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1,2-Dimethylpyrido[1,2-a]benzimidazole-4-carbonitrile

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Abstract

The title compound, $C_{14}H_{11}N_3$, is planar to within 0.030 Å (excluding H atoms). Wide bond angles are observed exocyclic to the five-membered ring [maximum 134.2 (2)°]. Molecules are connected into zigzag chains by hydrogen bonds of the form C_{arom}—H···N≡C, with an H···N distance of 2.47 Å.

Comment

In the course of our preparative studies of fused heterocyclic nitrogen compounds utilizing readily obtainable nitrile intermediates (Elgemeie *et al.*, 1992, 1997; Elgemeie & Fathy, 1995), we have reported new approaches starting from 2-cyanomethylazolyl derivatives (Elgemeie & Elaal, 1986; Elgemeie & Fathy, 1988). We report here a novel synthesis of a benzo[g]-imidazo[1,2-a]pyridine derivative from the readily obtainable 2-cyanomethylbenzimidazole, (1). Compound (1) reacted with the sodium salt of 3-(hydroxymethylene)-2-butanone, (2), in the molar ratio 1:1 to give a product for which several possible isomeric structures [*cf.* (3)–(6) in Scheme] were considered. The spectral data were ambiguous; an X-ray structure determination indicated form (6) for the product in the solid state. The formation of (6) from the reaction of (1) and (2)

is assumed to proceed *via* initial addition of the active methylene-C atom of form (1b) to the formyl group of (2) to give the favoured kinetically and thermodynamically controlled product (6).
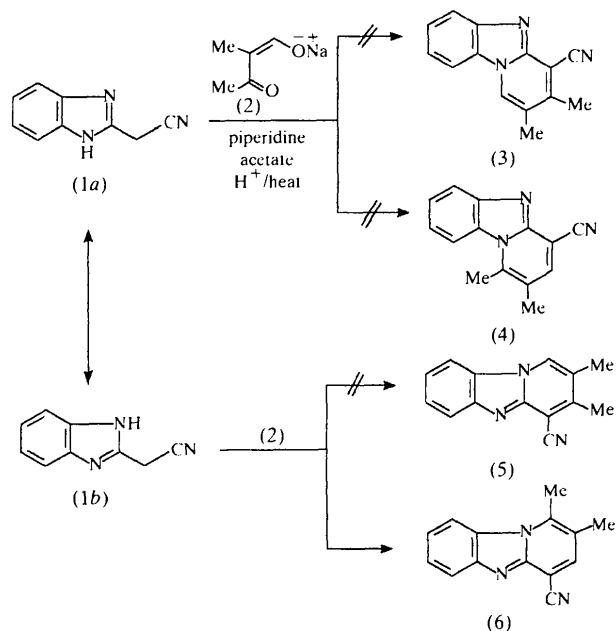
The molecule of (6) (Fig. 1) is planar, with an r.m.s. deviation of all non-H atoms from the least-squares plane of 0.030 Å. [The r.m.s. deviation is reduced to 0.014 Å on excluding atoms C14 and N3, which lie 0.109 (3) and 0.056 (3) Å, respectively, outside the improved plane.] The bond lengths and angles are closely similar to those of a benzimidazo[1,2-a]pyridine derivative with a further annelated seven-membered ring recently determined by us (Elgemeie *et al.*, 1998); in particular, wide angles are observed exocyclic to the five-membered ring [*e.g.* C1—N1—C9 132.41 (18) and C8—C9—N1 134.2 (2)°].
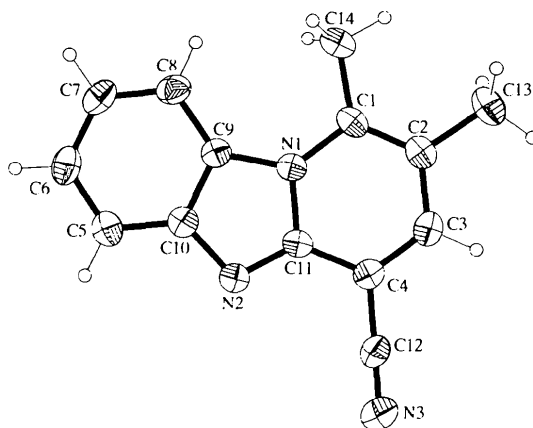

Fig. 1. The molecule of the title compound in the crystal. Ellipsoids are shown at 50% probability levels and H atoms are shown as circles of arbitrary radii.

A search of the Cambridge Structural Database (Allen & Kennard, 1993) revealed one other structure with the same tricyclic system, but substituted at C8 and C6 (our numbering) with a nitro and a trifluoromethyl group, respectively (Chidester *et al.*, 1986). Steric strain associated with the nitro substituent led to even wider exocyclic angles at N1 and C9 (our numbering), of 134.3 (3) and 138.2 (3)°, respectively; additionally, the ring system was slightly bowed, which is not the case in the current structure.

The crystal packing of (6) involves hydrogen bonds of the form C3—H3···N3, successive molecules related by screw axes being connected into zigzag chains parallel to the *y* axis. Such hydrogen bonds have been the subject of recent controversy (Steiner & Desiraju, 1998, and references therein).

Experimental

A solution of 2-cyanobenzimidazole [(1); 0.01 mol, 1.57 g], the sodium salt of 3-(hydroxymethylene)-2-butanone [(2); 0.01 mol, 1.22 g] and piperidine acetate (1 ml) in water (5 ml) and ethanol (50 ml) was refluxed for 15 min. Acetic acid (1.5 ml) was added to the hot solution. The precipitated solid was collected by filtration and recrystallized from ethanol in 50% yield (m.p. 525–527 K).

Crystal data

$C_{14}H_{11}N_3$	Mo $K\alpha$ radiation
$M_r = 221.26$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 46
$P2_1/n$	reflections
$a = 7.469\,(2)$ Å	$\theta = 10.0–11.5°$
$b = 8.106\,(2)$ Å	$\mu = 0.082$ mm^{-1}
$c = 18.238\,(4)$ Å	$T = 143\,(2)$ K
$\beta = 93.78\,(3)°$	Lath
$V = 1101.8\,(5)$ Å^3	$0.80 \times 0.25 \times 0.10$ mm
$Z = 4$	Pale yellow
$D_x = 1.334$ Mg m^{-3}	
D_m not measured	

Data collection

Stoe Stadi-4 diffractometer	$\theta_{max} = 25.03°$
ω/θ scans	$h = 0 \rightarrow 8$
Absorption correction: none	$k = -9 \rightarrow 3$
2722 measured reflections	$l = -21 \rightarrow 21$
1935 independent reflections	3 standard reflections
1448 reflections with	frequency: 60 min
$I > 2\sigma(I)$	intensity decay: none
$R_{int} = 0.028$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.049$	$\Delta\rho_{max} = 0.16$ e Å^{-3}
$wR(F^2) = 0.132$	$\Delta\rho_{min} = -0.18$ e Å^{-3}
$S = 1.043$	Extinction correction: none

1935 reflections
156 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0631P)^2 + 0.2377P]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1—C1	1.391 (3)	N2—C11	1.320 (3)		
N1—C11	1.401 (3)	N2—C10	1.386 (3)		
N1—C9	1.403 (3)	C9—C10	1.403 (3)		
C1—N1—C11	122.50 (17)	N2—C10—C5	127.1 (2)		
C1—N1—C9	132.41 (18)	N2—C10—C9	111.85 (18)		
C11—N1—C9	105.08 (16)	C5—C10—C9	121.04 (19)		
C11—N2—C10	103.91 (17)	N2—C11—N1	114.13 (17)		
C8—C9—N1	134.2 (2)	N2—C11—C4	128.46 (19)		
C8—C9—C10	120.8 (2)	N1—C11—C4	117.41 (18)		
N1—C9—C10	105.03 (17)				

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···N3^i	0.95	2.47	3.405 (3)	169.1

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

Methyl-H atoms were treated as rigid groups and allowed to rotate but not tip; the starting positions were from a difference synthesis. Others H atoms were refined as riding, starting from calculated positions.

Data collection: *DIF4* (Stoe & Cie, 1992*a*). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*97.

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Two Organic Diselenides: Dimesityl Diselenide and Bis(2,4,6-triisopropylphenyl) Diselenide

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Abstract

The organic diselenides dimesityl diselenide [$C_{18}H_{22}Se_2$, (I)] and bis(2,4,6-triisopropylphenyl) diselenide [$C_{30}H_{46}Se_2$, (II)] display normal diselenide geometries: Se—Se bond lengths are 2.3341 (6) in (I) and 2.3389 (6) Å in (II), and the absolute C—Se—Se—C torsion angles are 83.96 (12) in (I) and 73.38 (16)° in (II).

Comment

We are interested in the structural chemistry of organic disulfides and diselenides. The use of bulky organic groups might be expected to change the C—E—E—C (E = chalcogenide) torsion angle from the usual region of *circa* 90° as in 2,2′-dipyridyl diselenide [84.3 (2)°; Kienitz *et al.*, 1996] to larger (*trans*) values; this was indeed achieved for bis[tris(trimethylsilyl)methyl]-disulfane, which displays crystallographic inversion of symmetry and thus a C—S—S—C torsion angle of 180° (Ostrowski *et al.*, 1993). Here we present the structures of two diselenides: dimesityl diselenide, (I), and bis(2,4,6-triisopropylphenyl) diselenide, (II).
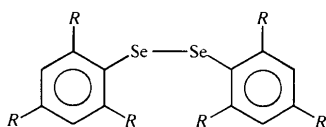
(I) R = Me
(II) R = ^{i}Pr

Both compounds (Figs 1 and 2) crystallize without imposed symmetry, although (II) displays non-crystallographic twofold symmetry to a good approximation. The absolute torsion angles about the Se—Se bonds lie in the normal region [(I) 83.96 (12); (II) 73.38 (16)°] and the organic groups are thus not bulky enough to promote a *trans* geometry. The bond lengths and angles involving the Se atoms are normal (Tables 1 and 2).
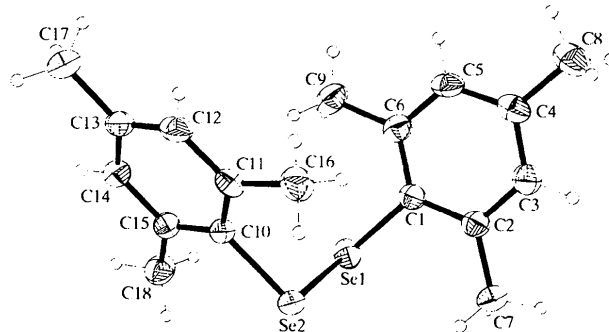

Fig. 1. Structure of dimesityl diselenide in the crystal. Ellipsoids represent 50% probability levels. H-atom radii are arbitrary.
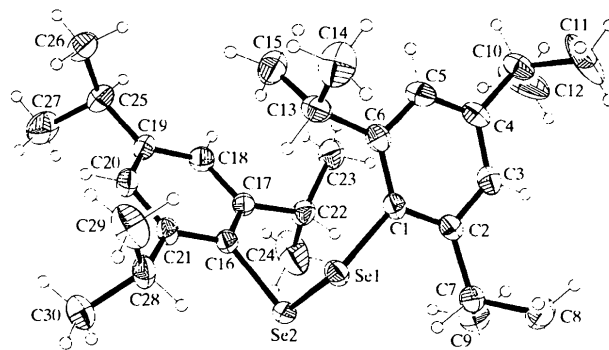

Fig. 2. Structure of bis(2,4,6-triisopropylphenyl) diselenide in the crystal. Ellipsoids represent 40% probability levels. H-atom radii are arbitrary.

The diselenide (II) is also known to form a 2:1 adduct with molecular iodine (du Mont *et al.*, 1990), involving weak Se···I contacts of 3.483 (1) Å; in this adduct, which has Se—Se 2.353 (2) Å and C—Se—Se—C 73.0°, the dimensions of (II) are closely similar to those reported here.

A search of the Cambridge Structural Database (October 1997 version; Allen & Kennard, 1993) revealed 16 diaryl diselenides, with Se—Se bond lengths ranging from 2.287 to 2.380 Å (mean 2.335 Å). Absolute torsion angles C—Se—Se—C lie in the range 70–100°, with the extremely bulky di(2,6-dimesitylphenyl) diselenide providing the exception at 128.3° (Ellison *et al.*, 1995).

The interplanar angles between the aromatic rings are 30.39 (11) for (I) and 39.10 (13)° for (II). In (II) the