Crystal Structures of Three Di- and Tetrabenzylterephthalamides

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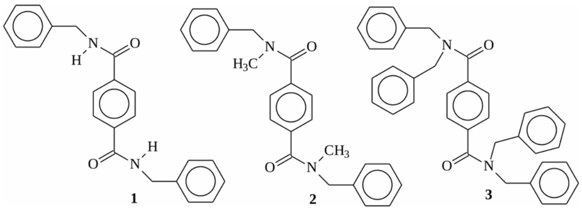
The X-ray crystal structures of the three compounds *N*,*N*′-dibenzylterephthalamide, **1**, *N*,*N*′-dibenzyl-*N*,*N*′-dimethylterephthalamide, **2**, and *N*,*N*,*N*′,*N*′-tetrabenzylterephthalamide, **3**, were determined. Compound **1** fits into the general pattern of disubstituted terephthalamides, with crystallographic inversion symmetry and classical hydrogen bonds linking the molecules into chains parallel to the short axis. Compound **2** also displays inversion symmetry, but the packing only involves two weak hydrogen bonds of the form $\text{C–H}_{\text{methyl}} \cdots \text{O}$. The complex packing of compound **3**, which possesses no crystallographic symmetry, involves only two C–H···O contacts; these are augmented by three C–H···π interactions.

Key words: Terephthalamides, X-Ray Structures, Secondary Interactions

Introduction

We are interested in terephthalamide derivatives, and especially in the hydrogen-bonding patterns in their packing diagrams. In our previous papers [1 – 3] we reported the crystal structures of a series of various terephthalic acid diamide derivatives in which nitrogen atoms are mono- or disubstituted. The disubstituted derivatives, which retain a hydrogen atom at each nitrogen atom, are easier to summarise: six out of seven structures displayed crystallographic inversion symmetry within the molecule, whereby the amide group was rotated by *ca.* 35 – 40° out of the central aromatic plane. The packing of five of these structures involved classical hydrogen bonds N–H···O=C, which linked the molecules into chains by translation. In the other two cases, bifurcated hydrogen bond systems of the form (N–H···, C–H···)O=C were involved, and each molecule was linked to four other, laterally displaced molecules by glide plane operators. A search of the Cambridge Database [4] for related molecules, but involving only hydrocarbon substituents, revealed the structure of the diphenyl derivative [5], which corresponds perfectly to the main structural type as described above. Three out of four tetrasubstituted amides [1] also displayed crystallographic inversion symmetry; in the packing diagrams, the lack of classical hydrogen bond donors meant that the main interactions were “weak”, but in some cases very short (H···O 2.2 Å), C–H···O hydrogen bonds with donors on the central ring. The packing types were however more hetereogeneous.



Scheme 1.

Here we present X-ray structure determinations of three benzyl derivatives of terephthalic amide (Scheme 1). Compound **1** is a disubstituted terephthalamide retaining one NH function at each nitrogen atom), whereas compounds **2** and **3** are tetrasubstituted amides, with one benzyl and one methyl substituent at each nitrogen atom in **2** and four benzyl N-substituents in **3**.

Discussion

Compound **1** fits perfectly into the general pattern of the monosubstituted derivatives. The molecule displays crystallographic inversion symmetry (Fig. 1a), and classical hydrogen bonds (Table 1) link the molecules into chains parallel to the short *a* axis (Fig. 1b). Three weak interactions, a bifurcated $(\text{C–H})_2 \cdots \text{O}$ and a C–H···π system, link the parallel

Table 1. Intermolecular contacts in compound **1** (Å and deg)[a,b].

D–H···A	$d(D$–H)	d(H···A)	$d(D$···A)	∠(DHA)
N–H01···O[#1]	0.881(16)	2.008(16)	2.8748(12)	167.9(14)
C5–H5A···O[#2]	0.99	2.60	3.5479(14)	162
C11–H11···O[#2]	0.95	2.59	3.4809(14)	156
C5–H5B···Cg(C6–11)[#3]	0.99	2.66	3.57	152

[a] Symmetry transformations used to generate equivalent atoms: [#1] $x+1, y, z$; [#2] $-x+1, -y+1, -z+1$; [#3] $-1+x, y, z$; [b] Cg = centre of gravity of the ring system.

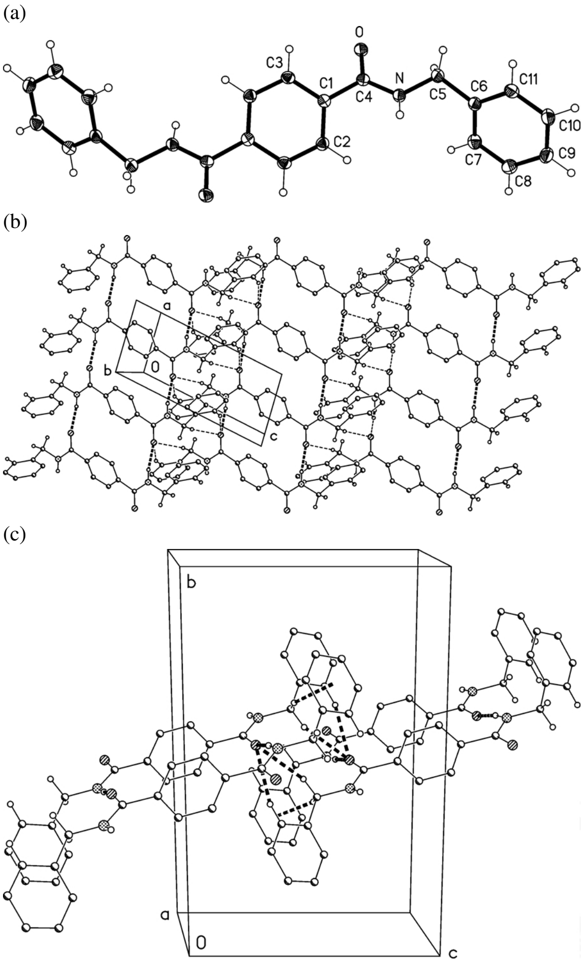


Fig. 1. (a) The molecule of compound **1** in the crystal. Ellipsoids represent 50 % probability levels. Only the asymmetric unit is numbered. Torsion angle C2–C1–C4=O = 150.4(1)°. (b) Packing diagram of compound **1** viewed parallel to the y axis. Thick dashed lines represent classical hydrogen bonds, thin dashed lines represent "weak" interactions. (c) Packing diagram of compound **1** viewed perpendicular to $(\bar{1}10)$, showing C–H···O and C–H···π interactions as thick dashed lines. The classical hydrogen bonds are seen almost end-on in this view.

Table 2. Intermolecular contacts in compound **2** (Å and deg)[a].

D–H···A	$d(D$–H)	d(H···A)	$d(D$···A)	∠(DHA)
C5–H5B···O[#1]	0.98	2.56	3.516(3)	166
C5–H5C···O[#2]	0.98	2.50	3.413(3)	156

[a] Symmetry transformations used to generate equivalent atoms: [#1] $x-1/2, y-1/2, z$; [#2] $x, y-1, z$.

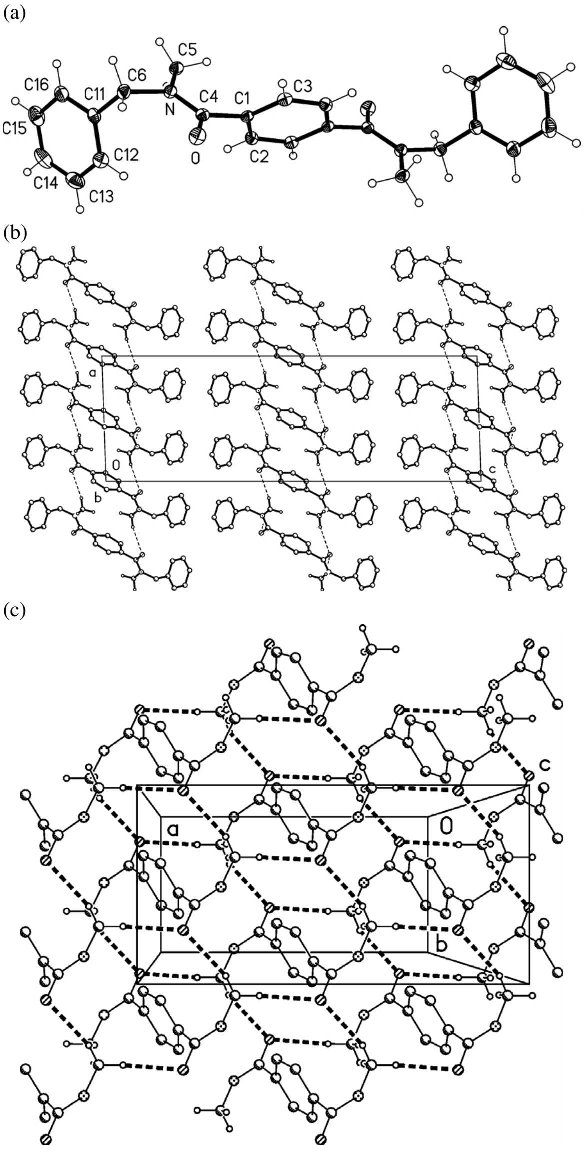


Fig. 2. (a) The molecule of compound **2** in the crystal. Ellipsoids represent 50 % probability levels. Only the asymmetric unit is numbered. (b) Packing diagram of compound **2** projected parallel to the y axis. Thin dashed lines represent C–H···O interactions. (c) Packing diagram of compound **2** viewed perpendicular to the xy plane in the region $z \approx 0$. Thick dashed lines represent C–H···O interactions. Benzyl groups are omitted for clarity.

Table 3. Intermolecular contacts in compound **3** (Å and deg)[a,b].

D–H···A	$d(D$–H)	d(H···A)	$d(D···A)$	∠(DHA)
C24–H24···O1$^{\#1}$	0.95	2.63	3.278(3)	126
C34–H34···O2$^{\#2}$	0.95	2.66	3.340(3)	129
C25–H25···Cg(C31–36)$^{\#3}$	0.95	2.80	3.60	143
C26–H26···Cg(C1–6)$^{\#4}$	0.95	2.92	3.71	140
C36–H36···Cg(C1–6)$^{\#5}$	0.95	2.82	3.66	148

[a] Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $x+1/2$, $-y+5/2$, z; $^{\#2}$ $x-1/2$, $-y-1/2$, z; $^{\#3}$ $x+1/2$, $-y+3/2$, z; $^{\#4}$ x, $y+1$, z; $^{\#5}$ x, $y-1$, z; [b] Cg = centre of gravity of the ring system.

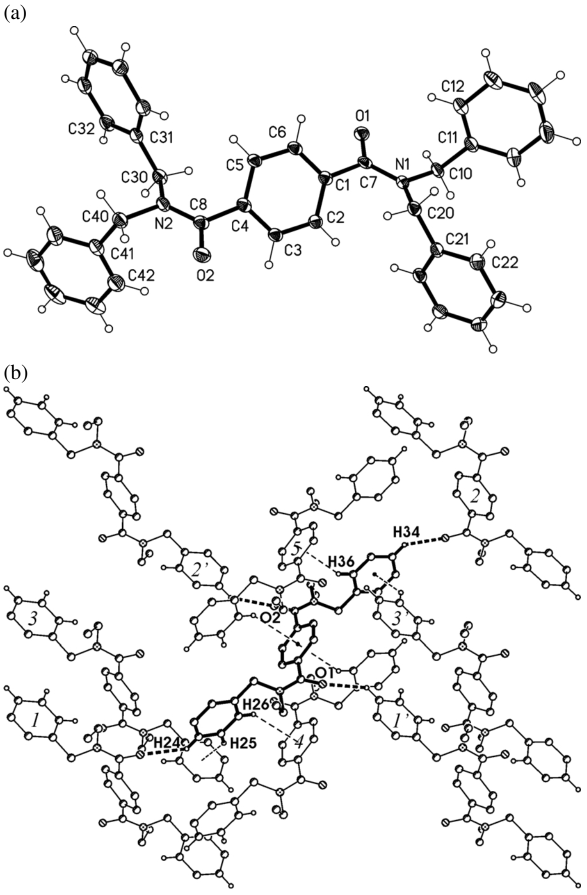


Fig. 3. (a) The molecule of compound **3** in the crystal. Ellipsoids represent 50 % probability levels. Torsion angles: C2–C1–C7=O1 135.2(3), C5–C4–C8=O2 −132.6(3)°. (b) Weak interactions from one central molecule of compound **3** (drawn with thicker bonds) to eight neighbouring molecules. Selected atoms of the central molecule are labelled. Thick dashed lines represent H···O, thin dashed lines H···π interactions. The neighbouring molecules are numbered in the same order as the interactions in Table 3; molecules without primes function as acceptors, molecules with primes function as donors in the secondary interactions. The label *4* is equivalent to *5′* and *5* to *4′*.

chains (Table 1; Figs. 1b, c). These interactions involve the benzyl fragments, whereas the central phenylene ring does not participate in secondary interactions.

The tetrasubstituted compound **2** also displays inversion symmetry, but the carbonyl group is rotated more than usual out of the plane of the central ring (C2–C1–C4=O 111.8(2)°). The only secondary contacts are two weak hydrogen bonds of the form C–H_{methyl}···O, which link the molecules to form thick layers parallel to the *xy* plane (Table 2, Fig. 2c); the view in projection parallel to the *y* axis (Fig. 2b) is however more informative.

The molecule of compound **3** (Fig. 3a) possesses no crystallographic symmetry, but is close to inversion symmetry (r. m. s. deviation 0.10 Å). The extended benzyl "arms" lead to an appreciable maximum molecular length C14···C44 (excluding hydrogens) of 16.4 Å. The bulkiness of the benzyl groups militates against close approaches to the carbonyl oxygens, and the only two moderately short contacts (H24···O1 2.63, H34···O1 2.66 Å) involve narrow angles (< 130°). In such cases, C–H···π contacts might be expected to become more important, and three of these are indeed observed (Table 3). Each molecule of **3** is thus involved as donor and acceptor in a total of ten weak contacts to eight neighbouring molecules (Fig. 3b). The packing diagrams consequently become extremely complicated (as is often the case in space group $Pna2_1$). The molecules pack so as to form thick layers parallel to the *ab* plane at $z \approx 1/4, 3/4$, *etc.*

The presence of various dispositions of the benzyl fragments in solution, and especially the alternative positions of their CH_2 groups, become clear from their NMR spectra. In both proton and carbon spectra there is a different signal for each CH_2 group, which reflects the different arrangements of these fragments with respect to the central ring, and also rules out fast rotation about the N–C bonds (*e. g.* N1–C7 and N2–C8 in **3**) at r. t. This is a characteristic feature of methyl or methylene groups directly bonded to the nitrogen atom of many N-substituted amides in solution at r. t., and is regarded (*e. g.* in *N*,*N*-dimethylformamide [6]) as a textbook example of rotational barriers in the amide unit. A second related example in the literature is that of tetraethylterephthalamide [7].

Experimental Section

Compounds **1**–**3** were synthesised from terephthaloyl chloride and the corresponding amines according to the procedure described earlier [1]. Analytical data of **1** and **3** were

Table 4. Crystal data and numbers pertinent to data collection and structure refinement for compounds **1** – **3**.

Compound	**1**	**2**	**3**
Formula	$C_{22}H_{20}N_2O_2$	$C_{24}H_{24}N_2O_2$	$C_{36}H_{32}N_2O_2$
M_r	344.40	372.45	524.64
Crystal size, mm^3	0.25 × 0.10 × 0.04	0.5 × 0.4 × 0.13	0.4 × 0.03 × 0.03
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$C2/c$	$Pna2_1$
Cell constants			
a, Å	4.90752(12)	10.8712(6)	19.162(2)
b, Å	16.6954(3)	5.5261(4)	5.3102(6)
c, Å	10.6955(2)	32.563(3)	26.803(4)
β, deg	100.886(3)	91.885(6)	90
V, Å^3	860.55(3)	1955.1(2)	2727.4(6)
Z	4	4	4
D_x, Mg m^{-3}	1.33	1.27	1.28
μ, mm^{-1}	0.7	0.1	0.6
F(000), e	364	792	1112
T, K	100	100	103
λ, Å	1.54184	0.71073	1.54148
$2\theta_{max}$, deg	152	56.6	142
Transmissions	0.77 – 1.00	no corr.	0.76 – 1.00
Refl. meas. / indep. / R_{int}	15799 / 1784 / 0.024	6199 / 2398 / 0.033	22443 / 2674 / 0.086
Ref. parameters	122	128	361
Restraints	0	0	407
R [$F \geq 4\,\sigma(F)$]	0.036	0.073	0.041
wR (F^2, all refl.)	0.089	0.139	0.102
S	1.06	1.20	0.99
$\Delta\rho_{max}$, e Å^{-3}	0.21	0.34	0.23

in agreement with literature values [8, 9]. Single crystals used for X-ray measurements were obtained from DMF, methanol and ethanol-hexane solutions, respectively, by slow evaporation of solvents. NMR spectra were obtained in $CDCl_3$ solutions using a Bruker apparatus. Mass spectra were recorded using a Varian MS 500 instrument and the direct injection method. Positive mode was used for all compounds measured.

N,N′-Dibenzylterephthalamide, ***1***: M. p. 281 – 282 °C (DMF) (lit. 264 – 266 °C from acetone [8]). – ^{1}H NMR (400 MHz, $CDCl_3$ + [D$_6$]DMSO): δ (ppm) = 8.30 (t, 2H, NH), 7.48 (s, 4H), 6.79 – 6.86 (m, 8H), 6.75 – 6.71 (m, 2H), 4.08 (d, 4H). – ^{13}C NMR (100 MHz, $CDCl_3$ + [D$_6$]DMSO): δ (ppm) = 166.5, 139.3, 136.9, 128.4, 127.6, 127.5, 127.1, 43.5. – ESI MS: m/z = 345 [M+H]$^+$, 689 [2M+H]$^+$.

N,N′-Dibenzyl-N,N′-dimethylterephthalamide, ***2***: M. p. 144 – 145 °C (methanol). – ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.48 (d, 4H), 7.26 – 7.35 (m, 8H), 7.15 (bs, 2H), 4.75 (s, 2H), 4.49 (s, 2H), 3.04 (s, 3H), 2.85 (s, 3H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 171.5, 170.8, 137.6, 136.8, 136.3, 128.9, 128.8, 128.3, 127.7, 127.2, 127.0, 126.7, 55.1, 50.9, 37.0, 33.3. – ESI MS: m/z = 373 [M+H]$^+$, 745 [2M+H]$^+$. – $C_{24}H_{24}N_2O_2$ (372.46): calcd. C 77.39, H 6.49, N 7.52; found C 77.22, H 6.60, N 7.38.

N,N,N′,N′-Tetrabenzylterephthalamide, ***3***: M. p. 179 – 181 °C (methanol) (lit. 173 – 174 °C from ethanol [9]). – ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.50 (s, 4H), 7.25 – 7.38 (m, 16H), 7.11 (d, 4H), 4.69 (s, 4H), 4.37 (s, 4H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 171.55, 137.60, 136.86, 136.22, 129.04, 128.90, 128.57, 127.89, 127.80, 127.11, 127.04, 51.62, 47.19. – ESI MS: m/z = 526 [M+H]$^+$, 1051 [2M+H]$^+$.

X-Ray structure determinations

Crystal data are summarised in Table 4. Data were registered on Oxford Diffraction diffractometers using mirror-focussed CuK_α (**1**, **3**) or monochromated MoK_α radiation (**2**) at low temperature (*ca.* 100 K). Absorption corrections were applied to CuK_α data using the multi-scan method. Structures were solved using routine Direct Methods and refined using the program SHELXL-97 [10]. Hydrogen atoms were included using free refinement (NH groups), rigid methyl groups, or a riding model for all other hydrogens. The crystal quality was only moderate for **2** (large but soft crystals that deformed slightly on cutting), and **3** (very long but thin needles with a tendency to bend or to shatter lengthwise on cutting). For **3**, the Flack parameter was indeterminate, and Friedel opposite reflections were therefore merged; the resulting data/parameter ratio was necessarily poor, and restraints to displacement parameters were employed.

CCDC 788627 – 788629 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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