Weak Hydrogen Bonds in the Molecular Packing of *N*-Tetraalkyl Terephthalamides

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We present the structures of eight terephthaldiamides, seven of which (**1** – **7**) are fully substituted at both nitrogens and so cannot form classical hydrogen bonds. The structure of *N*,*N*′-dimethyl-*N*,*N*′-diphenylterephthalamide (**7**) represents a new polymorph. Where possible, the molecules tend to exhibit inversion symmetry. The amide groups are rotated significantly out of the central aromatic plane, by 33° to 84° (average 54°). The carbonyl carbon of the amide group may lie significantly (*ca.* 0.1 – 0.2 Å) out of the aromatic ring plane. The packing patterns exploit those types of contact still available, namely C–H···O (especially) and C–H···π. The smaller substituents in general lead to simpler packing patterns such as layer structures; more complex substituents can lead to three-dimensional patterns of great complexity. The central ring tends to play less of a role as the substituents become larger. Phenyl substituents often use their *para* hydrogen atoms to form intermolecular contacts, presumably because they are sterically more exposed. One terephthaldiamide (**8**) with two NHR groups forms a mixed "classical and weak" bifurcated (N–H, *o*-C–H)···O hydrogen bond system.

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

Introduction

In our earlier papers [1 – 4] we have described several crystal structures of terephthalamides in which both nitrogen atoms are identically substituted. For monosubstituted nitrogens (disubstituted terephthalamides), the molecular packing is determined by classical "strong" hydrogen bonding of the form N–H···O=C between neighbouring molecules, often leading to a one-dimensional "ladder"-type arrangement. In some cases bifurcated hydrogen bond systems were observed, whereby the NH and a neighbouring aromatic CH group of the same molecule act as donors to the same oxygen acceptor. For disubstituted nitrogens (tetrasubstituted terephthalamides) classical hydrogen bonding is precluded by the absence of NH groups, so the packing is determined by "weak" hydrogen bonding between the carbonyl oxygens and hydrogen atoms, predominantly those of the central ring. The C–H···O distances can be as short as 2.2 Å, although more typical distances up to *ca.* 2.6 Å are also observed. Other interactions such as C–H···π are rarer, but are observed in *e. g.* the tetrabenzyl derivative.

In this paper we extend our studies by presenting the structures of eight terephthaldiamides **1** – **8**. Compounds **1** – **4** are simple tetraalkyl derivatives and **5**, where the nitrogen is incorporated into a saturated ring, may also be considered in this category. Compound **6** and by similar extension compound **7** are dialkyldiaryl derivatives. Compound **8** is an NH-functional dialkylderivative.

The crystal structures of **1** and **2** as pure substances were previously unknown, but the structures of their hydrogen-bonded adducts with hydroquinone were presented in [5]. The structure of **7** has been presented previously (denoted here as **7**′ [6, 7]), but we have measured a new polymorph.

Discussion

The molecular structures of compounds **1** – **8** are presented in Figs. 1a – 8a. "Weak" hydrogen bonds are presented in Tables 2 – 9. Packing diagrams are numbered correspondingly as Figs. "b" etc.; in general, hydrogen atoms not involved in hydrogen bonding are omitted for clarity. Since this is our last major publication of terephthalamide structures for the forese-

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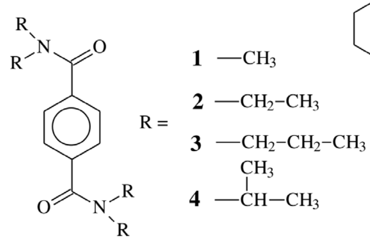

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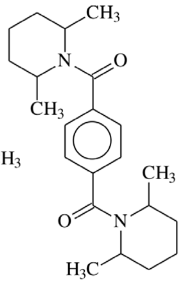

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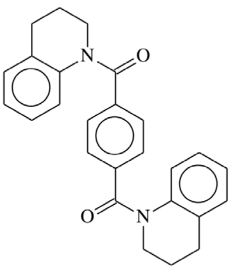

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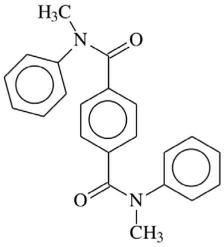

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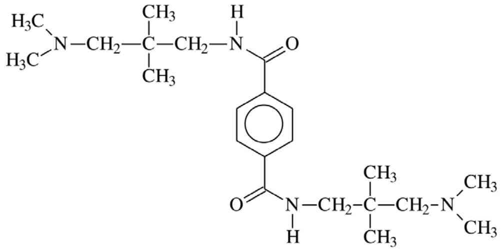

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able future, it is appropriate to summarise some of the general features of their molecular geometry, referring where necessary to the newer structures reported here. Many of these features have been mentioned in previous publications, or by other authors, but some aspects were only implicit or, in one case, escaped our attention at the time.

Molecular geometry

(i) Where possible, the compounds tend to display crystallographic inversion symmetry, whereby the asymmetric unit consists of half a molecule. Exceptions in this publication are compound **7**, which crystallises with one and a half molecules in the asymmetric unit (the molecule on a general position has approximate inversion symmetry, with an r. m. s. deviation of 0.13 Å; the previously known polymorph **7′** obeyed the general rule [6, 7]), and compound **4**, which crystallises with two independent inversion-symmetric molecules.

(ii) Compounds bearing a hydrogen atom at each nitrogen atom display a *trans* geometry of the amide group O=C–N–H, to facilitate the formation of hydrogen bonded "ladders" (see compound **8** below). The grouping C_{ipso}–C_{carbonyl}–N–R then necessarily displays an antiperiplanar configuration. If the nitrogen atoms are disubstituted by different groups R^1 and R^2, the amide configuration may be *cis* or *trans*. For compound **7′** and other related structures, the authors of the previous study [6, 7] interpreted the *cis* geometry (oxygen *cis* to methyl, thus methyl antiperiplanar to C_{ipso}) as a consequence of phenyl-phenyl interactions. However, the compound with R^1 = methyl, R^2 = benzyl [4] has the benzyl group antiperiplanar to C_{ipso}, perhaps because a methyl hydrogen is involved in CH···O interactions that lead to a packing pattern analogous to the "ladder" of the NH derivatives.

(iii) The amide groups are rotated significantly out of the central aromatic plane. For derivatives with NHR groups, with one major exception (see below), interplanar angles between the ring and the plane defined by all atoms of C_{ipso}–C(=O)–N range from 27.7° to 34.4° (av. 30°) for 8 structures. Higher values might preclude the efficient packing of hydrogen-bonded ladders because the central rings would project too far out of the ladder plane. For systems with disubstituted nitrogens, the angles are significantly larger (19 values in all, average 54°, ranging from 33.3° for **7** to 83.7° for **2**), presumably to reduce unfavourable steric interactions. One major exception to the general principles of NHR derivatives is the monoclinic polymorph of the compound with R = *p*-Et_2N-C_6H_4 [3]. The molecule has no symmetry and the N–H vectors are approximately perpendicular, so the ladder structure cannot be formed. The relevant interplanar angles involving the two independent amide groups are 51.2° and 7.5°.

Table 1. Selected aspects of the molecular geometry for compounds **1** – **8**.

Compound	Interplanar angle aromatic ring / amide group (deg)	Deviation of amide N from plane of substituents (Å)	Deviation of carbonyl C from central ring plane (Å)	Absolute torsion angle C_{ipso}–$C_{carbonyl}$–N–C (deg)[a]
1	63.7	0.03	0.08	
2	83.7	0.01	0.08	
3	52.8	0.09	0.16	
4	71.1, 61.5	0.00, 0.01	0.13, 0.11	
5	63.6	0.11	0.12	
6	37.3	0.02	0.14	163.2
7	38.5, 33.3, 40.5	0.10, 0.07, 0.17	0.12, 0.05, 0.10	178.9, 176.1, 178.7
7′	40.1	0.12	0.09	178.4
8	28.7	0.06	0.02	179.8

[a] Relevant for cases with different groups at nitrogen: **7**, **7′** to methyl C; **6**, **8** to methylene C.

A further serious irregularity of this structure is mentioned in paragraph (v).

(iv) The amide nitrogen displays a planar geometry. However, small deviations (up to *ca.* 0.1 Å) are common, and the largest is 0.17 Å for N3 of compound **7**. A fully pyramidalised nitrogen with three equal bond lengths would lie *ca.* 1/3 of a bond length above the pyramid base.

(v) The interplanar angles between the central ring and the amide group, as discussed above under (iii), may alternatively be given in terms of the absolute torsion angles C_{arom}–C_{ipso}–C_{amide}=O (generally numbered as C2–C1–C4=O or C3–C1–C4=O), although the relevant individual torsion angles may differ from the interplanar angle by a few degrees. While collating the molecular dimensions, we observed by chance for compound **3** that the two torsion angles C2–C1–C4=O and C3–C1–C4=O, the absolute values of which should add to 180°, in fact gave the value 172.6°. This can only occur if there is a significant loss of planarity. Closer inspection revealed that C4, the carbonyl carbon of the amide group, lies as much as 0.16 Å out of the aromatic ring plane. This is a general effect: especially for the systems with doubly substituted nitrogen, *the carbonyl carbon of the amide group may lie significantly (ca. 0.1 – 0.2 Å) out of the aromatic ring plane*. Whereas these deviations are less, indeed insignificant in some cases, for the NHR systems, the above-mentioned compound with R = *p*-Et_2N-C_6H_4 [3] shows deviations from the plane as high as 0.20 and 0.24 Å.

The comparative geometries of the polymorphs **7** and **7′** need brief comment (see Table 1). The conformations are determined by the atom sequence $C_{ortho,central}$–$C_{ipso,central}$–$C_{carbonyl}$–N–$C_{ipso,peripheral}$–$C_{ortho,peripheral}$, where "central" and "peripheral" refer to the ring position. In all relevant moieties, the sequence is helical, with all three torsion angles of the same sign. For **7**, the values are 40, 16, 55° at N1, −35, −13, −58° at N2, and 42, 30, 55° at N3 (rounded to the nearest degree; for exact values, see the Supplementary Material). For **7′**, the values are 41, 19, 55°. A least-squares fit of the two molecules of **7** to each other gives an r. m. s. deviation of 0.27 Å; a corresponding fit of the inversion-symmetric molecules of **7** to **7′** has an r. m. s. deviation of 0.15 Å.

Table 2. Weak hydrogen bonds in compound **1** (Å and deg)[a].

D–H···A	*d*(*D*–H)	*d*(H···*A*)	*d*(*D*···*A*)	∠(*D*H*A*)
C2–H2···$O^{\#1}$	0.95	2.46	3.4011(11)	173
C3–H3···$O^{\#2}$	0.95	2.57	3.3414(11)	139

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

Molecular packing patterns

The packing of the tetramethyl derivative **1** (Fig. 1b) confirms perfectly our previous suggestion [1, 4] that tetrasubstituted terephthalamides with smaller substituents tend to use the hydrogen atoms of the central aromatic ring to form "weak" and bifurcated $(C\text{–}H)_2\cdots O$ hydrogen bonds; all four of these hydrogens are involved (only two are independent, Table 2) to form a corrugated layer structure parallel to the *ac* plane. The hydrogen-bonded rings thus formed are of graph sets $R_2^2(10)$ and

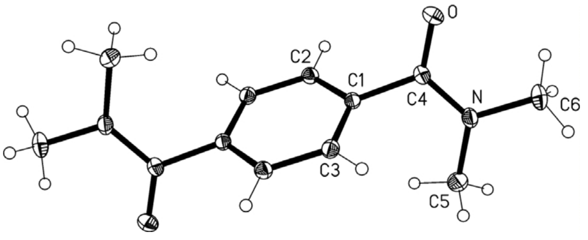

Fig. 1a. The molecule of compound **1** in the crystal. Ellipsoids represent 50 % probability levels. Only the asymmetric unit is numbered.

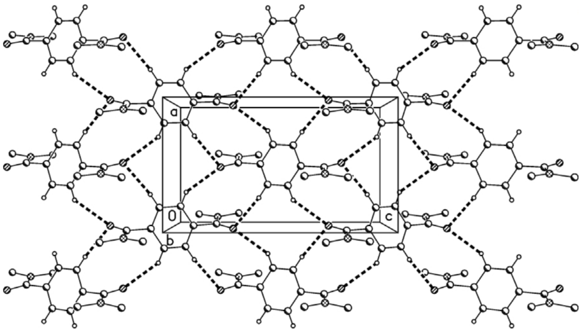

Fig. 1b. Packing diagram of compound **1** viewed parallel to the *b* axis. Thick dashed lines represent “weak” hydrogen bonds.

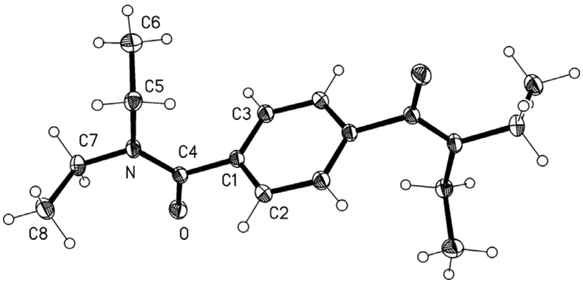

Fig. 2a. The molecule of compound **2** in the crystal. Ellipsoids represent 50 % probability levels. Only the asymmetric unit is numbered.

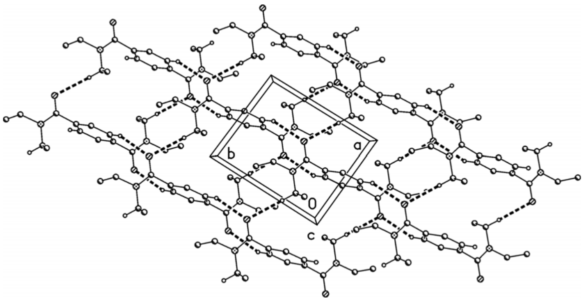

Fig. 2b. Packing diagram of compound **2** viewed parallel to the *c* axis in the region $z \approx 0$. Thick dashed lines represent “weak” hydrogen bonds.

$R_4^2(10)$. The borderline contact H5B···O (2.69 Å; $1-x$, $-1/2+y$, $1/2-z$) was omitted from this analysis.

The tetraethyl derivative **2** (Fig. 2b) uses only one independent aromatic hydrogen, together with one methylene hydrogen, to form two independent C–H···O hydrogen bonds (Table 3) and thereby a layer structure parallel to the *ab* plane; the aromatic rings subtend an angle of 88° with this plane. The C–H$_{\text{arom}}$···O contact forms inversion-symmetric $R_2^2(10)$ rings, but these are seen almost edge-on in Fig. 2b. The borderline contact H8C···O (2.71 Å; $-1+x$, y, z) was omitted from this analysis.

Table 3. Weak hydrogen bonds in compound **2** (Å and deg)[a].

D–H···A	*d*(*D*–H)	*d*(H···*A*)	*d*(*D*···*A*)	∠(*D*H*A*)
C2–H2···$O^{\#1}$	0.95	2.56	3.4225(10)	151
C5–H5B···$O^{\#2}$	0.99	2.59	3.5686(11)	171

[a] Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x+1$, $-y+1$, $-z$; $^{\#2}$ $x-1$, y, z.

The tetra-*n*-propyl derivative **3** (Fig. 3b) also uses only one independent aromatic hydrogen, together with one methylene hydrogen, to form two independent C–H···O hydrogen bonds (Table 4). This is sufficient to form a three-dimensional packing pattern. Chains of molecules parallel to the short *a* axis are

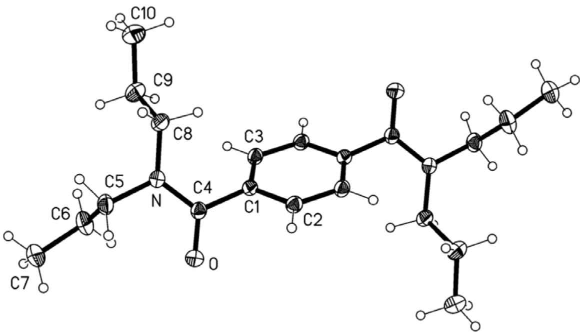

Fig. 3a. The molecule of compound **3** in the crystal. Ellipsoids represent 50 % probability levels. Only the asymmetric unit is numbered.

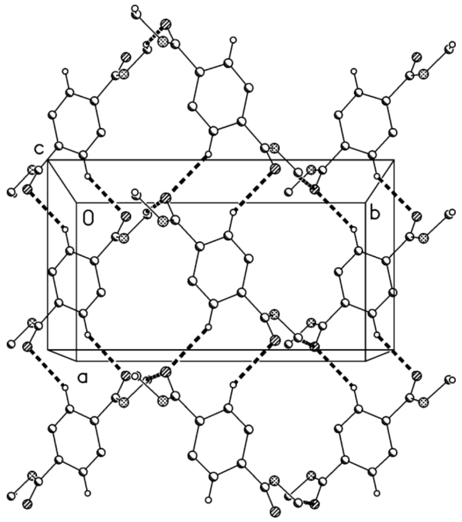

Fig. 3b. Packing diagram of compound **3** viewed perpendicular to the *ac* plane in the region $z \approx 0$. Thick dashed lines represent “weak” hydrogen bonds; C–H$_{\text{arom}}$···O are approximately parallel to the plane, C–H$_{\text{methylene}}$···O approximately perpendicular to it. *n*-Propyl groups are either omitted or shortened to the first methylene moiety for clarity.

Table 4. Weak hydrogen bonds in compound **3** (Å and deg)[a].

D–H···A	*d*(*D*–H)	*d*(H···*A*)	*d*(*D*···*A*)	∠(*DHA*)
C2–H2···O$^{\#1}$	0.95	2.47	3.3147(12)	148
C5–H5A···O$^{\#2}$	0.99	2.50	3.4380(12)	157

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

connected *via* $\mathrm{H_{arom}}\cdots\mathrm{O}$, again forming inversion-symmetric $R_2^2(10)$ rings; they are crosslinked in the other two dimensions by $\mathrm{H_{methylene}}\cdots\mathrm{O}$. The latter interactions, taken alone, link the molecules to layers parallel to *bc* (not shown).

The packing of the tetra-*i*-propyl derivative **4** (Fig. 4b) involves two independent molecules, which however play topologically identical roles. Each forms *via* translation two independent hydrogen bonds to an oxygen of the other molecule; one from a methine hydrogen of one independent *i*-Pr group and one from a methyl hydrogen of the other *i*-Pr group (Table 5). The bifurcated hydrogen bond systems thus formed each display $R_2^1(7)$ graph sets and are linked alternately to form chains parallel to $[1\bar{1}0]$, horizontal in Fig. 4b; the chains crosslink to form layers parallel to (110). The borderline contacts H10F···O (2.71 Å; x, $-1+y$, z) and H10C···O′ (2.72 Å; $1+x$, y, z) were omitted from this analysis, but would fit into the packing as already described. A borderline C–H···π contact, H7B···Cent(molecule 2), with H···π 2.92 Å and operator $1+x$, y, z, is also omitted from Fig. 4b, but its position can easily be inferred from the proximity of rings designated "2" in this figure to methyls of molecule 1.

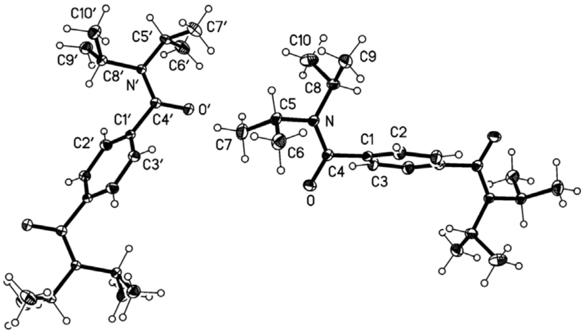

Fig. 4a. The structure of compound **4** in the crystal. Ellipsoids represent 50 % probability levels. Only the asymmetric unit (two half molecules) is numbered.

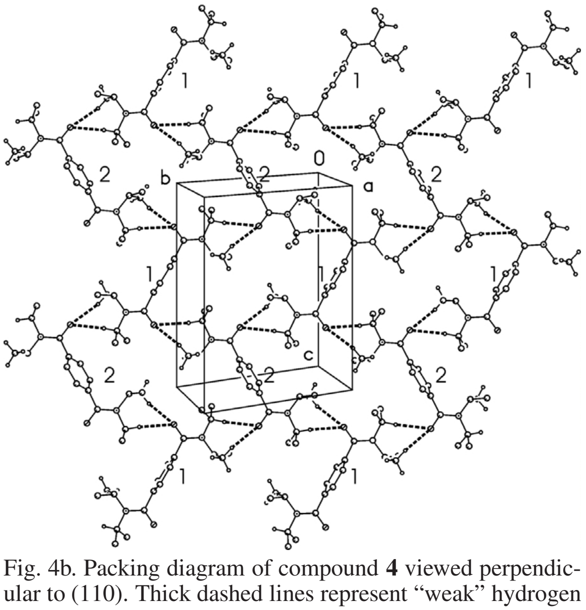

Fig. 4b. Packing diagram of compound **4** viewed perpendicular to (110). Thick dashed lines represent "weak" hydrogen bonds. The numbers "1" and "2" indicate the first and second independent molecules, respectively (unprimed and primed, respectively, in Fig. 4a).

Table 5. Weak hydrogen bonds in compound **4** (Å and deg)[a].

D–H···A	*d*(*D*–H)	*d*(H···*A*)	*d*(*D*···*A*)	∠(*DHA*)
C5′–H5′···O$^{\#1}$	1.00	2.50	3.5015(13)	175
C9′–H9′1···O$^{\#1}$	0.98	2.57	3.4688(13)	153
C5–H5···O′$^{\#2}$	1.00	2.53	3.5248(13)	175
C9–H9A···O′$^{\#2}$	0.98	2.52	3.4385(14)	155

[a] Symmetry transformations used to generate equivalent atoms: $^{\#1}$ x, $y-1$, z; $^{\#2}$ $x+1$, y, z.

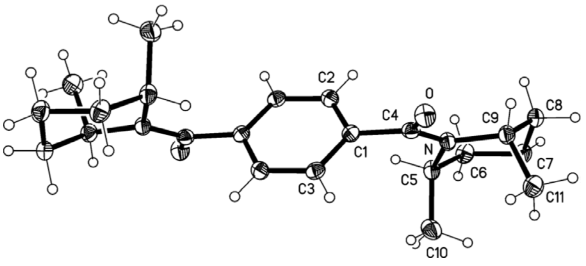

Fig. 5a. The molecule of compound **5** in the crystal. Ellipsoids represent 50 % probability levels. Only the asymmetric unit is numbered.

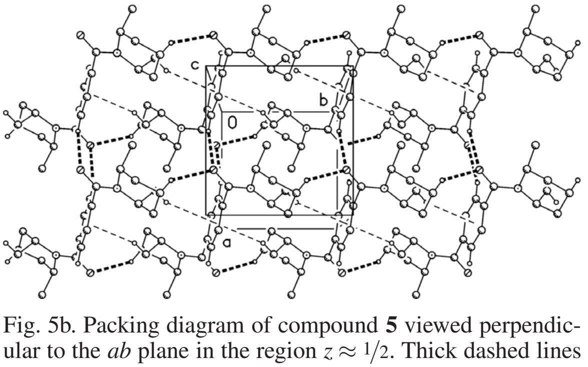

Fig. 5b. Packing diagram of compound **5** viewed perpendicular to the *ab* plane in the region $z \approx 1/2$. Thick dashed lines represent "weak" hydrogen bonds; thin dashed lines represent C–H···π interactions.

Table 6. Weak hydrogen bonds in compound **5** (Å and deg)[a].

D–H$\cdots$A	$d(D$–H)	$d(\mathrm{H}\cdots A)$	$d(D\cdots A)$	$\angle(D\mathrm{H}A)$
C3–H3$\cdots$O$^{\#1}$	0.95	2.55	3.449(2)	159
C7–H7B$\cdots$O$^{\#2}$	0.99	2.66	3.542(2)	149

[a] Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x+1$, $-y$, $-z+1$; $^{\#2}$ x, $y-1$, z.

Table 7. Weak hydrogen bonds in compound **6** (Å and deg)[a].

D–H$\cdots$A	$d(D$–H)	$d(\mathrm{H}\cdots A)$	$d(D\cdots A)$	$\angle(D\mathrm{H}A)$
C13–H13A$\cdots$O$^{\#1}$	0.99	2.64	3.6142(16)	167
C16–H16$\cdots$O$^{\#2}$	0.95	2.61	3.4127(15)	142
C17–H17$\cdots$O$^{\#3}$	0.95	2.45	3.3412(16)	156

[a] Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x+1$, $-y+1$, $-z+1$; $^{\#2}$ $-x+1^1/_2$, $y-{}^1/_2$, $-z+{}^1/_2$; $^{\#3}$ $x+{}^1/_2$, $-y+1^1/_2$, $z-{}^1/_2$.

In the dimethylpiperidine derivative **5**, a hydrogen bond C$_{\mathrm{arom}}$–H$\cdots$O (approximately vertical in Fig. 5b) forms inversion-symmetric $\mathrm{R}_2^2(10)$ rings; a rather long C$_{\mathrm{methylene}}$–H$\cdots$O interaction (Table 6) *via y* axis translation completes the formation of layers parallel to the *ab* plane. A long H$_{\mathrm{methyl}}\cdots\pi$ contact, H10B$\cdots$Cent, with H$\cdots\pi$ 2.94 Å, is included in Fig. 5b.

It is extremely difficult to construct an interpretable packing diagram of the tetrahydroquinoline derivative **6**. There are three C–H$\cdots$O interactions, all involving the tetrahydroquinoline ring system (Table 7) and one C$_{\mathrm{arom}}$–H$\cdots\pi$ contact from the central ring, H2$\cdots$Cent(C14–19) 2.86 Å (operator $x+{}^1/_2$, $-y+1^1/_2$, $z+{}^1/_2$). However, combined with the molecular inversion symmetry and the fact that both donors and acceptors are involved, this means that each molecule is involved with no fewer than 12 others. Even diagrams involving only the shortest contact H17$\cdots$O are three-dimensional (Fig. 6b).

We have determined the packing diagram of the previously determined structure **7′** [6, 7] from the deposited coordinates [8]. The structure involves just one independent C–H$\cdots$O interaction, from the *para* hydrogen of the terminal phenyl group (H$\cdots$O 2.44 Å, operator $x+{}^1/_2$, $-y+{}^1/_2$, $z+1$ in space group $P2_1/a$), but this is sufficient to establish a layer structure

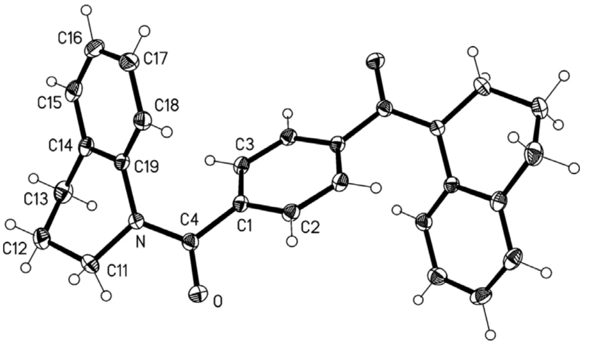

Fig. 6a. The molecule of compound **6** in the crystal. Ellipsoids represent 50 % probability levels. Only the asymmetric unit is numbered.

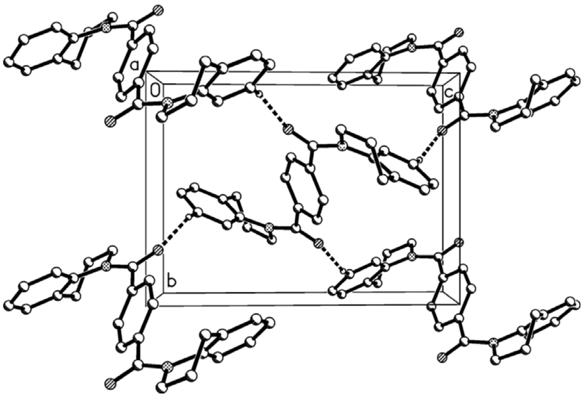

Fig. 6b. Highly simplified packing diagram of compound **6** viewed parallel to the *a* axis; environment of one molecule involving only the shortest contact. Thick dashed lines represent “weak” hydrogen bonds.

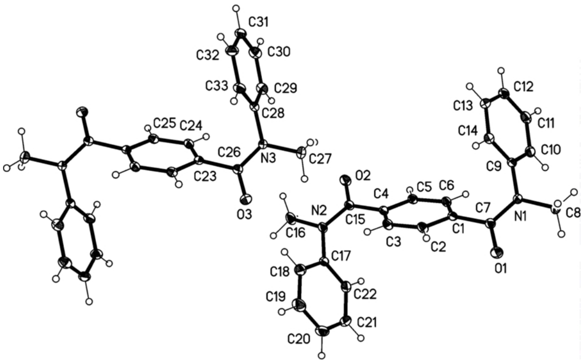

Fig. 7a. The structure of compound **7** in the crystal. Ellipsoids represent 50 % probability levels. Only the asymmetric unit (one complete and one half molecule) is numbered.

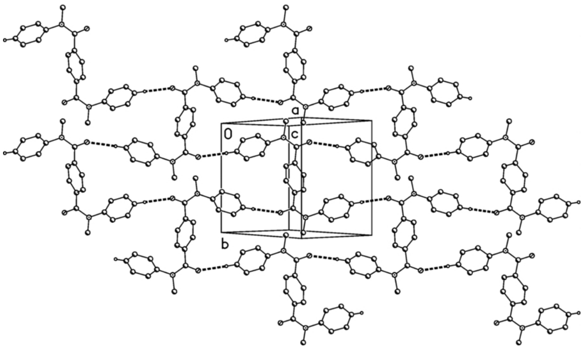

Fig. 7b. Packing diagram of the previously determined structure **7′** of compound **7** [4a, b] viewed perpendicular to ($20\bar{1}$). Thick dashed lines represent “weak” hydrogen bonds.

D–H···*A*	*d*(*D*–H)	*d*(H···*A*)	*d*(*D*···*A*)	∠(*DHA*)	Code
C3–H3···O2$^{\#3}$	0.95	2.47	3.1821(13)	132	*a*
C20–H20···O2$^{\#4}$	0.95	2.61	3.3881(15)	140	*b*
C24–H24···O1$^{\#1}$	0.95	2.56	3.3748(13)	145	*c*
C31–H31···O1$^{\#2}$	0.95	2.49	3.2758(14)	141	*d*
C5–H5···O3$^{\#1}$	0.95	2.67	3.4264(13)	137	*e*
C12–H12···O3$^{\#1}$	0.95	2.51	3.4579(14)	178	*f*
C18–H18···O3	0.95	2.49	3.4372(14)	175	*g*
C13–H13···Cent(1 – 6)$^{\#5}$	0.95	2.86	3.66	143	*h*
C27–H27···Cent(17 – 22)$^{\#5}$	0.95	2.76	3.65	151	*i*
C16–H16···Cent(28 – 33)$^{\#6}$	0.95	2.60	3.39	137	*j*

Table 8. Weak hydrogen bonds in compound **7** (Å and deg)[a,b].

[a] Symmetry transformations used to generate equivalent atoms: $^{\#1}$ x, $-y+1/2$, $z-1/2$; $^{\#2}$ $x-1$, $-y+1/2$, $z-1/2$; $^{\#3}$ x, $-y+1/2$, $z+1/2$; $^{\#4}$ $x+1$, $-y+1/2$, $z+1/2$; $^{\#5}$ $x-1$, y, z; $^{\#6}$ $x+1$, y, z; [b] Cent = centre of gravity of ring defined by carbon atom numbers.

parallel to $(20\bar{1})$ (Fig. 7b). The large homodromic rings thus constructed display graph set $R_4^4(42)$. An $H_{methyl}\cdots$Cent(phenyl) contact of 2.74 Å connects the layers in the third dimension.

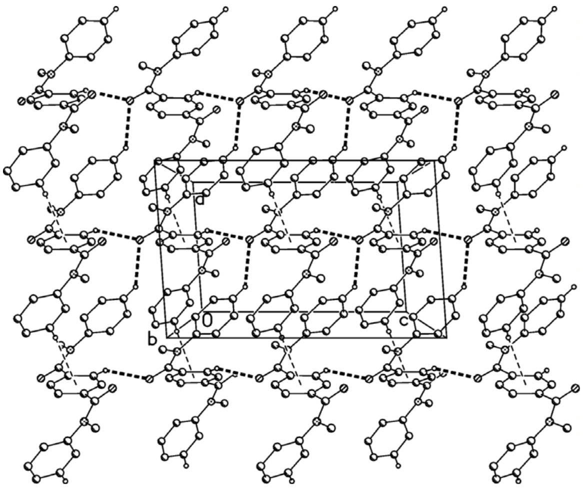

Fig. 7c. Packing diagram of the first independent molecule (general position) of compound **7** viewed parallel to the *b* axis in the region $y \approx 1/4$. Thick dashed lines represent C–H···O and thin dashed lines C–H···π interactions.

Our new modification **7** necessarily has a more complex packing, since the asymmetric unit is three times as large as that of **7′**. Contacts are summarised (and coded with italic letters) in Table 8; there are seven C–H···O and three C–H···π contacts, although some of these are quite long (H10···O1 2.75 Å was not included) or have narrower angles (< 140° in some cases). It is convenient to consider first the packing of the first molecule alone (Figs. 7c,d). Contacts *a*, *b* and *h* connect the molecules to form layers parallel to the *ac* plane in the regions $y \approx 1/4$, $3/3$, *etc.*, although parts of the molecules project far out of these layers; the central ring is the donor for *a* and the acceptor for *h*. The C–H···O interactions lead to rings of graph set $R_4^3(24)$.

There are no interactions involving exclusively the second independent molecule. The environment of molecule 1, surrounded *via* seven contacts by six inversion-symmetric molecules 2, is shown in Fig. 7c.

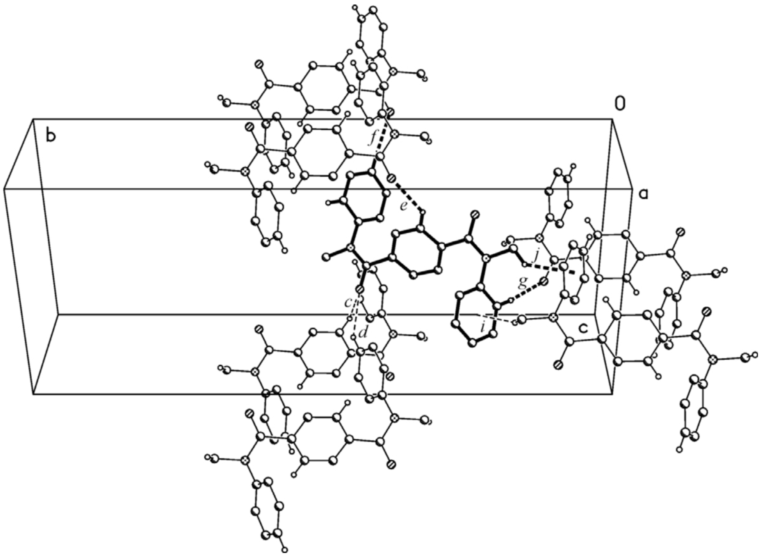

Fig. 7d. Environment of the molecule 1 of compound **7** viewed approximately perpendicular to $(10\bar{1})$. The central molecule is drawn with thicker bonds, whereas the surrounding molecules 2, each with inversion symmetry, are shown with thin bonds. Thick dashed lines represent interactions in which molecule 1 is the donor, and thin dashed lines interactions in which molecule 1 is the acceptor. Italic letters correspond to the identification in Table 8.

Table 9. Classical and weak hydrogen bonds in compound **8** (Å and deg)[a].

D–H···A	$d(D$–H)	d(H···A)	$d(D\cdots A)$	∠(DHA)
N1–H01···O$^{\#1}$	0.89(2)	1.96(2)	2.8534(17)	174.1(18)
C2–H2···O$^{\#1}$	0.95	2.46	3.0696(18)	122

[a] Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $x, -y+1^1/_2, z-{}^1/_2$.

It is noteworthy that all *para* hydrogen atoms of the peripheral phenyl groups are involved in secondary interactions.

Finally, as an addendum to the structures of the tetrasubstituted compounds, we present the structure of the disubstituted derivative **8**. The packing of **8** is topologically identical (but not isotypic) to our previously determined structure of the *t*-butyl derivative [1]: It forms a layer structure parallel to *bc* in which bifurcated (N–H, *o*-C–H)···O hydrogen bond systems of graph set $R^1_2(7)$ link each molecule with four neighbours (Fig. 8b, Table 9). The central rings subtend interplanar angles of 41° with the *bc* plane.

We conclude that *N*-tetrasubstituted terephthalamide molecules pack together utilising those types of contact available to them, namely C–H···O (especially) and C–H···π. Logically, the smaller substituents lead to more easily interpretable packing patterns such as layer structures; more complex substituents may lead to three-dimensional patterns of great complexity. The central ring tends to play less of a role as the substituents become larger. Phenyl substituents often use their *para* hydrogen atoms to form intermolecular contacts, presumably because they are sterically more exposed.

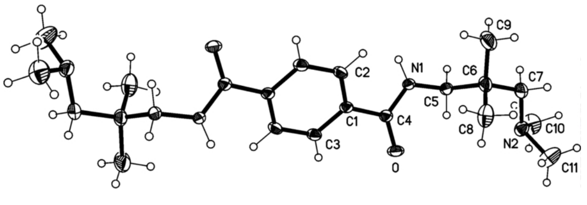

Fig. 8a. The molecule of compound **8** in the crystal. Ellipsoids represent 50 % probability levels. Only the asymmetric unit is numbered.

Experimental Section

Compounds **1**–**8** were synthesised from terephthaloyl chloride (Aldrich) and the corresponding amines (Aldrich, Acros) according to the procedure described earlier [3]. 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 [ESI MS (+)] was used for all compounds measured. Single crystals used for X-ray measurements were obtained from ethyl acetate (**2**, **3** and **8**), DMF (**4**), *p*-xylene (**6**), benzene (**1** and **5**), and methanol (**7**), by slow evaporation of solvents.

*N,N,N‘,N‘ Tetramethylterephthalamide, **1**:* M. p. 207 °C (lit. 204–206 °C [9]). – ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.44 (s, 4H), 3.11 (s, 6H), 2.96 (s, 6H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.34, 39.50, 127.11, 137.48, 170.86. – MS ((+)-ESI): m/z = 221 $[M+H]^+$.

*N,N,N‘,N‘-Tetraethylterephthalamide, **2**:* M. p. 140–142 °C (lit. 128–130 °C [10]). – ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.37 (s, 4H), 3.52 (d, 4H), 3.19 (d, 4H), 1.22 (t, 6H), 1.06 (t, 6H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.89, 14.18, 39.27, 43.22, 126.42, 138.02, 170.63. – MS ((+)-ESI): m/z = 277 $[M+H]^+$, 299 $[M+Na]^+$.

*N,N,N‘,N‘-Tetra-n-propylterephthalamide, **3**:* M. p. 114–116 °C (lit. 100–102 °C [10]). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (s, 4H), 3.45, 3.15 (2× t, 2× 4H), 1.69, 1.52 (2× m, 2× 4H), 0.99, 0.74 (2× t, 2× 6H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.89, 11.37, 20.63, 21.83, 46.24, 50.57, 126.56, 138.00, 171.08. – MS ((+)-ESI): m/z = 333 $[M+H]^+$.

*N,N,N‘,N‘-Tetra-iso-propylterephthalamide, **4**:* M. p. 254–256 °C (lit. 270–272 °C [10]). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (s, 4H), 3.81, 3.54 (2 × bs, 4H), 1.53, 1.14 (2 × bs, 24H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.65, 45.82, 50.97, 125.79, 139.21, 170.47. – MS ((+)-ESI): m/z = 333 $[M+H]^+$, 665 $[2M+H]^+$, 688 $[2M+Na]^+$.

*N,N′-Terephthaloyl-bis-(2,6-dimethylpiperidine), **5**:* M. p. 247–249 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (s, 4H), 1.85 (q, 2H), 1.51-1.68 (m, 12H), 1.26 (bs, 12H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.21, 21.30, 30.23, 126.23, 138.34, 170.94. – MS ((+)-ESI): m/z = 357 $[M+H]^+$. – $C_{22}H_{32}N_2O_2$: calcd. C 74.12, H 9.05, N 7.86; found C 74.22, H 9.15, N 7.90.

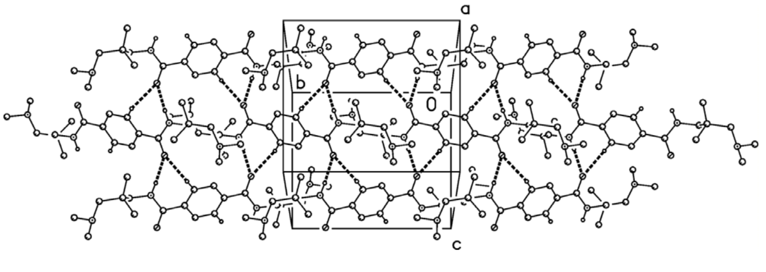

Fig. 8b. Packing diagram of compound **8** viewed perpendicular to the *bc* plane. Thick dashed lines represent hydrogen bonds.

Table 10. Crystallographic data for compounds **1** – **8**.

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Formula	$C_{12}H_{16}N_2O_2$	$C_{16}H_{24}N_2O_2$	$C_{20}H_{32}N_2O_2$	$C_{20}H_{32}N_2O_2$	$C_{22}H_{32}N_2O_2$	$C_{26}H_{24}N_2O_2$	$C_{22}H_{20}N_2O_2$	$C_{22}H_{38}N_4O_2$
M_r	220.27	276.37	332.48	332.48	356.50	396.47	344.40	390.56
Crystal size, mm^3	0.45 × 0.40 × 0.30	0.45 × 0.22 × 0.22	0.35 × 0.27 × 0.20	0.4 × 0.2 × 0.2	0.20 × 0.15 × 0.08	0.45 × 0.20 × 0.07	0.25 × 0.22 × 0.06	0.37 × 0.33 × 0.10
T, K	100(2)	133(2)	133(2)	133(2)	133(2)	133(2)	100(2)	133(2)
Crystal system	orthorhombic	triclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$Pbca$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$
Cell constants								
a, Å	7.3555(3)	6.4083(6)	6.8796(11)	6.1718(6)	7.2729(3)	7.9026(14)	7.6615(6)	11.5661(14)
b, Å	12.0170(4)	7.7630(8)	12.621(2)	11.4722(12)	7.1778(3)	9.6417(16)	29.056(2)	11.4421(13)
c, Å	12.7765(4)	7.8623(8)	11.530(2)	14.2366(15)	18.8643(9)	13.018(2)	12.0496(9)	9.8010(11)
α, deg	90	100.742(4)	90	84.415(4)	90	90	90	90
β, deg	90	103.295(4)	95.114(4)	77.725(4)	94.979(5)	94.251(5)	94.016(4)	112.353(4)
γ, deg	90	91.503(4)	90	81.835(5)	90	90	90	90
V, Å^3	1129.33(7)	373.00(6)	997.1(3)	972.63(17)	981.06(7)	989.2(3)	2675.8(3)	1199.6(2)
Z	4	1	2	2	2	2	6	2
$F(000)$, e	472	150	364	364	388	420	1092	428
μ, mm^{-1}	0.09	0.08	0.07	0.07	0.60	0.09	0.08	0.07
λ, Å	0.71073	0.71073	0.71073	0.71073	1.54184	0.71073	0.71073	0.71073
$2\theta_{\max}$, deg	60	61	61	61	142.2	61	63.3	56.6
Transmissions	0.969, 1.000	no corr.	no corr.	no corr.	0.787, 1.000	no corr.	no corr.	no corr.
Reflections meas.	27041	5365	11529	11560	9567	9252	70055	11997
indep.	1642	2254	3031	5817	1817	3017	8609	2974
R_{int}	0.022	0.028	0.043	0.038	0.018	0.048	0.047	0.067
Ref. parameters	75	93	111	225	120	136	355	135
wR (F^2, all refl.)	0.111	0.113	0.116	0.125	0.137	0.126	0.120	0.134
$R1$ [$F \geq 4\,\sigma(F)$]	0.039	0.039	0.043	0.046	0.051	0.047	0.045	0.060
S	1.09	1.08	1.05	1.04	1.16	1.04	1.03	1.06
$\Delta\rho_{\max/\min}$, e Å^{-3}	0.42 / −0.24	0.41 / −0.18	0.43 / −0.17	0.39 / −0.17	0.30 / −0.26	0.44 / −0.20	0.43 / −0.22	0.32 / −0.28

N,N‘–Terephthaloyl-bis-(1,2,3,4-tetrahydroquinoline), ***6:*** M. p. 148 – 150 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (s, 4H), 7.14 (d, 2H), 7.01 (t, 2H), 6.87 (t, 2H), 6.63 (d, 2H), 3.90 (t, 4H), 2.83 (t, 4H), 2.06 (q, 4H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.08, 26.91, 44.29, 124.85, 125.47, 125.87, 128.36, 128.44, 131.84, 137.78, 139.00, 169.35. – MS ((+)-ESI): m/z = 397 $[M+H]^+$. – $C_{26}H_{24}N_2O_2 \times 1/3$ H_2O: calcd. C 77.59, H 6.18, N 6.96; found C 77.68, H 6.04, N 6.86.

N,N′-Dimethyl-N,N′-diphenylterephthalamide, ***7:*** M. p. 225 – 226 °C (lit. 214 – 215 °C [7]). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10 – 7.20 (m, 6H), 7.08 (s, 4H), 6.92 (d, 4H), 3.43 (s, 6H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.30, 126.67, 126.81, 128.15, 129.21, 136.90, 144.46, 169.86. – MS ((+)-ESI): m/z = 346 $[M+H]^+$.

N,N′-Bis-(3-dimethylamino-2,2-dimethylpropyl)terephthalamide), ***8:*** M. p. 168 – 169 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.42 (bs, 2H), 7.84 (s, 4H), 3.37 (d, 4H), 2.38 (s, 4H), 2.37 (s, 12H), 1.03 (s, 12H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.55, 34.82, 48.64, 52.23, 71.93, 127.30, 137.64, 166.62. – MS ((+)-ESI): m/z = 391 $[M+H]^+$. – $C_{22}H_{38}N_4O_2$: calcd. C 67.66, H 9.81, N 14.35; found C 67.71, H 9.52, N 14.34.

X-Ray structure determinations

Crystal data are summarised in Table 10. Data were registered on a Bruker SMART 1000 CCD diffractometer using monochromated MoK_α radiation, except for **1**, Oxford Diffraction Xcalibur, MoK_α; **7**, Oxford Diffraction Xcalibur Nova, mirror-focussed CuK_α; **8**, Bruker APEX-2, MoK_α. Absorption corrections were applied in some cases using the multi-scan method. Structures were solved using routine Direct Methods and refined on F^2 using the program SHELXL-97 [11]. Hydrogen atoms were included using free refinement (NH groups), rigid methyl groups, or a riding model for all other hydrogens.

Complete crystallographic data have been deposited at The Cambridge Crystallographic Data Centre under the numbers CCDC 809554 (**1**), 809555 (**2**), 809556 (**3**), 809557 (**4**), 809558 (**6**), 809559 (**8**), 809560 (**5**), 809561 (**7**). Copies can be obtained free of charge *via* www.ccdc.ac.uk/data_request/cif.

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