Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Dispiro[2*H*-benzimidazole-2,1′-cyclohexane-4′,2″-[2*H*]benzimidazole] 1-oxide and dispiro[2*H*-benzimidazole-2,1′-cyclohexane-4′,2″-[2*H*]benzimidazole] 1,1″-dioxide

Menahem Kaftory,* Vitaly Shteiman and Mark Botoshansky

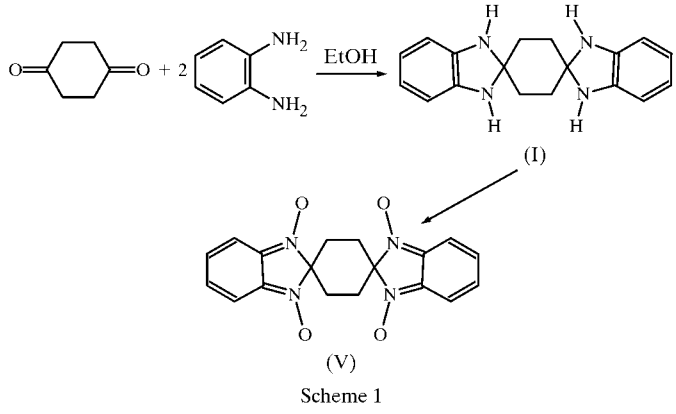
Department of Chemistry, Technion–Israel Institute of Technology, Haifa, Israel 32000
Correspondence e-mail: kaftory@tx.technion.ac.il

Received 15 November 2001
Accepted 21 January 2002
Online 28 February 2002

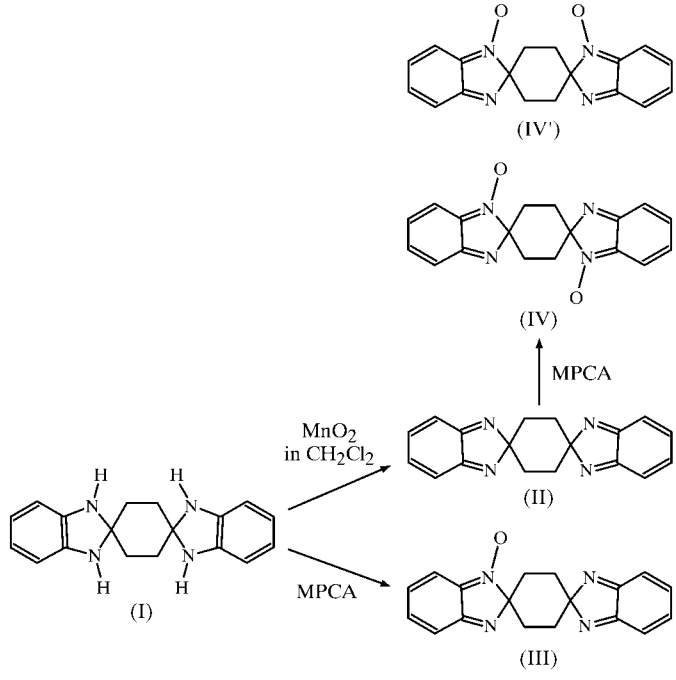
Oxidation of tetrahydrodispirobenzimidazole by *m*-chloroperbenzoic acid did not produce dispiro-2*H*-benzimidazole, which is the product obtained by oxidation with MnO_2. Instead, a mixture of two compounds was identified, namely dispiro[2*H*-benzimidazole-2,1′-cyclohexane-4′,2″-[2*H*]benzimidazole] 1-oxide, $C_{18}H_{16}N_4O$, (III), and dispiro[2*H*-benzimidazole-2,1′-cyclohexane-4′,2″-[2*H*]benzimidazole] 1,1″-dioxide, $C_{18}H_{16}N_4O_2$, (IV). In (III), the molecules are disordered about a twofold rotation axis and have 2/*m* site symmetry. In (IV), the crystals are triclinic and the molecules occupy crystallographic inversion centers. Although the two compounds are very similar and are arranged in layers, they adopt completely different packing modes within the layers, *viz*. herring-bone in (III) and parallel molecules in (IV). The molecules within the layers are held together by C—H···O and C—H···N hydrogen bonds.

Comment

We have attempted to prepare tetranitroxide (V) (see Scheme 1) by a procedure similar to that described by Keana *et al.* (1967, 1978). Following the guidelines of Davies *et al.* (1984) and Herbert *et al.* (1988), dispiro[2*H*-benzimidazole-2,1′-cyclohexane-4,2″-[2*H*]benzimidazole], (I), was prepared. Oxidation of (I) by MnO_2 led to the dispiro-2*H*-benzimidazole (II) (Herbert *et al.*, 1988) (see Scheme 2). Further oxidation by *m*-chloroperbenzoic acid (von Glahn *et al.*, 1999) produced (*E*)- and (*Z*)-dispiro[2*H*-benzimidazole-2,1′-cyclohexane-4′,2″-[2*H*]benzimidazole] 1,1″-dioxide, *i.e.* (IV) and (IV′), respectively (see Scheme 2). We carried out the oxidation of (I) by *m*-chloroperbenzoic acid, skipping the oxidation step with MnO_2. Two major products were identified, namely dispiro[2*H*-benzimidazole-2,1′-cyclohexane-4′,2″-[2*H*]benzimidazole] 1-oxide, (III), and dispiro[2*H*-benzimidazole-2,1′-cyclohexane-4′,2″-[2*H*]benzimidazole] 1,1″-dioxide, (IV). Although the chemical difference between the two compounds is small, the crystal structures are completely different.



Scheme 1



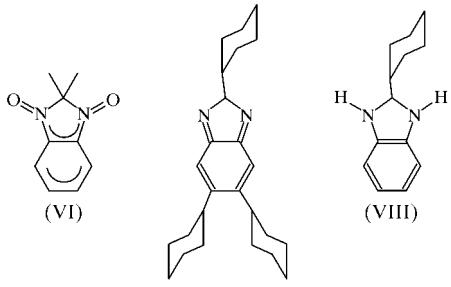
Scheme 2

Monoxide (III) crystallizes in the orthorhombic space group *Cmca*, displaying 2/*m* crystallographic site symmetry. This means that the O atom is equally disordered between two sites related by a twofold symmetry axis. The crystals of dioxide (IV) are triclinic and the molecule occupies a crystallographic inversion center. The packing of the molecules of (III) and (IV) in the unit cells are shown in Figs. 1 and 2, respectively. In both, the molecules form layers but the arrangement of molecules within the layer is different. While the molecules in (III) adopt a herring-bone packing motif, the molecules are parallel in (IV). The molecules within a layer are held together by short intermolecular O···H—C and N···H—C contacts. Only two such contacts that were observed in the crystal structure of (III) could be considered hydrogen bonds: O1···H4 2.205 (3) Å, O1···C4 3.110 (3) Å and O1···H4—C4

 DOI: 10.1107/S0108270102001099

158.7 (2)°; N2···H3 2.605 (3) Å, N2···C3 3.510 (3) Å and N2···H3—C3 159.3 (2)°. In (IV), there is only one hydrogen bond; O1···H2 2.470 (4) Å, O1···C2 3.327 (4) Å and O1···H2—C2 153.4 (3)°.

The packing of the layers is also very different. While the molecules between successive layers in (IV) are related by translation, those in (III) are related by a twofold rotation axis perpendicular to the benzimidazole portions of the molecules (see Figs. 3 and 4). A comparison of bond lengths and angles is given in Table 1; also compared in Table 1 are the bond lengths of the relevant moiety in benzimidazole dioxide (VI) (Keller *et al.*, 1977), benzimidazole (VII), and dihydrobenzimidazole (VIII) (Hazelton *et al.*, 1995) (see Scheme 3).



Scheme 3

The localization of double bonds in the benzene ring is clearly observed in (III), (IV) and (VII), where the C2—C3 and C4—C5 bonds are significantly shorter than C1—C2, C3—C4, C5—C6 and C1—C6 (see notation in Fig. 1), while in (VI) and (VIII), these bonds are normal for aromatic compounds.

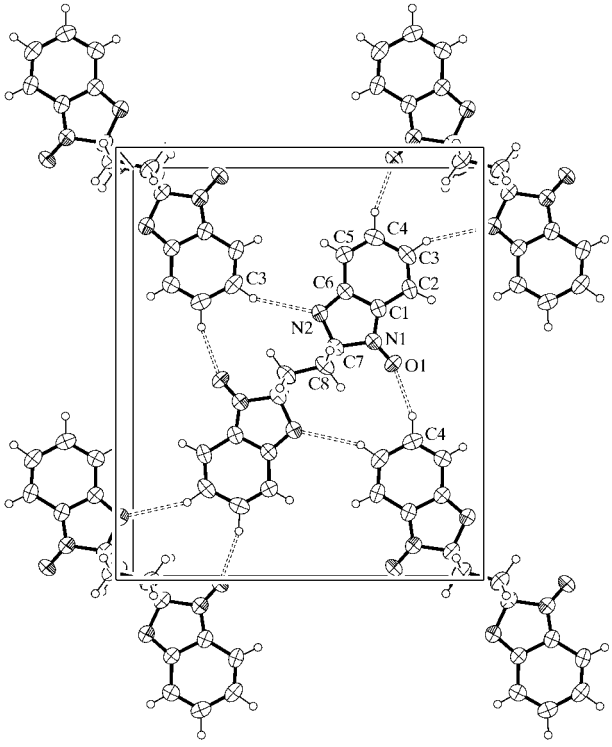


Figure 1
The structure of a layer of (III) viewed down the *a* axis (the *c* axis is pointing upwards) (*ORTEP*-3; Farrugia, 1997).

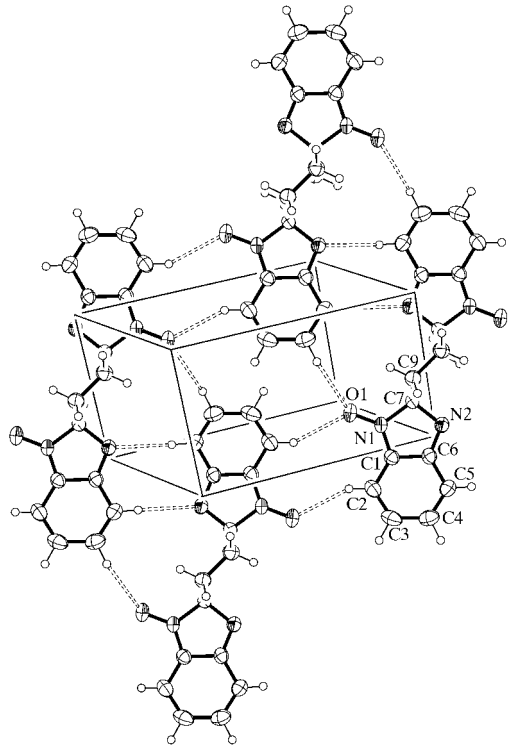


Figure 2
The structure of a layer of (IV) (the *b* axis is pointing upwards and the *a* axis is pointing to the right) (*ORTEP*-3; Farrugia, 1997).

Some bond lengths should be noted; the N1—O1 bond length is significantly shorter in monooxyl (III) [1.152 (3) Å] than in both dioxyl (IV) [1.274 (3) Å] and (VI) [1.28 (2) and 1.34 (3) Å]. The experimental geometry at the nitroxide group in (III) is strongly affected by the disorder. The disordered moiety is an average between benzimidazole [such as (VI)] and benzimidazole oxide [such as (VII)]. The position of atom N1 is an average between two sites. The distance between the

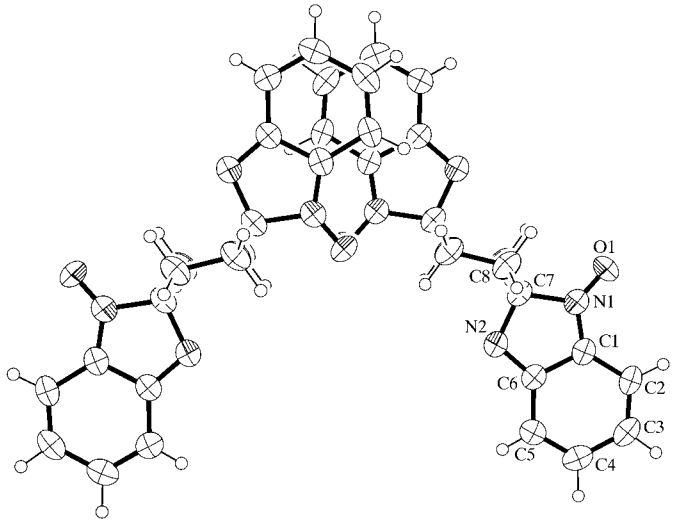


Figure 3
Overlap diagram of (III) (*ORTEP*-3; Farrugia, 1997).

theoretical positions of the two sites is only 0.12 Å and all attempts to refine these positions separately or by fixing them failed to provide more reliable geometry. The N1═C1 and N2═C6 bond lengths are chemically equivalent within each of compounds (VI), (VII) and (VIII), and therefore the bond lengths are equal within each molecule either as localized double bonds in (VII) [1.30 (1) and 1.30 (1) Å], localized Nsp^3—Csp^2 single bonds in (VIII) [1.399 (7) and 1.403 (7) Å] or delocalized double bonds in (VII) [1.34 (3) and 1.33 (3) Å]. These bonds in (IV) are significantly different [N1═C1 1.320 (3) Å and N2═C6 1.307 (3) Å] because only one of the two N atoms is connected to the electronegative atom O1; therefore, the later is compared to the equivalent bond in (VI), and the former should be compared with that in (VII).

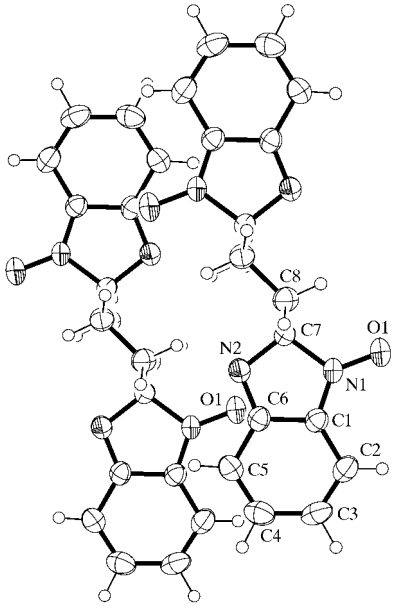


Figure 4
Overlap diagram of (IV) (*ORTEP*-3; Farrugia, 1997).

The N2═C6 bond in (IV) is not affected by the disorder and therefore the bond length of 1.303 (3) Å is similar to that found in (VII). The N1═C1 bond length in (III) is somewhat longer [1.312 (3) Å] as a result of the disorder. The presence of (III) in the reaction bath might suggest that the oxidation takes place in two steps. In the first step, the monooxyl is formed and in the second step, the second N atom is oxidized.

Experimental

Compound (I) was synthesized according to the procedure of Herbert *et al.* (1988) (see Scheme 1). Monooxyl (III) and dioxyl (IV) were prepared by the oxidation of (I) (0.29 g, 1 mmol) by dropwise addition over 20 min of an ether solution of *m*-chloroperbenzoic acid (MPCA; 0.95 g, 5.5 mmol) at 273 K. Overnight stirring produced a yellow solution which was washed with 5% Na_2CO_3, dried (K_2CO_3) and evaporated. After chromatography of the resulting solid over silica gel with $CHCl_3$, two substances were isolated, namely monooxyl (III) [90 mg, 30%; MS: (M^+ + 1) 305] and dioxyl (IV) [118 mg, 37%; MS: (M^+ + 1) 321].

Compound (III)

Crystal data

$C_{18}H_{16}N_4O$
M_r = 304.35
Orthorhombic, *Cmca*
a = 6.774 (2) Å
b = 15.875 (3) Å
c = 13.477 (3) Å
V = 1449.3 (6) Å^3
Z = 4
D_x = 1.395 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 902 reflections
θ = 0.9–27.5°
μ = 0.09 mm^{-1}
T = 150 (2) K
Prism, orange–red
0.50 × 0.35 × 0.30 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
3482 measured reflections
902 independent reflections
658 reflections with $I > 2\sigma(I)$
R_{int} = 0.054
θ_{max} = 27.5°
$h = 0 \rightarrow 8$
$k = -20 \rightarrow 20$
$l = -16 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.119
S = 1.02
902 reflections
77 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0602P)^2 + 0.5909P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.038 (5)

Compound (IV)

Crystal data

$C_{18}H_{16}N_4O_2$
M_r = 320.34
Triclinic, $P\overline{1}$
a = 5.416 (2) Å
b = 7.290 (2) Å
c = 10.426 (3) Å
α = 104.39 (3)°
β = 104.15 (3)°
γ = 98.41 (3)°
V = 377.1 (2) Å^3
Z = 1
D_x = 1.411 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 3.1–12.2°
μ = 0.10 mm^{-1}
T = 293 (2) K
Plate, yellow
0.40 × 0.30 × 0.25 mm

Data collection

Philips PW1100 diffractometer
$\omega/2\theta$ scans
1422 measured reflections
1339 independent reflections
885 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 25.0°
$h = -6 \rightarrow 6$
$k = -8 \rightarrow 8$
$l = 0 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity decay: 7.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.139
S = 1.06
1339 reflections
117 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0567P)^2 + 0.0683P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

The positions of all H atoms were located in a difference Fourier map and they were refined as riding on their attached atoms (C—H = 0.95 and 0.99 Å).

For compound (III), data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; for compound (IV), data collection: *Philips PW*1100/20 *Software* (Philips, 1973); cell refinement: *Philips*

Table 1
Comparison of bond lengths (Å) for (III), (IV), (VI), (VII) and (VIII), and bond angles (°) for (III) and (IV).

Atoms marked with an asterisk (*) are related by either twofold symmetry [in (III)] or by an inversion center [in (IV)].

	(III)	(IV)	(VI)	(VII)	(VIII)
O1—N1	1.152 (3)	1.273 (3)	1.28 (2)/1.34 (3)		
N1—C1	1.312 (3)	1.322 (3)	1.34 (3)	1.30 (1)	1.399 (7)
N1—C7	1.491 (3)	1.505 (3)	1.54 (3)	1.506 (8)	1.491 (7)
N2—C6	1.299 (2)	1.308 (3)	1.33 (3)	1.30 (1)	1.403 (7)
N2—C7	1.455 (3)	1.449 (3)	1.52 (3)	1.48 (1)	1.480 (8)
C1—C2	1.430 (3)	1.420 (4)	1.42 (3)	1.463 (9)	1.383 (7)
C1—C6	1.456 (3)	1.447 (4)	1.41 (3)	1.48 (1)	1.375 (7)
C2—C3	1.349 (3)	1.337 (4)	1.41 (4)	1.36 (1)	1.402 (7)
C3—C4	1.448 (3)	1.438 (4)	1.41 (4)	1.51 (2)	1.389 (9)
C4—C5	1.348 (3)	1.351 (4)	1.40 (4)	1.36 (1)	1.402 (9)
C5—C6	1.446 (3)	1.434 (4)	1.45 (4)	1.43 (2)	1.363 (8)
C7—C8	1.530 (2)	1.522 (4)			
C7—C8*	1.530 (2)	1.530 (4)			
C8—C8*	1.531 (3)	1.518 (3)			
O1—N1—C1	130.0 (2)	129.2 (2)			
O1—N1—C7	123.5 (2)	122.3 (2)			
C1—N1—C7	106.5 (2)	108.5 (2)			
C6—N2—C7	105.7 (2)	106.3 (2)			
N1—C1—C2	129.6 (2)	131.2 (3)			
N1—C1—C6	108.5 (2)	106.4 (2)			
C2—C1—C6	121.8 (2)	122.4 (3)			
C3—C2—C1	117.2 (2)	116.6 (3)			
C2—C3—C4	121.9 (2)	122.5 (3)			
C5—C4—C3	122.8 (2)	122.6 (3)			
C4—C5—C6	118.2 (2)	117.8 (3)			
N2—C6—C5	129.6 (2)	128.3 (2)			
N2—C6—C1	112.4 (2)	113.6 (2)			
C5—C6—C1	118.0 (2)	118.1 (2)			
N2—C7—N1	106.9 (2)	105.1 (2)			
N2—C7—C8	110.8 (1)	112.0 (2)			
N1—C7—C8	109.0 (1)	108.6 (2)			
N2—C7—C8*	110.8 (1)	111.1 (2)			
N1—C7—C8*	108.6 (1)	107.9 (2)			
C8—C7—C8*	110.9 (2)	111.7 (2)			
C8*—C8—C7	111.2 (1)	112.1 (2)			
C8—C8*—C7	111.2 (1)	112.0 (2)			

*PW*1100/20 *Software*; data reduction: *Philips PW*1100/20 *Software*; for both compounds, program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997).

This research was mainly supported by the United States–Israel Binational Science Foundation, and partially supported by the Technion VPR Fund, and by the Fund for the Promotion of Research at the Technion.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1128). Services for accessing these data are described at the back of the journal.

References

Davies, K. E., Domany, G. E., Farhat, M., Herbert, J. A. L., Jefferson, A. M., Guttierez-Martin, M. de los A. & Suschitzky, H. (1984). *J. Chem. Soc. Perkin Trans.* 1, pp. 2465–2475.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Glahn, B. von, Kramer, W., Neidlein, R. & Suschitzky, H. (1999). *J. Heterocycl. Chem.* **36**, 1001–1012.
Hazelton, J. C., Iddon, B., Redhouse, A. D. & Suschitzky, H. (1995). *Tetrahedron*, **51**, 5597–5608.
Herbert, J. A. L., Iddon, B., Robinson, A. G. & Suschitzky, H. (1988). *J. Chem. Soc. Perkin Trans.* 1, pp. 991–997.
Keana, J. F. W., Keana, S. B. & Beetham, D. (1967). *J. Am. Chem. Soc.* **89**, 3055–3056.
Keana, J. F. W., Norton, R. S., Morello, M., van Engen, D. & Clardy, J. (1978). *J. Am. Chem. Soc.* **100**, 934–937.
Keller, H. J., Leichtert, I., Uhlmann, G. & Weiss, J. (1977). *Chem. Ber.* **110**, 1684–1690.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter & R. M. Sweet, pp. 307–326. London: Academic Press.
Philips (1973). *Philips PW*1100/20 *Software*. Natuurkundig Laboratorium, NV Philips Gloeilampenfabrieken, Eindhoven, The Netherlands.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.