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Octafluoronaphthalene–1,8-diaminonaphthalene (1/1)

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
R factor = 0.030
wR factor = 0.083
Data-to-parameter ratio = 6.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The structure of $C_{10}H_{10}N_2{\cdot}C_{10}F_8$, (I), comprises mixed stacks of parallel (within 2°) neutral molecules, overlapping in a 'graphitic' mode. Molecular geometry and UV–visible spectra indicate the absence of charge transfer. Structure (I) in space group $P2_1$ is close to $P2_1/c$ and pseudo-isostructural with the 1:1 complex of naphthalene and $C_{10}F_8$, hence the crystal packing of (I) is governed largely by quadrupole–quadrupole interactions, hydrogen bonding of NH_2 groups (including a relatively strong N—H···F bond of 2.16 Å) being less important.

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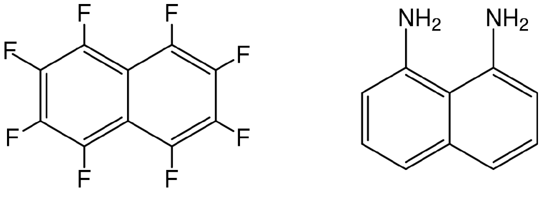
Arene–perfluoroarene interactions in crystal engineering, Part 6. For Part 5, see Batsanov, Collings *et al.* (2001).

Comment

Some aromatic amines, such as *N*,*N*-dimethylaniline and *N*,*N*,*N*′,*N*′-tetramethylphenylene-*p*-diamine, form 1:1 complexes with hexafluorobenzene (HFB). The presence of characteristic bands in UV-vis absorption spectra of these complexes in hexane solutions (Beaumont & Davis, 1967, 1968) indicated a charge-transfer (CT) component, in contrast to the complexes formed between HFB and non-functionalized aromatic hydrocarbon atoms, *e.g.* benzene (Patrick & Prosser, 1960), which are held together by quadrupole–quadrupole and van der Waals interactions. Subsequent crystallographic studies of a series of CT complexes HFB·Q have been reported, where Q is Me_2NPh, p-$Me_2NC_6H_4NMe_2$, p-$MeC_6H_4NMe_2$ and 3,5-$Me_2C_6H_3NMe_2$ (Dahl, 1977, 1979, 1981, 1985, 1989).



(I)

One widely used class of aromatic amines are *N,N*′-substituted derivatives of 1,8-diaminonaphthalene (DAN), the exceptionally high basicity of which earned them the name of 'proton sponges' (*e.g.* pK_a of *N*,*N*,*N*′,*N*′-tetramethyl-1,8-diaminonaphthalene is 12.1). Therefore, the parent compound DAN also attracted interest, although it is not a proton sponge itself, having pK_a = 4.6 (Staab & Saupe, 1988). Numerous salts with the $[(DAN)H]^+$ cation have been structurally characterized, but to our knowledge, no structure containing a neutral (non-protonated) DAN molecule has been reported, except that of pure DAN (Llamas-Saiz *et al.*, 1991; Basaran *et al.*, 1993). While studying arene-perfluoroarene interactions (Dai

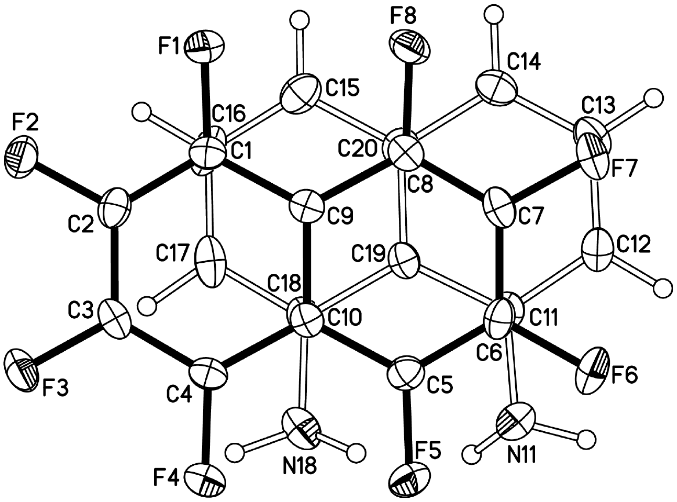


Figure 1
DAN and OFN molecules in (I), viewed normally to their planes. Displacement ellipsoid are drawn at the 50% probability level.

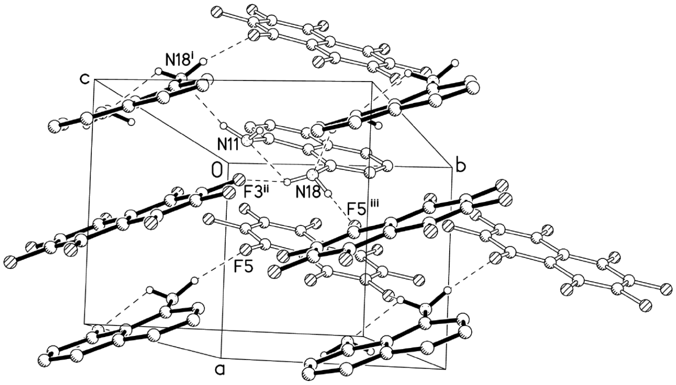


Figure 2
Crystal packing of (I); dashed lines show hydrogen bonds, naphthalene H atoms have been omitted. Symmetry codes: (i) $-x, y-\frac{1}{2}, 1-z$; (ii) $1-x, y-\frac{1}{2}, 1-z$; (iii) $1-x, y+\frac{1}{2}, 1-z$.

et al., 1999; Collings, Batsanov *et al.*, 2001; Collings, Roscoe *et al.*, 2001; Batsanov, Howard *et al.*, 2001; Batsanov, Collings *et al.*, 2001), we obtained the first molecular complex, (I), of neutral DAN with octafluoronaphthalene (OFN) in a 1:1 ratio.

The C atoms of the OFN molecule (Fig. 1) lie in one plane, with a mean deviation of 0.008 (2) Å, F atoms deviating from this plane by up to 0.050 (2) Å. The DAN adopts the usual, slightly twisted, conformation (Llamas-Saiz *et al.*, 1991). The C11 and C18 atoms tilt by 0.070 (3) and −0.086 (3) Å [and N11 and N18 by 0.130 (4) and −0.207 (3) Å] from the mean plane of the other eight naphthalene C atoms, which are coplanar with a mean deviation of 0.025 (2) Å and a maximum of 0.039 (2) Å. The average torsion angle around the central C19—C20 bond [4.4 (3)°] is essentially the same as in the structure of pure DAN [5.1 (4)°; Llamas-Saiz *et al.*, 1991]. In pure DAN, the NH_2 groups have different orientations: an N—H bond of one and the lone electron pair of another lie approximately in the naphthalene plane, thus forming an intramolecular N—H···N hydrogen bond with the N···N and H···N distances of 2.72 (1) and 2.04 (7) Å, and an N—H···N angle of 123 (5)°. In (I), the intramolecular N11···N18 distance is essentially the same [2.713 (2) Å] as in pure DAN, due to rigidity of the molecule. However, the lone electron pairs (EP) of both N atoms are almost normal to the naphthalene plane, with the torsion angles C19—C11—N11—EP of −77° and C19—C18—N18—EP of 84°, providing an unfavourable orientation for intramolecular hydrogen bonding. Although one H atom of each NH_2 group is directed 'inward', neither points directly to the opposite N atom. The intramolecular distances H111···N18 of 2.31 (3) Å and H181···N11 of 2.12 (3) Å are somewhat longer than the main range for (N)H···N hydrogen bonds, 1.9–2.1 Å (Dunitz & Taylor, 1997). It is not clear whether these interactions should be regarded as hydrogen bonds or as weaker (and probably forced) interactions.

The two remaining amino–H atoms participate in intermolecular hydrogen bonds. The N11—H112···N18($-x$, $-1-y$, $1-z$) bond is relatively weak: the N···N distance of 3.154 (3) Å is above the average (2.98 Å) for intermolecular hydrogen bonds (Kuleshova & Zorkii, 1981); the H···N distance of 2.30 (3) Å is also longer than usual (see above). The N18—H182···F5($1-x$, $-1-y$, $1-z$) bond is noteworthy. It is well known that an 'organic' (*i.e.* bonded to carbon) F atom is an exceedingly poor acceptor of hydrogen bonds. Howard *et al.* (1996) found only 26 crystal structures with N—H···F—C contacts with an H···F distance of 2.35 Å or less, while Dunitz & Taylor counted only 12 unequivocal cases of N—H···F—C hydrogen bonds (H···F 2.10–2.33 Å). Thus, the H182···F5 distance of 2.16 (3) Å and N—H···F angle of 158 (3)° in (I) correspond to relatively strong bonding. The intermolecular contact N18—H181···F3 ($1-x$, $-1-y$, $1-z$) has an H···F distance of 2.53 (3) Å, *i.e.* it falls within the usual range (2.5–2.6 Å) of H···F contacts, which are not proper hydrogen bonds (Howard *et al.*, 1996), and close to the sum of van der Waals radii, variously estimated from 2.56 Å (Rowland & Taylor, 1996) to 2.67 Å (Bondi, 1964). Every C-bonded H atom of the DAN molecule participates in one inter-stack H···F contact, with the H···F distances ranging from 2.47 to 2.67 Å and the C—H···F angles from 122 to 162°, to which the previous statement fully applies.

The structure contains infinite stacks of alternating DAN and OFN molecules, overlapping in a 'graphitic' mode (see Fig. 2). The naphthalene moieties of the DAN and OFN are parallel within 2°; the mean interplanar separations alternate between 3.35 and 3.42 Å along the stack. The general direction of the stack is parallel to the '*a*' axis. Similar stacks have been observed in the 1:1 complex, (II), of naphthalene and OFN (Potenza & Mastropaolo, 1975) and, indeed, in all previously studied molecular complexes of arenes with OFN (Clyburne *et al.*, 2001; Collings, Roscoe *et al.*, 2001; Batsanov, Collings *et al.*, 2001). Indeed, compound (I) is pseudo-isomorphous with (II), which crystallizes in the space group $P2_1/c$. The unit cell of (II), a = 7.457 (5), b = 8.503 (2), c = 12.710 (2) Å and β = 99.48 (5)°, is very similar to that of (I). Structure (I), except the amino groups, has an approximate symmetry of the space group $P2_1/c$ (shifting the origin by $c/4$ from the present setting), with the DAN and OFN molecules occupying the

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inversion centres at $0,\frac{1}{2},0$ and $\frac{1}{2},\frac{1}{2},0$.

Bond lengths in the DAN and OFN moieties in (I) do not differ substantially from those in pure DAN (Llamas-Saiz *et al.*, 1991) and OFN (Batsanov & Collings, 2001). The UV-visible absorption spectrum of (I) in hexane solution shows no additional features compared to the spectrum of pure DAN, indicating the absence of CT. Thus, (I) can be regarded as a cocrystal of neutral molecules, in contrast with the CT complexes of HFB with Me_2NPh and its derivatives (see above). The pattern of hydrogen bonds, formed by the NH_2 groups, is far less favourable than could be imagined *a priori*. Hence the structure is not defined by hydrogen bonds (to whose network other factors have to adapt) but rather by quadrupole–quadrupole and van der Waals interactions between the naphthalene and perfluoronaphthalene systems, to whose stacking motif the hydrogen bonding has to adjust. This is evident from the fact that the packing of (I) is similar to that of complexes between simple (non-functionalized) arenes and perfluoroarenes. The inter-stack $C-H\cdots F-C$ interactions are not hydrogen bonds in a proper sense, rather one of the manifestations of the electrostatic (quadrupole–quadrupole) interactions. However, although the introduction of amino groups does not alter the packing geometry of (I) compared to (II), it does increase the strength of intermolecular interactions. Thus (I) has a melting point (460–463 K), much higher than that of (II) (405 K), the more surprising in that the melting point of pure DAN (339.5 K) is actually lower than that of pure naphthalene (353.6 K) (Weast, 1972).

Experimental

Large colourless needle-shaped single crystals of (I) were grown by slow (3 d) evaporation at room temperature of a solution of OFN (0.1 mmol, 0.027 g) and DAN (0.1 mmol, 0.016 g) in freshly distilled CH_2Cl_2 (1 ml). DAN (Aldrich) had been purified by sublimation (at 0.1 Torr and 373 K) and recrystallized from aqueous ethanol prior to use (on storage, DAN acquires a brown colour, which is then passed on to the complex). M.p. of (I): 460–463 K, *cf.* 360 K for OFN and 339.5 K for DAN. Analysis, found: C 55.42, H 2.30, N 6.94%; calculated for $C_{20}H_{10}F_8N_2$: C 55.81, H 2.32, N 6.51.

Crystal data

$C_{10}F_8{\cdot}C_{10}H_{10}N_2$
$M_r = 430.30$
Monoclinic, $P2_1$
$a = 7.309$ (1) Å
$b = 8.541$ (1) Å
$c = 13.412$ (1) Å
$\beta = 96.89$ (1)°
$V = 831.21$ (16) $Å^3$
$Z = 2$
$D_x = 1.719$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 818 reflections
$\theta = 12.1$–$26.4°$
$\mu = 0.17$ mm^{-1}
$T = 120$ (2) K
Prism, colourless
0.44 × 0.25 × 0.16 mm

Data collection

SMART 1K CCD area-detector diffractometer
ω scans
6791 measured reflections
2031 independent reflections
1797 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.037$
$\theta_{\rm max} = 27.5°$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.083$
$S = 1.03$
2031 reflections
311 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0612P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.26$ e $Å^{-3}$
$\Delta\rho_{\rm min} = -0.25$ e $Å^{-3}$
Absolute structure: indeterminate, Friedel pairs merged, all $\Delta f''$ set to 0

All H atoms were refined in isotropic approximation; bond lengths C—H 0.93 (3)–0.98 (3) Å and N—H 0.89 (4)–0.95 (3) Å. However, all calculations for hydrogen bonds and intermolecular contacts were made with N—H bond lengths normalized to 1.009 Å and C—H to 1.083 Å, as determined by neutron diffraction (Allen *et al.*, 1987).

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.
Basaran, R., Dou, S. Q. & Weiss, A. (1993). *Struct. Chem.* **4**, 219–233.
Batsanov, A. S. & Collings, J. C. (2001). *Acta Cryst.* B**57**. In the press.
Batsanov, A. S., Howard, J. A. K., Marder, T. B. & Robins, E. G. (2001). *Acta Cryst.* C**57**. In the press.
Batsanov, A. S., Collings, J. C., Howard, J. A. K., Marder, T. B. & Perepichka, D. F. (2001). *Acta Cryst.* C**57**. In the press.
Beaumont, T. G. & Davis, K. M. C. (1967). *J. Chem. Soc. B*, pp. 1131–1134.
Beaumont, T. G. & Davis, K. M. C. (1968). *Nature*, **218**, 865.
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Bruker (1997). *SHELXTL*. Version 5.10 DOS/WIN95/NT. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (1999). *SMART* (Version 5.049) and *SAINT* (Version 5.00). Bruker AXS Inc., Madison, Wisconsin, USA.
Clyburne, J. A. C., Hamilton, T. & Jenkins, H. A. (2001). *Cryst. Eng.* **4**, 1–9.
Collings, J. C., Batsanov, A. S., Howard, J. A. K. & Marder, T. B. (2001). *Acta Cryst.* C**57**, 870–872.
Collings, J. C., Roscoe, K. P., Thomas, R. Ll., Batsanov, A. S., Stimson, L. M., Howard, J. A. K. & Marder, T. B. (2001). *New J. Chem.* In the press.
Dahl, T. (1977). *Acta Cryst.* B**33**, 3021–3024.
Dahl, T. (1979). *Acta Chem. Scand. Ser. A*, **33**, 665–669.
Dahl, T. (1981). *Acta Cryst.* B**37**, 98–101.
Dahl, T. (1985). *Acta Cryst.* C**41**, 931–933.
Dahl, T. (1989). *Acta Chem. Scand.* **43**, 172–176.
Dai, C., Nguyen, P., Marder, T. B., Scott, A. J., Clegg, W. & Viney, C. (1999). *Chem. Commun.* pp. 2493–2494.
Dunitz, J. D. & Taylor, R. (1997). *Chem. Eur. J.* **3**, 89–98.
Howard, J. A. K., Hoy, V. J., O'Hagan, D. & Smith, G. T. (1996). *Tetrahedron*, **52**, 12613–12622.
Kuleshova, L. N. & Zorkii, P. M. (1981). *Acta Cryst.* B**37**, 1363–1366.
Llamas-Saiz, A. L., Foces-Foces, C., Molina, P., Alajarin, M., Vidal, A., Claramunt, R. M. & Elguero, J. (1991). *J. Chem. Soc. Perkin Trans.* 2, pp. 1025–1031.
Patrick, C. R. & Prosser, G. S. (1960). *Nature*, **187**, 1021.
Potenza, J. & Mastropaolo, D. (1975). *Acta Cryst.* B**31**, 2527–2529.
Rowland, R. S. & Taylor, R. (1996). *J. Phys. Chem.* **100**, 7384–7391.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Staab, H. A. & Saupe, T. (1988). *Angew. Chem. Int. Ed.* **27**, 865–878.
Weast, R. C. (1972). Editor. *Handbook of Chemistry and Physics*, 53rd ed. Cleveland, Ohio: The Chemical Rubber Co.

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