

4-Amino derivatives of 7-nitro-2,1,3-benzoxadiazole: the effect of the amino moiety on the structure of fluorophores

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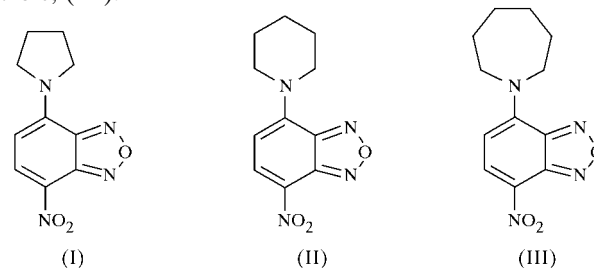
The crystal structures of three 4-amino derivatives of 7-nitro-2,1,3-benzoxadiazole with increasing substituent ring size, *viz.* 7-nitro-4-(pyrrolidin-1-yl)-2,1,3-benzoxadiazole, $C_{10}H_{10}N_4O_3$, 7-nitro-4-(piperidin-1-yl)-2,1,3-benzoxadiazole, $C_{11}H_{12}N_4O_3$, and 4-(azepan-1-yl)-7-nitro-2,1,3-benzoxadiazole, $C_{12}H_{14}N_4O_3$, have been determined in order to understand their photophysical behaviour. All three were found to crystallize in centrosymmetric space groups. There is considerable electron delocalization compared with the parent compound, although the five-membered oxadiazole ring apparently does not participate in this. The length of the C–N bond between the amino N atom and the 7-nitrobenzoxadiazole system is found to be shorter than in similar compounds, as is the C–N_{nitro} bond. In each structure, the nitro group lies in the plane of the benzoxadiazole unit.

Comment

Although 4-amino derivatives of 7-nitro-2,1,3-benzoxadiazole (NBD) are considered to be highly efficient fluorophores and have widespread applications (Chattopadhyay, 1990), so far only a few crystal structures of these have been reported (Saha & Samanta, 1999*a*). As benzoxadiazole is considered a complex heterocyclic moiety, the standard input data for initial parameterization for sophisticated theoretical calculations are not yet available. Crystal structure determinations also provide information about whether a crystal exhibits non-linear optical (NLO) activity; a non-centrosymmetric crystal is a precondition for second-order NLO activity.

It has been shown (Suzuki *et al.*, 1988) that 4-chloro-7-nitrobenzoxadiazole (NBD-chloride) is NLO active. Although the Cl atom is thought to be part of the π -system and has some electron-donating capacity, the double bonds in the six-membered ring of the benzoxadiazole moiety are localized, *i.e.* no resonance is detected. It was therefore of interest to determine the structure when this benzoxadiazole unit is attached to a strongly electron-donating group, such as amine,

so we report here the crystal structures of three new 4-amino NBD derivatives, namely 7-nitro-4-(pyrrolidin-1-yl)-2,1,3-benzoxadiazole, (I), 7-nitro-4-(piperidin-1-yl)-2,1,3-benzoxadiazole, (II), and 4-(azepan-1-yl)-7-nitro-2,1,3-benzoxadiazole, (III).



In addition, to follow the details of the structural changes in the intramolecular charge-transfer (ICT) state that accompanies and governs the excited-state ICT process, knowledge of the ground-state crystal structure is important. The present studies were also carried out in order to obtain information on the electron flow and its direction, the change in the order of the C4–N4 bond that connects the amine moiety to the benzoxadiazole subunit in the three derivatives, the pyramidalicity of the amine N atom, and the change of the twist angle with change of substituent amine. It is known that the character of the C4–N4 bond and the configuration of the amine N atom determine the photophysical properties of some donor–acceptor (*D–A*) molecules (Saha & Samanta, 1998). It is also known that the ground-state twist angle can be a useful predictor of the excited-state conformation (Saha & Samanta, 1999*b*).

The molecular structures of compounds (I)–(III) are shown in Figs. 1–3, respectively. Unlike the parent NBD-chloride compound, derivatives (I)–(III) are centrosymmetric and show reversal of bond order in the six-membered ring of the benzoxadiazole unit. The C4–C5 bond has appreciable

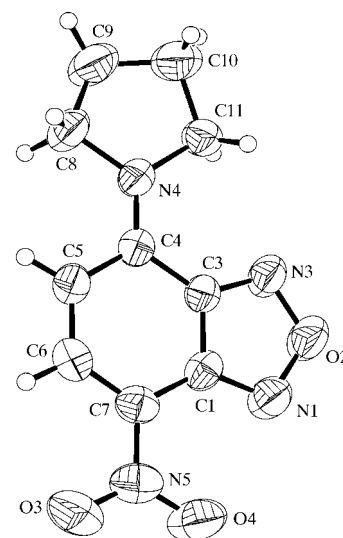


Figure 1

A view of the molecular structure of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. One of the H atoms bound to C9 is wholly obscured by it.

double-bond character in NBD-chloride [1.349 (9) Å; Suzuki *et al.*, 1988], whereas in the present systems, this bond has considerable single-bond character, with a mean bond length of 1.406 (3) Å. Similarly, the C5—C6 bond in NBD-chloride is 1.435 (9) Å, whereas in (I)–(III) it has an average length of 1.383 (1) Å, indicating that the reversal of bond order of these compounds is due to substitution with a stronger donor.

The C4—N4 bond, which is very important for photo-physical behaviour, is found to be considerably shortened in each of (I), (II) and (III). In similar donor–acceptor molecules with ICT states, for example, 3,5-dimethyl-4-dimethylamino-benzonitrile, the corresponding C4—N4 bond length is 1.414 (3) Å, and at 173 K, it is also twisted by 59.3 (2)° (Heine *et al.*, 1994). However, this is shorter than the corresponding bond in the salt 4-aminobenzonitrile hydrochloride [1.467 (2) Å], which is considered to be a pure single bond (Colapietro *et al.*, 1981). In the case of 4-dimethylamino-benzonitrile (DMABN), the corresponding bond length is 1.367 (3) Å, with a twist angle of 10.8 (2)° (Heine *et al.*, 1994), where considerable double-bond character has been predicted on the basis of photophysical properties. For the present NBD derivatives, the mean C4—N4 length is 1.336 (5) Å. Comparing this with all the data mentioned above, we can conclude that there is a considerable charge flow from donor to acceptor, making the bond appreciably shorter. The double-bond character of C4—N4 can also be explained by a formal valence-bond approach.

Another noteworthy point is that the N5—C7 bond is considerably shorter in the present NBD derivatives [mean 1.422 (4) Å] compared with NBD-chloride [1.470 (8) Å; Suzuki *et al.*, 1988]. This indicates that the nitro group acts as the acceptor, a conclusion which is supported by the observation that the nitro group is almost coplanar with the benzoxadiazole unit. The adjacent five-membered ring of the

benzoxadiazole does not contribute to electron flow, which is evident from the fact that its geometry does not change much on substitution with an amino group. Hence, the dipole moment is directed from the amino to the nitro group, removing the complexity and controversy about the involvement of the benzoxadiazole unit.

Comparing the derivatives studied, it can be seen that (I) has the shortest C4—N4 bond. This is due to the maximum overlap of the amine lone pair with the benzoxadiazole moiety, resulting from the favourable nitrogen conformation retarding rotation around the bond. This observation supports the dynamic NMR data that indicate (I) has a higher barrier to rotation compared with other compounds (Saha & Samanta, 1998).

The cyclic amino moiety in (II) is found to be in the stable chair conformation. The three angles around the amine N atom indicate the pyramidity at the N atom; in these derivatives, the amino N atom is almost planar. Furthermore, it can be seen from the data that (III) is more planar than the others. This is due to the lower barrier to inversion for larger rings (Ōki, 1985), and also supports the photophysical observations that (III) has the maximum non-radiative rate-constant value (Saha & Samanta, 1998).

There is a small increase in the twist angle between the amine and NBD moieties on going from (I) to (III). The maximum twist angle detected for (III) is 10.9 (5)° [$\tau(\text{C8—N4—C4—C5})$], which indicates that the excited state is unlikely to be twisted, contrary to the speculation that a twisted intramolecular charge-transfer (TICT) state is involved (Forgues *et al.*, 1993). This supports our earlier findings (Saha & Samanta, 1998).

In summary, from the structure determinations on these three NBD derivatives, we have been able to extract valuable data about the effect of amino substitutions, and some of these data supplement photophysical observations.

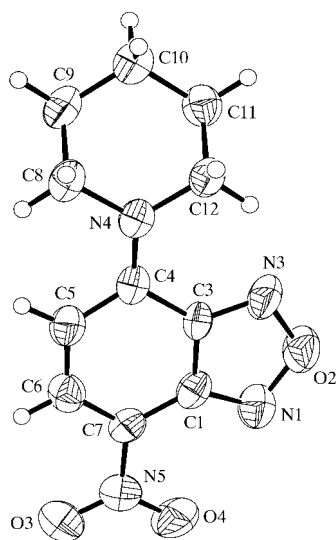


Figure 2
A view of the molecular structure of (II) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. One H atom on each of C9 and C11 is wholly obscured by the parent atom.

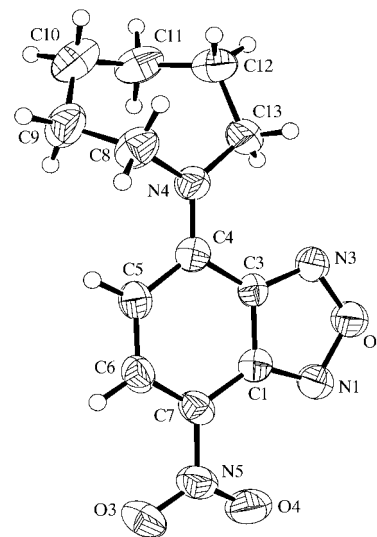


Figure 3
A view of the molecular structure of (III) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Experimental

Compounds (I)–(III) were prepared according to the general procedure of Saha & Samanta (1998). In a typical synthesis, a solution of the amine (1.2 mmol) in ethyl acetate (2 ml) was added dropwise to a solution of NBD-chloride (1 mmol) in ethyl acetate (3 ml) cooled in an ice bath. After stirring for 30 min in the ice bath, the mixture was stirred for a further 2 h at room temperature. The product, which appeared as a red precipitate in all cases, was filtered off and purified by column chromatography, using a silica-gel column and different proportions of hexane and ethyl acetate as eluent. The purified compounds were recrystallized from absolute ethanol by slow evaporation.

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

N4–C4	1.328 (4)	N5–C7	1.417 (4)
C4–N4–C8	123.3 (2)	C8–N4–C11	110.9 (3)
C4–N4–C11	125.8 (2)		
C8–N4–C4–C5	–3.2 (4)	O3–N5–C7–C6	0.1 (4)

Compound (I)

Crystal data

C₁₀H₁₀N₄O₃
M_r = 234.22
Monoclinic, *P*2₁/*c*
a = 7.0305 (12) Å
b = 7.686 (2) Å
c = 18.951 (4) Å
 β = 93.69 (2)°
V = 1022.0 (4) Å³
Z = 4

D_x = 1.522 Mg m^{–3}
Mo *K*α radiation
Cell parameters from 25 reflections
 θ = 11.3–12.6°
 μ = 0.12 mm^{–1}
T = 293 (2) K
Plate, red
0.7 × 0.4 × 0.2 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω scans
1792 measured reflections
1792 independent reflections
973 reflections with *I* > 2σ(*I*)
 θ_{\max} = 25°

h = 0 → 8
k = 0 → 9
l = –22 → 22
3 standard reflections
frequency: 90 min
intensity decay: none

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.130$
S = 1.11
1792 reflections
154 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0537P)^2 + 0.1481P]$
where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ)_{max} = 0.012
 $\Delta\rho_{\max} = 0.17 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.17 \text{ e } \text{Å}^{-3}$

Table 2
Selected geometric parameters (Å, °) for (II).

N4–C4	1.337 (6)	N5–C7	1.431 (7)
C4–N4–C8	121.2 (5)	C8–N4–C12	113.2 (4)
C4–N4–C12	125.5 (4)		
C8–N4–C4–C5	–3.5 (9)	O3–N5–C7–C6	0.4 (8)

Compound (II)

Crystal data

C₁₁H₁₂N₄O₃
M_r = 248.25
Monoclinic, *P*2₁/*c*
a = 6.7644 (19) Å
b = 21.277 (6) Å
c = 7.788 (6) Å
 β = 94.22 (5)°
V = 1117.8 (10) Å³
Z = 4

D_x = 1.475 Mg m^{–3}
Mo *K*α radiation
Cell parameters from 25 reflections
 θ = 7.8–10.4°
 μ = 0.11 mm^{–1}
T = 293 (2) K
Plate, red
0.40 × 0.29 × 0.16 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω scans
2122 measured reflections
1955 independent reflections
732 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.137

θ_{\max} = 25°
h = 0 → 8
k = 0 → 25
l = –9 → 9
3 standard reflections
frequency: 90 min
intensity decay: none

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.069$
 $wR(F^2) = 0.224$
S = 1.05
1955 reflections
163 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0751P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ)_{max} = 0.005
 $\Delta\rho_{\max} = 0.25 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.28 \text{ e } \text{Å}^{-3}$

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

N4–C4	1.344 (4)	N5–C7	1.424 (4)
C4–N4–C8	120.3 (3)	C8–N4–C13	117.0 (3)
C4–N4–C13	122.7 (3)		
C8–N4–C4–C5	10.9 (5)	O3–N5–C7–C6	–0.7 (5)

Compound (III)

Crystal data

C₁₂H₁₄N₄O₃
M_r = 262.27
Monoclinic, *P*2₁/*c*
a = 7.4909 (16) Å
b = 10.8002 (14) Å
c = 15.1001 (19) Å
 β = 98.958 (14)°
V = 1206.7 (3) Å³
Z = 4

D_x = 1.444 Mg m^{–3}
Mo *K*α radiation
Cell parameters from 25 reflections
 θ = 9.3–10.6°
 μ = 0.11 mm^{–1}
T = 293 (2) K
Plate, red
0.32 × 0.21 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω scans
2115 measured reflections
2115 independent reflections
1043 reflections with *I* > 2σ(*I*)
 θ_{\max} = 25°

h = 0 → 8
k = 0 → 12
l = –17 → 17
3 standard reflections
frequency: 90 min
intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.174$
 $S = 1.03$
 2115 reflections
 173 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0918P)^2]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.22 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL97*
 (Sheldrick, 1997)
 Extinction coefficient: 0.010 (3)

For all three compounds, H atoms were placed geometrically and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. C–H distances were fixed at 0.97 Å for methylene H and at 0.93 Å for aromatic H atoms.

For all compounds, data collection: *CAD-4 Software* (Enraf-Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *Xtal3.5* (Hall *et al.*, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEX6.0* (McArdle, 1995); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1482). Services for accessing these data are described at the back of the journal.

References

- Chattopadhyay, A. (1990). *Chem. Phys. Lipids*, **53**, 1–15.
 Colapietro, M., Domenicano, A., Marciante, C. & Portalone, G. (1981). *Acta Cryst.* **B37**, 387–394.
 Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
 Forgues, F. S., Fayet, J. P. & Lopez, A. (1993). *J. Photochem. Photobiol. A*, **70**, 229–243.
 Hall, S. R., Flack, H. D. & Stewart, J. M. (1995). Editors. *Xtal3.5 Reference Manual*. Universities of Western Australia, Australia, Geneva, Switzerland, and Maryland, USA.
 Heine, A., Herbst-Irmer, R., Stalke, D., Kühnle, W. & Zachariasse, K. A. (1994). *Acta Cryst.* **B50**, 363–373.
 McArdle, P. (1995). *J. Appl. Cryst.* **28**, 65.
 Ōki, M. (1985). *Applications of Dynamic NMR Spectroscopy to Organic Chemistry*, p. 315. Deerfield Beach: VCH.
 Saha, S. & Samanta, A. (1998). *J. Phys. Chem. A*, **102**, 7903–7912.
 Saha, S. & Samanta, A. (1999a). *Acta Cryst.* **C55**, 252–254.
 Saha, S. & Samanta, A. (1999b). *Acta Cryst.* **C55**, 1299–1300.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
 Suzuki, H., Kurihara, T., Kaino, T. & Ebisawa, F. (1988). *Acta Cryst.* **C44**, 484–486.