independent reflections |
| Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2008) | 2167 reflections with $I > 2\sigma(I)$ |
| | $R_{int}$ = 0.022 |
| $T_{min}$ = 0.810, $T_{max}$ = 1.000 | |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$ = 0.055 | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2)$ = 0.153 | |
| $S$ = 1.10 | |
| 2182 reflections | $\Delta\rho_{max}$ = 0.34 e Å$^{-3}$ |
| 319 parameters | $\Delta\rho_{min}$ = −0.31 e Å$^{-3}$ |
| 303 restraints | |

For polymorph (I$t$), the NH hydrogen was refined freely. Methyl H atoms were located in difference syntheses, idealized to C—H = 0.98 Å and H—C—H = 109.5°, and refined as rigid groups which were allowed to rotate but not tip. Other H atoms were placed in calculated positions (C—H = 0.95 Å for aromatic and 0.99 Å for methylene H atoms) and refined using a riding model. $U_{iso}$(H) values were set at 1.5$U_{eq}$(C) for methyl H atoms and 1.2$U_{eq}$(C) for other H atoms.

The initial $R$ values were rather high and inspection showed that the crystal was nonmerohedrally twinned by rotation of 180° about $c^*$. For refinement, the HKLF 5 option was employed. Scale factors of five reflection batches, corresponding to different extents of twin overlap, indicated that the main component was occupied to the extent of 92%. The untwinning routines merge all equivalent reflections and thus no $R_{int}$ value can be given. Data are only 93% complete to $\theta$ = 67°, which may also be a consequence of the untwinning routines (rejection of poorly determined intensities).

For polymorph (I$m$), H atoms were refined as above, except that the N—H distances were restrained to be equal (SADI). The Flack (1987) parameter originally refined to 0.2 (4), which is essentially indeterminate (although successful determinations of absolute structure are, in principle, possible for Cu radiation and structures containing oxygen); for this reason, Friedel opposite reflections were merged and the resulting Flack parameter is meaningless. The necessarily poor data/parameter ratio was to some extent ameliorated by the use of restraints (SIMU and DELU) to the displacement parameters. Data are 98% complete to $\theta$ = 67°.

For both compounds, data collection: CrysAlis CCD (Oxford Diffraction, 2008); cell refinement: CrysAlis RED (Oxford Diffraction, 2008); data reduction: CrysAlis RED; program(s) used to solve

# organic compounds

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3326). Services for accessing these data are described at the back of the journal.

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