

N—H... π hydrogen bonding in
2-aminofluorene

Thomas Steiner

Institut für Chemie – Kristallographie, Freie Universität Berlin, Takustrasse 6,
D-14195 Berlin, Germany

Correspondence e-mail: steiner@chemie.fu-berlin.de

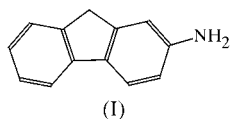
Received 7 December 1999

Accepted 4 April 2000

The amino group of the title compound, $C_{13}H_{11}N$, does not form N—H...N hydrogen bonds, but is engaged only in weaker N—H...Ph and C—H...N interactions. An aromatic ring acts as a double hydrogen-bond acceptor, leading to an infinite H—N—H...Ph...H—N—H...Ph array.

Comment

The primary amino group ($-NH_2$) has a double-donor single-acceptor hydrogen-bond function. As a consequence, primary amines often have a surplus of strong hydrogen-bond donors that cannot be satisfied by conventional hydrogen bonding (N—H...X with X = O, N, S *etc.*). If π -bonded moieties are present, weaker N—H... π hydrogen bonds are often formed as a result (Hanton *et al.*, 1992). Most important of all π acceptors is the phenyl group and today there is a large volume of experimental material on N—H...Ph hydrogen bonds (surveyed by Malone *et al.*, 1997; Desiraju & Steiner, 1999). Several neutron diffraction studies have even been performed (Allen *et al.*, 1997; Steiner & Mason, 2000; also see Starikov & Steiner, 1998). Nevertheless, the roles played by N—H...Ph interactions in hydrogen-bond networks have been poorly explored and deserve further investigation. In this



context, 2-aminofluorene, (I), is an obviously interesting molecule. Therefore, its crystal structure was determined in order to characterize the hydrogen-bond pattern formed.

The molecular structure of (I) is shown in Fig. 1. The geometry of the fluorene moiety is unremarkable [for relevant references see, for example, the structure reports on fluorene by Gerkin *et al.* (1984), on 2-acetylaminofluorene by van Meerssche *et al.* (1980) and on 9-fluorenone by Luss & Smith (1972)]. The C—N bond length is 1.372 (4) Å. The amino group is significantly pyramidal, with the sum of the angles at N being 347 (4)°; the H—N—H angle is 117 (4)°. Both N—H vectors are oriented out of the plane of the neighboring

aromatic ring, with torsion angles C1—C2—N—H1N = 163 (3) and C1—C2—N—H2N = 21 (3)°.

The crystal packing of (I) is depicted in Fig. 2. No N—H...N hydrogen bonds are formed, but both N—H vectors point at the faces of aromatic rings of neighboring molecules.

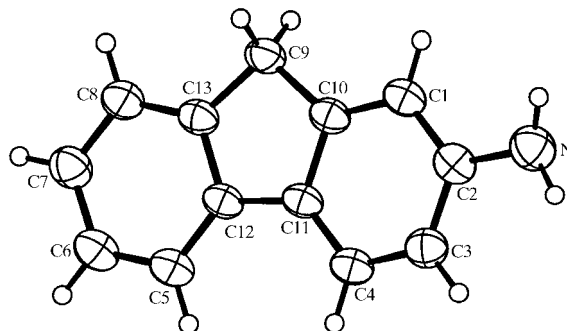


Figure 1

The molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level.

The geometries of these contacts are typical for N—H...Ph hydrogen bonding [for N—H normalized to 1.01 Å, M is an aromatic center: N—H1...Ph($x - \frac{1}{2}, \frac{1}{2} - y, z$) with H... M = 2.55, N... M = 3.54 Å, N—H... M = 167° and H...C range = 2.60–3.17 Å; N—H2...Ph($1 - x, -y, z - \frac{1}{2}$) with H... M = 2.86, N... M = 3.82 Å, N—H... M = 160° and H...C range 2.53–3.71 Å]. Since the aromatic ring involved acts as a double acceptor, the resulting hydrogen-bond pattern is an infinite H—N—H...Ph...H—N—H...Ph chain. More commonly, Ph groups act only as single hydrogen-bond acceptors (X—H...Ph) and can then play only very simple roles in hydrogen-bond arrays (*i.e.* isolated X—H...Ph bonds, Ph...H—X—H...Ph pairs or X—H...Y—H...Ph chain terminators).

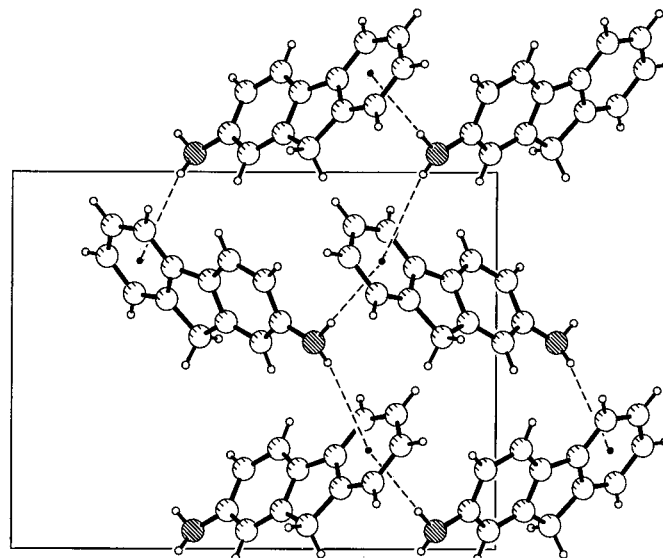


Figure 2

The crystal packing of (I) drawn in projection onto the xz plane. N—H... π hydrogen bonds are indicated by dashed lines.

Owing to its pyramidal geometry, the amino group of (I) can also act as a hydrogen-bond acceptor. Apart from the amino group, (I) contains only the weakly polar C—H groups as potential donors. The shortest intermolecular contact formed by the amino N atom is to C4—H(1 - x, 1 - y, $\frac{1}{2}$ + z), with H...N = 2.65, C...N = 3.723 (6) Å and C—H...N = 170° (for C—H normalized to 1.08 Å; not shown in Fig. 2). This is a typical geometry for a weak C—H...N hydrogen bond (Steiner, 1998).

The crystal structure of 2-aminofluorene is an example of a structure containing no conventional hydrogen bonds, although they could be formed in principle. Instead, the amino group is involved only in weak hydrogen bonds of the types N—H...Ph and C—H...N, which were generally neglected not so long ago.

Experimental

2-Aminofluorene, (I), was obtained from Aldrich and was recrystallized from MeOH by slow evaporation of the solvent.

Crystal data

C ₁₃ H ₁₁ N	Mo K α radiation
<i>M_r</i> = 181.23	Cell parameters from 33 reflections
Orthorhombic, <i>Pna</i> 2 ₁	θ = 8.1–17.3°
<i>a</i> = 14.790 (14) Å	μ = 0.075 mm ⁻¹
<i>b</i> = 5.681 (9) Å	<i>T</i> = 293 K
<i>c</i> = 11.187 (11) Å	Rod, yellow
<i>V</i> = 940 (2) Å ³	0.80 × 0.25 × 0.15 mm
<i>Z</i> = 4	
<i>D_x</i> = 1.281 Mg m ⁻³	

Data collection

Stoe four-circle diffractometer	<i>h</i> = -19 → 16
ω scans	<i>k</i> = -7 → 3
2226 measured reflections	<i>l</i> = -14 → 13
1358 independent reflections	3 standard reflections
1037 reflections with <i>I</i> > 2 σ (<i>I</i>)	frequency: 90 min
<i>R</i> _{int} = 0.033	intensity decay: none
θ _{max} = 27.51°	

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0579P)^2 + 0.1454P]$
$R[F^2 > 2\sigma(F^2)] = 0.043$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.128$	$(\Delta/\sigma)_{\max} < 0.001$
<i>S</i> = 1.032	$\Delta\rho_{\max} = 0.13 \text{ e } \text{Å}^{-3}$
1358 reflections	$\Delta\rho_{\min} = -0.15 \text{ e } \text{Å}^{-3}$
145 parameters	Extinction correction: <i>SHELXL97</i>
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.019 (5)

H atoms bonded to C atoms were treated with the default riding model and the amino H atoms were located in difference Fourier calculations and refined isotropically. All H-atom displacement parameters refined to realistic values [H atoms bonded to C: 0.057–0.096 Å²; amino-H atoms: 0.119 (16) and 0.100 (16) Å² for H1N and H2N, respectively]. At first glance, the *U*_{iso} values of the amino-H atoms appear to be relatively high, but when compared with the *U*_{eq} value of N [0.0836 (9) Å²] they can be considered as normal.

Data collection: Stoe diffractometer software; cell refinement: Stoe diffractometer software; data reduction: Stoe diffractometer software; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXL97*.

Dr D. Lentz is thanked for providing access to the single-crystal diffractometer.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1132). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H., Hoy, V. J., Howard, J. A. K., Thalladi, V. R., Desiraju, G. R., Wilson, C. C. & McIntyre, G. J. (1997). *J. Am. Chem. Soc.* **119**, 3477–3480.
- Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond in Structural Chemistry and Biology*, pp. 130–164. Oxford University Press.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Gerkin, R. E., Lundstedt, A. P. & Reppart, W. J. (1984). *Acta Cryst.* **C40**, 1892–1894.
- Hanton, L. R., Hunter, C. A. & Purvis, D. H. (1992). *J. Chem. Soc. Chem. Commun.* pp. 1134–1136.
- Luss, H. R. & Smith, D. L. (1972). *Acta Cryst.* **B28**, 884–889.
- Malone, J. F., Murray, C. M., Charlton, M. H., Docherty, R. & Lavery, A. J. (1997). *J. Chem. Soc. Faraday Trans.* **93**, 3429–3436.
- Meerssche, M. van, Germain, G., Declercq, J.-P., Touillaux, R., Roberfroid, M. & Razzouk, C. (1980). *Cryst. Struct. Commun.* **9**, 515–518.
- Sheldrick, G. M. (1985). *SHELXS86*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.
- Starikov, E. B. & Steiner, T. (1998). *Acta Cryst.* **B54**, 94–96.
- Steiner, T. (1998). *New J. Chem.* **22**, 1099–1103.
- Steiner, T. & Mason, S. A. (2000). *Acta Cryst.* **B56**, 254–260.