2,2′,3,3′,4,4′,5,5′,6,6′-Decafluoro-diphenylamine and its 1:1 cocrystal with diphenylamine

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In the structures of decafluorodiphenylamine, $C_{12}HF_{10}N$, and its 1:1 cocrystal with diphenylamine, $C_{12}HF_{10}N \cdot C_{12}H_{11}N$, the molecules are located on special positions of C_2 symmetry. The NH groups are not involved in hydrogen bonding and the usual face-to-face stacking interactions between phenyl and pentafluorophenyl rings are not observed in the cocrystal.

Comment

2,2′,3,3′,4,4′,5,5′,6,6′-Decafluorodiphenylamine, (I), belongs to the family of strong NH acids and its pK_a has been determined to be very similar to those of trifluoroacetic acid and pentafluorobenzoic acid (Koppel *et al.*, 1994). The highly electron-withdrawing properties of the $(C_6F_5)_2N$ ligand have recently been employed in organolanthanide (Click *et al.*, 1999), transition metal (Giesbrecht *et al.*, 2003) and lithium chemistry (Khvorost *et al.*, 2004). The structural studies of (I) and its cocrystal with diphenylamine, (II), reported in this paper originate from our interest in organic fluorine as an acceptor in hydrogen bonding (Pham *et al.*, 1998), as well as from our exploitation of phenyl–perfluorophenyl interactions for crystal engineering (Gdaniec *et al.*, 2003).

(I)

(II)
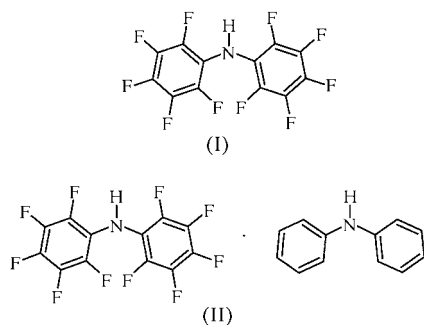
The low propensity of organic fluorine to participate in hydrogen bonding has been the subject of several reports and is now well documented and recognized (Shimoni & Glusker, 1994; Howard *et al.*, 1996; Dunitz & Taylor, 1997; Dunitz, 2004). In compound (I), there is only one strongly acidic hydrogen-bond donor and as many as ten weak F-atom

acceptors, with no other accepting groups to compete with fluorine for hydrogen bonding. The crystal structure reveals that, as in previous cases, intermolecular N—H···F hydrogen bonds do not contribute to the stabilization energy of the crystal lattice because all intermolecular H···F contacts are longer than 2.9 Å.

A view of the molecular structure of (I) is shown in Fig. 1. The molecule has crystallographic C_2 symmetry, with the NH group situated on the twofold axis. The pentafluorophenyl rings are twisted by 31.54 (8)° in opposite directions relative to the plane of the amine group defined by atoms C1, N1 and C1($-x, y, 1 - z$). This twist brings two symmetry-related F6 atoms into close contact at 2.767 (3) Å, *i.e.* a distance slightly
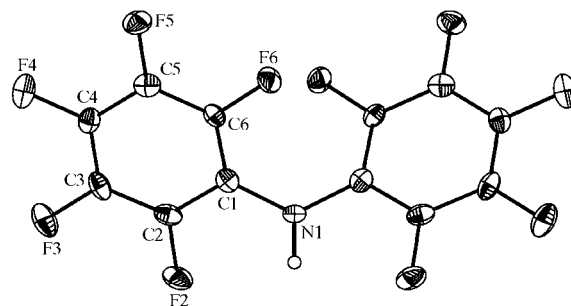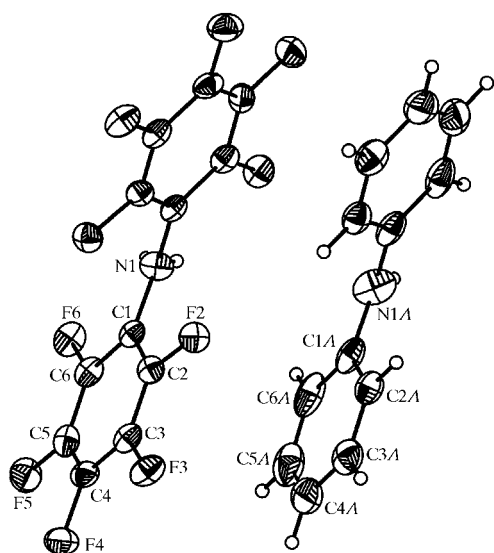

Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Unlabelled atoms are related to labelled atoms by the symmetry code ($-x, y, 1 - z$).

(a)

(b)
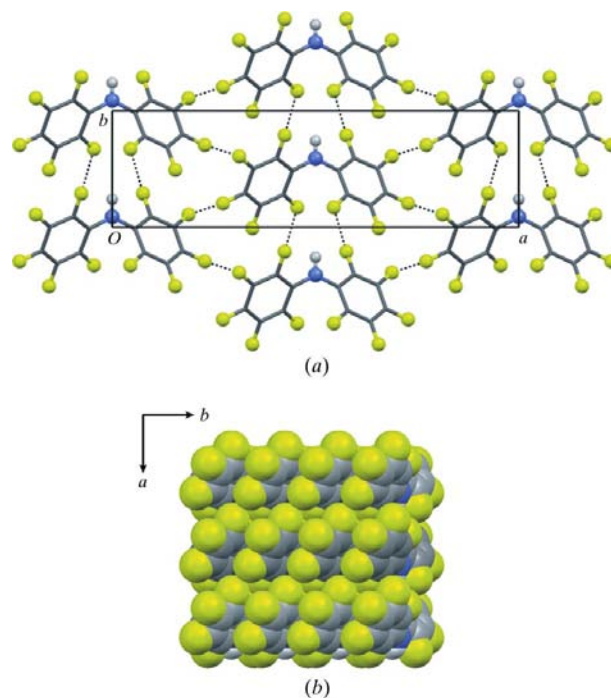
Figure 2
The crystal structure of (I), showing (*a*) the packing of the molecules viewed down the *c* axis, with the shortest F···F contacts shown as dashed lines, and (*b*) the arrangement of pentafluorophenyl rings on a surface of the (100) layer.

organic compounds

shorter than the sum of the van der Waals radii of two F atoms (1.46 Å; Rowland & Taylor, 1996). This molecular conformation also orients the local $N^{\delta-}$—$H^{\delta+}$ dipole and two closely situated $C2^{\delta+}$—$F2^{\delta-}$ dipoles nearly antiparallel (H1···F2 = 2.46 Å and N1—H1···F2 = 97°), thus providing some electrostatic stabilization to the conformation adopted by the

Figure 3
The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Unlabelled atoms are re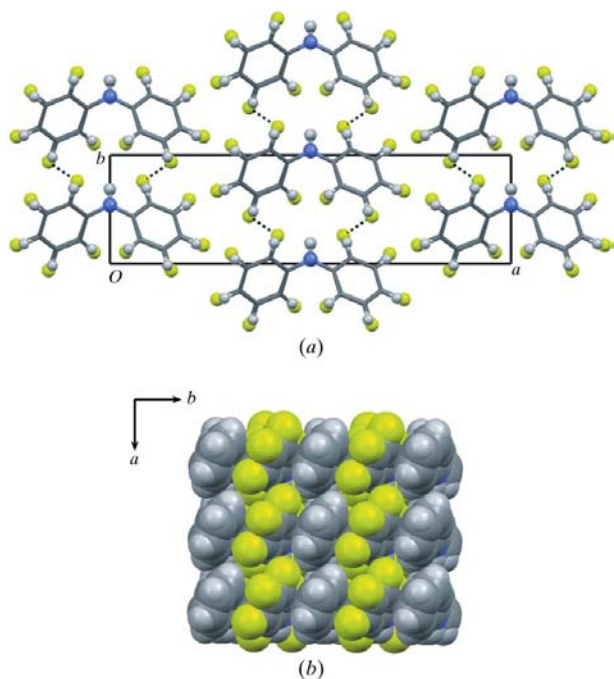lated to labelled atoms by the symmetry code $(-x, y, -z)$ for decafluorodiphenylamine and by $(-x, y, 1 - z)$ for diphenylamine.

Figure 4
The crystal structure of (II), showing (a) the packing of the molecules projected down the c axis, with the shortest F···F contacts shown as dashed lines, and (b) the arrangement of pentafluorophenyl and phenyl rings on a surface of the (100) layer.

molecule of (I). Atoms F2 and F2$(-x, y, 1 - z)$ in the molecule of (I) hinder access to the NH group by other potential acceptors and therefore no intermolecular N—H···F hydrogen bonds are formed.

The crystal packing of (I) is shown in Fig. 2. The pentafluorophenyl rings related by translation along [001] are arranged into stacks with a large offset (Fig. 2a), which brings atoms F3 and F6 from adjacent molecules along the stack directly above and below the centroid of an electron-deficient phenyl ring, with F···centroid distances of 3.26 and 3.22 Å, respectively. Additionally, the stacks of (I) along [001] assemble into (100) layers, where pentafluorophenyl rings related by unit translations along [011] or [01$\bar{1}$], and situated on one side of the layer, are nearly coplanar and contact via their edges with a shortest F···F distance of 2.826 (3) Å (Fig. 2b).

We expected that (I), with its two pentafluorophenyl rings, would be prone to forming molecular complexes via phenyl–perfluorophenyl interactions, but our attempts to obtain its benzene solvate were unsuccessful. However, when an equimolar mixture of (I) and diphenylamine was dissolved in ethanol, plate-like 1:1 cocrystals of (II) (m.p. 335 K) precipitated. These crystals have the same space group as (I) and very similar unit-cell parameters, with the exception that the c parameter is nearly twice as long as in (I).

A view of the molecular structure of (II) is shown in Fig. 3 and a view of the crystal packing along [001] is presented in Fig. 4. The crystal structure is very similar to that of (I), with the exception that the homomolecular stacks in (I) are substituted in (II) by heteromolecular stacks, with alternating fluorinated and non-fluorinated molecules (Fig. 4a). Both molecules possess crystallographic C_2 symmetry, with the N atom situated on the twofold axis. The amine N atoms are slightly pyramidal because the H atoms are not located on the twofold axis but are displaced from it and are, in effect, disordered over two positions. As in (I), the amine groups are not involved in hydrogen bonding because the closest (N)H···F distance is 2.75 Å.

Interestingly, in this cocrystal there are negligible face-to-face aromatic ring interactions, typical for this type of molecular complex (Collings et al., 2002, and references therein; Gdaniec et al., 2003). Here, a large slip angle of the phenyl–pentafluorophenyl stacks leaves the centroids of adjacent rings more than 4 Å apart, i.e. there is practically no overlap of the aromatic π-systems (Fig. 4b). Instead, lateral interactions between the fluorinated and non-fluorinated rings of neighbouring stacks seem to play a more important role in (II), because each phenyl-ring H atom makes a conact shorter than 3 Å with an F atom situated close to the plane of the phenyl ring.

Experimental

Compound (I) was prepared according to the literature procedure of Koppang (1971) and was recrystallized from ethanol. Compound (II) was prepared from an equimolar mixture of (I) and diphenylamine, dissolved in ethanol, by slow evaporation of the solvent at room temperature.

Compound (I)

Crystal data

$C_{12}HF_{10}N$
$M_r = 349.14$
Monoclinic, $C2$
$a = 21.293 (3)$ Å
$b = 5.9659 (8)$ Å
$c = 4.4306 (6)$ Å
$\beta = 101.702 (11)°$
$V = 551.13 (13)$ Å^3

$Z = 2$
$D_x = 2.104$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.24$ mm^{-1}
$T = 130 (2)$ K
Plate, colourless
$0.3 \times 0.3 \times 0.03$ mm

Data collection

Kuma KM-4 CCD κ-geometry diffractometer
ω scans
1458 measured reflections
532 independent reflections

513 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 25.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.080$
$S = 1.09$
532 reflections
106 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0625P)^2 + 0.0243P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.009 (1)

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

N1—C1	1.397 (3)		
C1^i—N1—C1	127.0 (4)	C6—C1—N1	124.5 (2)
C6—C1—C2	116.3 (2)	C2—C1—N1	119.2 (3)
C1^i—N1—C1—C6	−32.8 (2)	C1^i—N1—C1—C2	149.7 (2)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$F2	0.90	2.46	2.720 (2)	97

Compound (II)

Crystal data

$C_{12}HF_{10}N\cdot C_{12}H_{11}N$
$M_r = 518.36$
Monoclinic, $C2$
$a = 21.417 (3)$ Å
$b = 5.7778 (11)$ Å
$c = 8.1895 (14)$ Å
$\beta = 94.312 (13)°$
$V = 1010.5 (3)$ Å^3

$Z = 2$
$D_x = 1.704$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.17$ mm^{-1}
$T = 130 (2)$ K
Plate, colourless
$0.50 \times 0.25 \times 0.02$ mm

Data collection

Kuma KM-4 CCD κ-geometry diffractometer
ω scans
2852 measured reflections
965 independent reflections

924 reflections with $I > 2\sigma(I)$
$R_{int} = 0.057$
$\theta_{max} = 25.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.114$
$S = 1.16$
965 reflections
164 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0692P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}

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

C1—N1	1.395 (4)	C1A—N1A	1.402 (5)
C2—C1—C6	116.4 (3)	C6A—C1A—C2A	118.6 (4)
C2—C1—N1	124.7 (3)	C6A—C1A—N1A	118.9 (4)
C6—C1—N1	118.7 (3)	C2A—C1A—N1A	122.4 (4)
C1^i—N1—C1	128.3 (4)	C1A^{ii}—N1A—C1A	128.2 (5)
C2—C1—N1—C1^i	−32.4 (3)	C6A—C1A—N1A—C1A^{ii}	153.4 (4)
C6—C1—N1—C1^i	151.7 (3)	C2A—C1A—N1A—C1A^{ii}	−30.0 (3)

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

All H atoms of NH groups were located in electron-density difference maps and refined as riding, with N—H distances in the range 0.82–0.91 Å and U_{iso}(H) values of $1.2U_{eq}$(N). In (II), the H atoms of the NH groups were disordered over two symmetry-related positions. All H atoms bonded to C atoms were placed in calculated positions, with C—H distances in the range 0.93 Å, and were refined as riding, with U_{iso}(H) values of $1.2U_{eq}$(C).

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989) and *MERCURY* (Version 1.4; Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

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