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Acta Cryst. (1995). C**51**, 1590–1593

2-(2-Methoxyphenyl)pyridine 1-Oxide and its 3-Methyl Derivative

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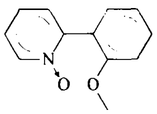
(*Received* 13 *December* 1994; *accepted* 13 *February* 1995)

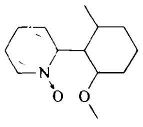
Abstract

The crystal structures of 2-(2-methoxyphenyl)pyridine 1-oxide, $C_{12}H_{11}NO_2$ (1), and 2-(2-methoxyphenyl)-3-methylpyridine 1-oxide, $C_{13}H_{13}NO_2$ (2), have been determined. The dihedral angle between the least-squares planes of the aromatic rings is 66.6 (1) for (1) and 74.70 (6)° for (2). Weak C—H···O hydrogen bonds govern the crystal packing.

Comment

Orellanine (3,3′,4,4′-tetrahydroxy-2,2′-bipyridine 1,1′-dioxide) was shown to lose both *N*-oxide groups at a surprisingly low temperature (Antkowiak & Gessner, 1979) compared with other bipyridine *N,N*′-dioxides (Wenkert & Woodward, 1983). As part of our studies on the mechanism of this deoxygenation reaction, we reported the structure of a model compound, 2-(2-hydroxyphenyl)pyridine 1-oxide (Kubicki, Borowiak, Antkowiak & Antkowiak, 1990), which has all the structural features necessary for the proposed mechanism of this deoxygenation process (Antkowiak & Gessner, 1984). In this structure, we found a strong intramolecular O—H···O—N hydrogen bond and the dihedral angle between the two aromatic rings was 38.2 (1)°. Since decrease of the twist angle is supposed to play a crucial role in the transition state of the deoxygenation process, we decided to check the influence of intramolecular hydrogen bonding on the molecular conformation by studying related compounds having no possibility of forming such a bond. In this paper, we present the structure determinations of two compounds, 2-(2-methoxyphenyl)pyridine 1-oxide, (1), and its 3-methyl derivative, (2).


(1)


(2)

The twist angle between the two almost perfectly planar aromatic rings is 66.6 (1) in (1) and 74.70 (6)° in (2). This seems to prove the role of intramolecular hydrogen bonding in stabilizing the conformation, reflected in a smaller dihedral angle, for this class of compounds. Comparing the conformations of (1) and (2), it was found that the rings were twisted in opposite directions; the absolute values of the torsion angles N1—C2—C1′—C2′ are 69.2 (3) and 106.8 (2)° in compounds (1) and (2), respectively. Thus, if one imagines a plane perpendicular to the pyridine ring and containing the central C2—C1′ bond, in (1) both O atoms will be on the same side of this plane, while in (2) they will lie on opposite sides. In the case of (1), even despite the lack of steric hindrance at positions 3 and 6′, a relatively short non-bonded O1···O2′ distance of 3.032 (3) Å is found. A similar situation is observed in 2,2′-bipyridine 1,1′-dioxide, where the absolute value of the torsion angle N1—C2—C2′—N1′ is 70.9 (2)° and the O1···O1′ distance is 3.040 (2) Å (Dutkiewicz, 1995). It is also noteworthy that the crystal structure of (2) contains both conformational enantiomers, while in (1) there are only homochiral molecules. The disposition of the methoxy group with respect to the phenyl ring is also slightly different in both compounds. In (1), the methoxy group is almost coplanar with the phenyl ring, while in (2) it is significantly tilted out of the plane; the torsion angles C3′—C2′—O2′—C2′1 are −3.3 (5) and −15.9 (3)° for compounds (1) and (2), respectively. This is accompanied by a statistically significant difference in the values of the C—O—C bond angles: 118.1 (3) for (1) and 116.5 (2)° for (2). The introduction of the methyl substituent in the 3-position changes the bond-angle pattern in the pyridine ring.

The differences between (2) and (1) are in agreement with the observations of Domenicano & Murray-Rust (1979) on mono- and disubstituted benzene derivatives. The N—O bond lengths of 1.307 (4) for (1) and 1.309 (2) Å for (2) are close to the typical values for N—O groups not involved in hydrogen bonding (Eichhorn, 1987).

In both structures, the molecular packing is determined by C—H···O hydrogen bonds. Compound (1) has a two-dimensional structure with chains of molecules along the [100] and [010] directions, interconnected with the rings of four other molecules. In (2), there are chains along the [010] direction and centrosymmetric dimers connect the chains into a three-dimensional structure.

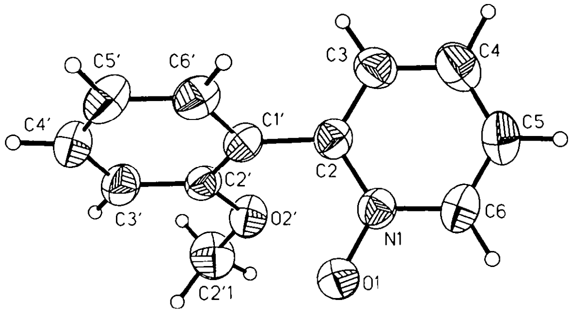


Fig. 1. Displacement ellipsoid representation of (1) with the labelling scheme. The ellipsoids are drawn at the 50% probability level, with H atoms drawn as spheres of arbitrary radii.

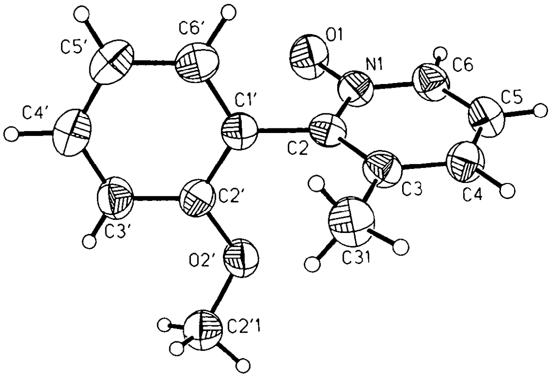


Fig. 2. Displacement ellipsoid representation of (2) with the labelling scheme. The ellipsoids are drawn at the 50% probability level, with H atoms drawn as spheres of arbitrary radii.

Experimental

The syntheses of the title compounds have been described elsewhere [Antkowiak & Gessner (1984) for (1), Antkowiak *et al.* (1994) for (2)]. Crystals of (1) were grown from toluene by slow evaporation, while those of (2) were grown by vapour diffusion from a dioxan–*n*-heptane system.

Compound (1)

Crystal data

$C_{12}H_{11}NO_2$
$M_r = 201.22$
Orthorhombic
$P2_12_12_1$
$a = 7.032\,(1)$ Å
$b = 7.443\,(1)$ Å
$c = 19.574\,(4)$ Å
$V = 1024.5\,(3)$ Å^3
$Z = 4$
$D_x = 1.305$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 29 reflections
$\theta = 9.06$–$25.99°$
$\mu = 0.729$ mm^{-1}
$T = 293\,(2)$ K
Prism
0.35 × 0.3 × 0.2 mm
Colourless

Data collection

Kuma KM-4 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: none
960 measured reflections
960 independent reflections
931 observed reflections [$I > 2\sigma(I)$]

$\theta_{\max} = 69.99°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 23$
3 standard reflections monitored every 100 reflections
intensity decay: 1.0%

Refinement

Refinement on F^2
$R(F) = 0.0398$
$wR(F^2) = 0.1164$
$S = 1.098$
960 reflections
180 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0825P)^2 + 0.1931P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.133$ e Å^{-3}
$\Delta\rho_{\min} = -0.204$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (1)

$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
N1	1.0982 (4)	0.1325 (3)	0.31704 (11)	0.0439 (6)
O1	0.9167 (3)	0.1522 (3)	0.30461 (10)	0.0524 (6)
C2	1.1606 (4)	−0.0099 (4)	0.35479 (13)	0.0429 (7)
C3	1.3552 (5)	−0.0325 (5)	0.3636 (2)	0.0537 (8)
C4	1.4839 (5)	0.0881 (6)	0.3369 (2)	0.0645 (9)
C5	1.4163 (5)	0.2327 (5)	0.3010 (2)	0.0607 (9)
C6	1.2241 (5)	0.2540 (4)	0.29109 (15)	0.0548 (8)
C1′	1.0179 (4)	−0.1367 (4)	0.38241 (12)	0.0421 (7)
C2′	0.8935 (4)	−0.0864 (3)	0.43394 (12)	0.0406 (6)
O2′	0.9103 (3)	0.0861 (2)	0.45742 (9)	0.0504 (6)
C2′1	0.7807 (7)	0.1451 (6)	0.5082 (2)	0.0669 (10)
C3′	0.7616 (5)	−0.2084 (4)	0.46000 (15)	0.0525 (8)
C4′	0.7583 (6)	−0.3818 (4)	0.4340 (2)	0.0590 (8)
C5′	0.8805 (6)	−0.4359 (4)	0.3837 (2)	0.0611 (9)
C6′	1.0131 (5)	−0.3120 (4)	0.35869 (15)	0.0519 (8)

Table 2. *Selected geometric parameters* (Å, °) *for* (1)

N1—O1	1.307 (4)	C1′—C6′	1.386 (4)
N1—C6	1.363 (4)	C1′—C2′	1.387 (4)
N1—C2	1.365 (4)	C2′—O2′	1.369 (3)
C2—C3	1.390 (4)	C2′—C3′	1.394 (5)
C2—C1′	1.480 (4)	O2′—C2′1	1.417 (4)
C3—C4	1.378 (5)	C3′—C4′	1.388 (4)
C4—C5	1.370 (5)	C4′—C5′	1.368 (5)
C5—C6	1.375 (5)	C5′—C6′	1.400 (5)
O1—N1—C6	119.4 (3)	C6′—C1′—C2	119.6 (3)
O1—N1—C2	120.1 (2)	C2′—C1′—C2	121.4 (2)
C6—N1—C2	120.6 (3)	O2′—C2′—C1′	116.3 (3)
N1—C2—C3	118.5 (3)	O2′—C2′—C3′	123.1 (3)
N1—C2—C1′	118.4 (3)	C1′—C2′—C3′	120.6 (2)
C3—C2—C1′	123.1 (3)	C2′—O2′—C2′1	118.1 (3)
C4—C3—C2	121.4 (3)	C4′—C3′—C2′	118.9 (3)
C5—C4—C3	118.6 (3)	C5′—C4′—C3′	121.8 (3)
C4—C5—C6	120.3 (3)	C4′—C5′—C6′	118.4 (3)
N1—C6—C5	120.6 (3)	C1′—C6′—C5′	121.3 (3)
C6′—C1′—C2′	118.9 (3)		

Table 3. *Hydrogen-bonding geometry* (Å, °) *for* (1)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···O1^{i}	1.09 (4)	2.22 (4)	3.145 (4)	142 (3)
C5′—H5′···O1^{ii}	0.98 (3)	2.47 (4)	3.444 (4)	174 (3)

Symmetry codes: (i) $1 + x, y, z$; (ii) $x, y - 1, z$.

Compound (2)

Crystal data

$C_{13}H_{13}NO_2$
$M_r = 215.24$
Monoclinic
$P2_1/c$
$a = 10.677$ (2) Å
$b = 7.750$ (1) Å
$c = 13.961$ (3) Å
$\beta = 104.77$ (1)°
$V = 1117.1$ (3) Å^3
$Z = 4$
$D_x = 1.280$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 15 reflections
$\theta = 13.19$–45.81°
$\mu = 0.701$ mm^{-1}
$T = 293$ (2) K
Prism
0.28 × 0.23 × 0.18 mm
Colourless

Data collection

Syntex $P2_1$ diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1586 measured reflections
1497 independent reflections
1284 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.0125$

$\theta_{\rm max} = 57.28°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 8$
$l = -15 \rightarrow 14$
2 standard reflections monitored every 100 reflections intensity decay: 2%

Refinement

Refinement on F^2
$R(F) = 0.0371$
$wR(F^2) = 0.1047$
$S = 1.176$
1497 reflections
198 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0534P)^2 + 0.2859P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 0.155$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.160$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0251 (16)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$
N1	0.86813 (14)	0.3236 (2)	0.88232 (10)	0.0394 (4)
O1	0.88111 (14)	0.3168 (2)	0.97800 (9)	0.0553 (5)
C2	0.8010 (2)	0.1971 (2)	0.82183 (12)	0.0360 (5)
C3	0.7873 (2)	0.2064 (2)	0.71996 (13)	0.0394 (5)
C31	0.7157 (2)	0.0677 (3)	0.6528 (2)	0.0547 (6)
C4	0.8416 (2)	0.3447 (3)	0.68159 (14)	0.0440 (5)
C5	0.9092 (2)	0.4690 (3)	0.74442 (14)	0.0465 (5)
C6	0.9226 (2)	0.4565 (3)	0.84435 (15)	0.0444 (5)
C1′	0.7507 (2)	0.0526 (2)	0.87182 (12)	0.0379 (5)
C2′	0.6184 (2)	0.0391 (2)	0.86649 (13)	0.0401 (5)
O2′	0.54097 (12)	0.1655 (2)	0.81422 (10)	0.0502 (4)
C2′1	0.4051 (2)	0.1308 (3)	0.7858 (2)	0.0548 (6)
C3′	0.5735 (2)	−0.0971 (3)	0.91259 (14)	0.0488 (5)
C4′	0.6579 (2)	−0.2202 (3)	0.9629 (2)	0.0543 (6)
C5′	0.7887 (2)	−0.2099 (3)	0.96852 (15)	0.0534 (6)
C6′	0.8340 (2)	−0.0734 (3)	0.92299 (14)	0.0471 (5)

Table 5. *Selected geometric parameters* (Å, °) *for* (2)

N1—O1	1.309 (2)	C1′—C6′	1.390 (3)
N1—C6	1.356 (2)	C1′—C2′	1.399 (3)
N1—C2	1.371 (2)	C2′—O2′	1.367 (2)
C2—C3	1.394 (2)	C2′—C3′	1.385 (3)
C2—C1′	1.490 (3)	O2′—C2′1	1.429 (2)
C3—C4	1.390 (3)	C3′—C4′	1.375 (3)
C3—C31	1.501 (3)	C4′—C5′	1.381 (3)
C4—C5	1.376 (3)	C5′—C6′	1.384 (3)
C5—C6	1.369 (3)		
O1—N1—C6	119.05 (15)	C6′—C1′—C2′	118.7 (2)
O1—N1—C2	120.17 (14)	C6′—C1′—C2	120.6 (2)
C6—N1—C2	120.8 (2)	C2′—C1′—C2	120.7 (2)
N1—C2—C3	119.6 (2)	O2′—C2′—C3′	124.1 (2)
N1—C2—C1′	116.31 (14)	O2′—C2′—C1′	116.1 (2)
C3—C2—C1′	124.1 (2)	C3′—C2′—C1′	119.8 (2)
C4—C3—C2	119.2 (2)	C2′—O2′—C2′1	116.5 (2)
C4—C3—C31	120.5 (2)	C4′—C3′—C2′	120.5 (2)
C2—C3—C31	120.3 (2)	C3′—C4′—C5′	120.7 (2)
C5—C4—C3	119.8 (2)	C4′—C5′—C6′	119.0 (2)
C6—C5—C4	120.1 (2)	C5′—C6′—C1′	121.3 (2)
N1—C6—C5	120.5 (2)		

Table 6. *Hydrogen-bonding geometry* (Å, °) *for* (2)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···O1^{i}	0.96 (2)	2.44 (2)	3.230 (2)	140 (2)
C6—H6···O1^{ii}	0.92 (2)	2.41 (2)	3.314 (2)	168 (2)

Symmetry codes: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $2 - x, 1 - y, 2 - z$.

The background and integrated intensity for each reflection were obtained by the profile-analysis method of Lehmann & Larsen (1974).

Data collection: *Kuma KM*-4 *Software* (Kuma, 1992) for (1); $P2_1$ software for (2). Cell refinement: *Kuma KM*-4 *Software* for (1); $P2_1$ software for (2). Data reduction: *Kuma KM*-4 *Software* for (1); *PRADIR* (Jaskólski, 1990) for (2). For both compounds, program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *Stereochemical Workstation* (Siemens, 1989); software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1113). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 1593–1594

Dispiro(fluorene-9,4′-[1,3]dithiolane-5′,9″-fluorene)

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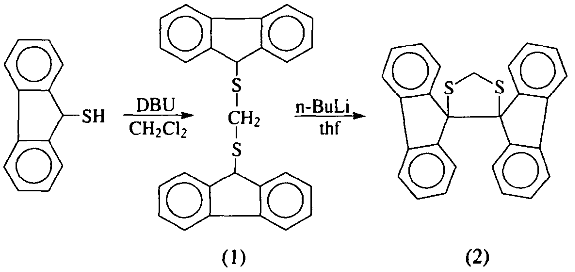
(*Received* 4 *November* 1994; *accepted* 3 *February* 1995)

Abstract

The crystal structure of dispiro(fluorene-9,4′-[1,3]dithiolane-5′,9″-fluorene), $C_{27}H_{18}S_2$, is reported. The C4—C5 bond connecting the two fluorenyl groups is 1.580 (4) Å, which is slightly longer than the C—C bond lengths [1.36–1.49 Å] in other 1,3-dithiolanes.

Comment

Only a few X-ray crystal structure determinations of compounds containing the 1,3-dithiolane moiety have been carried out. The structure of the title compound, (2), with atomic numbering scheme is illustrated in Fig. 1.



(1) (2)

The S1—C2, S1—C5, S3—C2 and S3—C4 bond lengths, and the S1—C2—S3, C2—S3—C4 and C5—S1—C2 bond angles are similar to those reported for other dithiolanes (Lynch, Lee, Martin & Davis, 1992; Mentzafors, Polisiou & Georgiadis, 1988; Noordik, Smits, Sicherer-Roetman, Jansen & De Groot, 1985; Dubourg *et al.*, 1984; Barrière, Chiaroni, Cléophax, Géro & Riche, 1984). The C4—C5 bond, however, is slightly longer compared with those of the related 1,3-dithiolanes [1.580 (4) *versus* 1.36–1.49 Å], causing a decrease in the corresponding S3—C4—C5 and S1—C5—C4 bond angles [106.8 (2) and 105.5 (3) compared with 107.5–113.6°]. This may be due to steric effects caused by the large fluorenyl groups attached to C4 and C5. The fluorenyl groups show minimal distortion from ideal geometry, with the C—C distances very close to the expected values for aromatic rings.

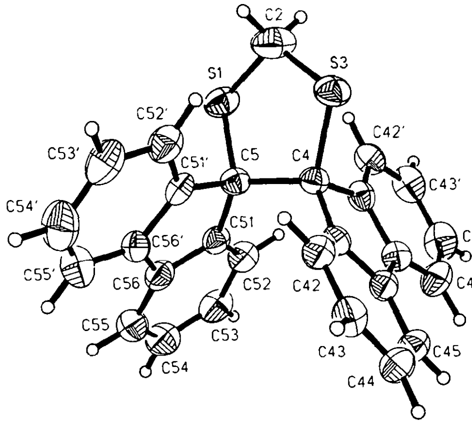


Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

Bis(fluorenyl-9-thio)methane, (1) (see the scheme above), was prepared by reacting fluorene-9-thiol with 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) in dichloromethane. Addition of *n*-butyllithium (2.5 M in hexanes) to (1) in thf gave the title compound (2). Colourless crystals were obtained by crystallization from toluene. The synthesis of (2) from thiofluorenone and diazomethane has been published (Schoenberg, Koenig & Singer, 1967). The NMR spectra of (1) and (2), along with other sulfur-containing 9-substituted fluorenes, are discussed elsewhere (Leino, Luttikhedde, Näsman & Mattinen, 1995).

Crystal data

$C_{27}H_{18}S_2$
$M_r = 406.56$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å