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**Structures of 1,4-Bis(3,5-dichloro-2-pyridyloxy)benzene (1), C₁₆H₈Cl₄N₂O₂,
1,4-Bis(5-chloro-2-pyridyloxy)benzene (2), C₁₆H₁₀Cl₂N₂O₂ and
1,4-Bis(3-chloro-2-pyridyloxy)benzene (3), C₁₆H₁₀Cl₂N₂O₂**

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Abstract. (1): $M_r = 402.1$, triclinic, $P\bar{1}$, $a = 3.964$ (1), $b = 7.344$ (2), $c = 14.546$ (2) Å, $\alpha = 87.28$ (2), $\beta = 84.97$ (1), $\gamma = 73.20$ (2)°, $V = 403.7$ (2) Å³, $Z = 1$, $D_x = 1.654$ Mg m⁻³, $\text{Cu } K\alpha$, $\lambda = 1.5418$ Å, $\mu = 6.75$ mm⁻¹, $F(000) = 202$, room temperature, $R = 0.116$ for 1257 observations. (2): $M_r = 333.2$, monoclinic, $P2_1/c$, $a = 3.987$ (2), $b = 5.587$ (1), $c = 31.910$ (2) Å, $\beta = 91.20$ (2)°, $V = 710.6$ (4) Å³, $Z = 2$, $D_x = 1.557$ Mg m⁻³, $\mu(\text{Cu } K\alpha) = 4.18$ mm⁻¹, $F(000) = 340$, room temperature, $R = 0.052$ for 1013 observations. (3): $M_r = 333.2$, monoclinic, $P2_1/c$, $a = 7.367$ (4), $b = 9.611$ (1), $c = 21.035$ (4) Å, $\beta = 99.61$ (2)°, $V = 1468.5$ (1.3) Å³, $Z = 4$, $D_x = 1.507$ Mg m⁻³, $\mu(\text{Cu } K\alpha) = 4.05$ mm⁻¹, $F(000) = 680$, room temperature, $R = 0.078$ for 1919 observations. (1) and (2) induce mouse hepatic monooxygenase activity and are found to have very similar conformations, with the pyridyl rings *anti* (with respect to the phenyl ring), and phenyl–ether dihedral angles of 52.7 (3) and 59.1 (2)°, respectively. In (3), which lacks biological activity, the pyridyl rings are *syn* and the phenyl–ether dihedral angles average 84.0°. In all three compounds the pyridyl rings are nearly coplanar with the C–O–C planes of the ethers and the pyridyl N atoms are proximal to the phenyl ring.

Introduction. The title compounds are members of a series of bis(pyridyloxy)benzene analogs tested for their

ability to induce certain monooxygenase enzymes in the liver and proximal intestines of mice (Poland, Mak, Glover, Boatman, Frank & Kende, 1980; Poland, 1982). The majority of these analogs involve variations in the placement and nature of the substituents of the lateral (pyridyl) rings. (1) is the most active compound tested, (2) has significant activity and (3) is inactive. To gain an understanding of the conformational properties of these substances we have performed structure determinations of the title compounds.

Experimental. Experimental parameters are given in Table 1. All data collection: Enraf–Nonius CAD-4 diffractometer; $2\theta_{\text{max}} = 154^\circ$; crystals of (1) and (2) grown from chloroform/toluene in sealed dish with a reservoir of ethyl acetate; crystals of (3) grown similarly from chloroform with 2-propanol reservoir; all crystals long, thin needles from which data crystals were cut; Lorentz and polarization corrections applied; empirical (ρ curve) absorption corrections applied for (2) and (3); structures solved using *MULTAN74* (Main, Woolfson, Lessinger, Germain & Declercq, 1974); H atoms located by difference Fourier synthesis; all atoms refined by block-diagonal least squares, using modified counting-statistics weighting scheme; anisotropic temperature factors used for non-H atoms and isotropic temperature factors for H atoms; two low-angle reflections removed from refinement of (2) for

secondary extinction; atomic scattering factors taken from Cromer & Waber (1965) for non-H atoms and from Stewart, Davidson & Simpson (1965) for H atoms; all calculations performed on a PDP 11/35

computer with programs developed in this laboratory (Rao, Haromy, McAlister & Merritt, unpublished).

Discussion. Positional and thermal parameters are listed in Table 2,* bond lengths and bond angles in Table 3, and torsion angles and dihedral angles in Table 4. Fig. 1 shows the molecules and the atom-numbering schemes. Crystal-packing diagrams are shown in Fig. 2.

Table 1. *Experimental parameters*

	(1)	(2)	(3)
Crystal size (mm)	0.5 × 0.1 × 0.02	0.35 × 0.07 × 0.02	0.6 × 0.06 × 0.03
Standard reflections (monitored every 2 h)	023, 007	013, 102, 0, 0, 10	1, 2, 11, 3, 0, 12, 139
Decay correction (%)	2	10	2
Maximum absorption correction (%)	—	35	19
Unique intensities	1689	1483	3092
Reflections used F > 3σ(F)	1257	1013	1919
R	0.116	0.052	0.078
wR	0.133	0.068	0.114
w = [σ ² (F) + (p F) ²] ⁻¹	p = 0.04	p = 0.03	p = 0.03
Residual densities (Δρ) (e Å ⁻³)	-0.34 ≤ Δρ ≤ 0.46	-0.28 ≤ Δρ ≤ 0.37	-0.25 ≤ Δρ ≤ 0.38
(d/σ) _{max} for non-H atoms	0.02	0.09	0.09
S, the goodness of fit	2.13	1.45	2.27

Table 2. *Fractional positional parameters (×10⁴) and B_{eq} values for non-hydrogen atoms*

$$B_{eq} = \frac{4}{3} \sum_i \sum_j B_{ij} a_i \cdot a_j$$

Compound (1)	x	y	z	B _{eq} (Å ²)
Cl(3)	16211 (5)	-6312 (2)	-2243 (1)	3.76 (5)
Cl(5)	9263 (5)	-2304 (2)	-5047 (1)	3.84 (5)
C(3)	13353 (17)	-4284 (8)	-2681 (4)	2.70 (15)
C(4)	12664 (17)	-4159 (8)	-3592 (4)	2.87 (17)
C(5)	10266 (17)	-2527 (8)	-3906 (4)	2.81 (16)
C(6)	8636 (18)	-1108 (9)	-3297 (4)	3.22 (17)
N(1)	9336 (16)	-1236 (7)	-2418 (4)	3.46 (14)
C(2)	11656 (17)	-2759 (8)	-2117 (4)	2.76 (16)
O(1)	12391 (15)	-2947 (6)	-1220 (3)	4.04 (14)
C(7)	11125 (18)	-1400 (9)	-630 (4)	3.20 (16)
C(8)	9382 (19)	-1755 (9)	186 (4)	3.32 (18)
C(9)	8216 (19)	-322 (10)	835 (4)	3.41 (17)
Compound (2)				
Cl(5)	4158 (2)	6017 (2)	2123 (1)	3.95 (2)
C(5)	2598 (8)	4062 (6)	1742 (1)	3.06 (6)
C(4)	838 (8)	2047 (6)	1860 (1)	3.33 (7)
C(3)	-315 (9)	526 (6)	1554 (1)	3.45 (7)
C(2)	341 (8)	1094 (6)	1139 (1)	3.11 (6)
N(1)	2016 (8)	3002 (5)	1021 (1)	3.38 (6)
C(6)	3129 (9)	4493 (6)	1324 (1)	3.29 (7)
O(1)	-834 (7)	-510 (4)	852 (1)	4.10 (6)
C(7)	-356 (9)	-155 (6)	422 (1)	3.30 (7)
C(8)	1309 (9)	-1962 (6)	216 (1)	3.58 (7)
C(9)	1640 (10)	-1800 (6)	-215 (1)	3.69 (7)
Compound (3)				
Cl(3)	3355 (3)	-5800 (1)	11103 (1)	5.91 (5)
C(3)	3307 (9)	-4148 (6)	11410 (2)	3.88 (14)
C(4)	3492 (10)	-3933 (6)	12061 (3)	4.74 (16)
C(5)	3463 (10)	-2566 (7)	12287 (3)	5.07 (18)
C(6)	3237 (10)	-1509 (6)	11846 (3)	4.86 (17)
N(1)	3014 (7)	-1717 (5)	11207 (2)	4.29 (13)
C(2)	3039 (8)	-3006 (5)	11003 (2)	3.59 (13)
O(1)	2818 (7)	-3272 (4)	10355 (2)	5.24 (13)
Cl(3')	1339 (3)	2420 (1)	7282 (1)	5.22 (4)
C(3')	1534 (8)	3043 (5)	8051 (2)	3.50 (13)
C(4')	1434 (10)	4441 (5)	8167 (3)	4.48 (15)
C(5')	1629 (11)	4910 (6)	8795 (3)	5.16 (20)
C(6')	1961 (11)	3966 (6)	9276 (3)	5.22 (18)
N(1')	2046 (8)	2586 (5)	9180 (2)	4.62 (14)
C(2')	1843 (8)	2147 (5)	8585 (2)	3.79 (14)
O(1')	1917 (7)	756 (4)	8458 (2)	5.28 (13)
C(7)	2597 (9)	-2152 (5)	9921 (2)	3.85 (15)
C(8)	889 (10)	-1646 (7)	9701 (3)	4.94 (17)
C(9)	646 (10)	-634 (6)	9223 (3)	4.81 (17)
C(10)	2153 (10)	-182 (5)	8970 (2)	4.25 (16)
C(11)	3859 (10)	-685 (6)	9187 (3)	4.80 (20)
C(12)	4098 (9)	-1697 (6)	9675 (3)	4.53 (16)

Table 3. *Bond lengths (Å) and bond angles (°)*

	(1)	(2)	(3)
C(2)–C(3)	1.391 (8)	1.392 (5)	1.386 (7)
C(2')–C(3')	—	—	1.403 (6)
C(3)–C(4)	1.370 (8)	1.367 (5)	1.369 (8)
C(3')–C(4')	—	—	1.370 (7)
C(4)–C(5)	1.384 (9)	1.383 (5)	1.399 (9)
C(4')–C(5')	—	—	1.380 (9)
C(5)–C(6)	1.373 (9)	1.376 (5)	1.367 (9)
C(5')–C(6')	—	—	1.351 (9)
C(6)–N(1)	1.325 (8)	1.344 (5)	1.342 (8)
C(6')–N(1')	—	—	1.345 (8)
N(1)–C(2)	1.311 (8)	1.317 (4)	1.312 (7)
N(1')–C(2')	—	—	1.306 (6)
C(3)–Cl(3)	1.723 (6)	—	1.717 (6)
C(3')–Cl(3')	—	—	1.708 (5)
C(5)–Cl(5)	1.730 (6)	1.740 (3)	—
C(2)–O(1)	1.354 (7)	1.358 (4)	1.370 (6)
C(2')–O(1')	—	—	1.366 (6)
O(1)–C(7)	1.402 (8)	1.403 (5)	1.403 (6)
O(1')–C(10)	—	—	1.393 (6)
C(7)–C(8)	1.373 (9)	1.382 (5)	1.356 (11)
C(8)–C(9)	1.396 (9)	1.387 (5)	1.389 (9)
C(9)–C(7')	1.378 (10)	1.370 (5)	—
C(9)–C(10)	—	—	1.379 (11)
C(10)–C(11)	—	—	1.353 (11)
C(11)–C(12)	—	—	1.404 (9)
C(12)–C(7)	—	—	1.368 (10)
C(2)–N(1)–C(6)	119.3 (7)	117.2 (4)	117.5 (6)
C(2')–N(1')–C(6')	—	—	117.5 (6)
C(3)–C(2)–N(1)	122.4 (7)	124.3 (4)	123.7 (6)
C(3')–C(2')–N(1')	—	—	123.1 (6)
C(4)–C(3)–C(2)	118.7 (7)	118.1 (4)	118.6 (6)
C(4')–C(3')–C(2')	—	—	117.8 (6)
C(5)–C(4)–C(3)	118.3 (7)	118.5 (4)	118.5 (7)
C(5')–C(4')–C(3')	—	—	119.4 (7)
C(6)–C(5)–C(4)	119.2 (7)	119.7 (4)	118.3 (7)
C(6')–C(5')–C(4')	—	—	118.3 (7)
N(1)–C(6)–C(5)	122.0 (7)	122.2 (4)	123.4 (7)
N(1')–C(6')–C(5')	—	—	123.9 (7)
Cl(3)–C(3)–C(2)	121.0 (5)	—	120.7 (5)
Cl(3')–C(3')–C(2')	—	—	121.3 (4)
Cl(3)–C(3)–C(4)	120.4 (5)	—	120.7 (5)
Cl(3')–C(3')–C(4')	—	—	121.0 (5)
Cl(5)–C(5)–C(4)	120.3 (6)	119.8 (3)	—
Cl(5')–C(5')–C(4')	120.5 (6)	120.5 (3)	—
O(1)–C(2)–N(1)	120.7 (7)	120.8 (4)	119.7 (5)
O(1')–C(2')–N(1')	—	—	120.1 (6)
O(1)–C(2)–C(3)	116.8 (6)	115.0 (4)	116.6 (5)
O(1')–C(2')–C(3')	—	—	116.8 (5)
C(2)–O(1)–C(7)	120.4 (6)	121.0 (4)	119.1 (5)
C(2')–O(1')–C(10)	—	—	119.1 (5)
O(1)–C(7)–C(8)	115.5 (7)	116.0 (4)	119.8 (7)
O(1')–C(7')–C(9)	—	—	119.8 (7)
O(1)–C(7)–C(9') or C(12)	—	—	118.5 (6)
O(1')–C(7')–C(11)	—	—	118.8 (7)
C(9') or C(12)–C(7)–C(8)	122.5 (7)	122.1 (4)	121.2 (8)
C(7)–C(8)–C(9)	119.1 (7)	118.7 (4)	119.9 (8)
C(8)–C(9)–C(7') or C(10)	118.4 (8)	119.2 (4)	119.0 (8)
C(9)–C(10)–C(11)	—	—	121.3 (8)
C(10)–C(11)–C(12)	—	—	119.4 (7)
C(11)–C(12)–C(7)	—	—	119.2 (7)

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42024 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

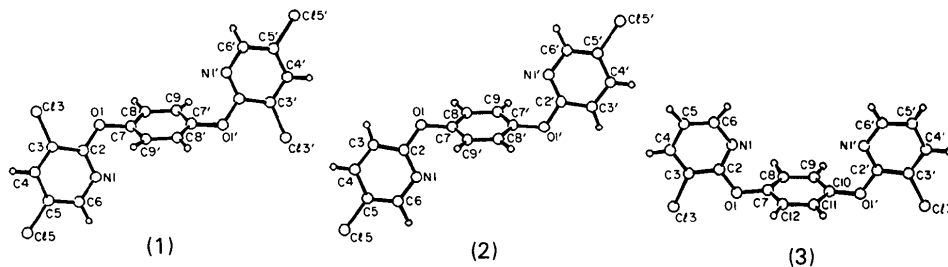


Fig. 1. Comparison of the molecular conformations viewed with a fixed orientation of the central (phenyl) ring.

Table 4. Selected torsion and dihedral angles ($^{\circ}$)

	(1)	(2)	(3)
φ_1 (swing)			
Torsion angles			
C(2)—O(1)—C(7)—C(8)	129.0 (1.0)	122.6 (5)	-88.5 (8)
C(2')—O(1')—C(10)—C(9)	—	—	84.7 (8)
C(2)—O(1)—C(7)—C(9') or C(12)	-54.8 (1.0)	-61.1 (6)	98.6 (8)
C(2')—O(1')—C(10)—C(11)	—	—	-98.6 (8)
Dihedral angles			
Phenyl to C—O—C	52.7 (3)	59.1 (2)	84.7 (4)
Phenyl to C'—O'—C'	—	—	83.2 (4)
φ_2 (twist)			
Torsion angles			
N(1)—C(2)—O(1)—C(7)	-10.3 (1.0)	-1.3 (5)	1.0 (9)
N(1')—C(2')—O(1')—C(10)	—	—	2.0 (1.0)
C(3)—C(2)—O(1)—C(7)	172.5 (1.0)	179.8 (5)	-178.1 (9)
C(3')—C(2')—O(1')—C(10)	—	—	-177.9 (9)
Dihedral angles			
Pyridyl to C—O—C	9.0 (3)	1.0 (2)	1.17 (4)
Pyridyl to C'—O'—C'	—	—	2.44 (5)
Ring—ring dihedral angles			
Phenyl to pyridyl	58.7 (2)	60.1 (1)	83.7 (2)
Phenyl to pyridyl'	—	—	83.9 (2)
Pyridyl to pyridyl'	0	0	1.69 (2)

(1) and (2) sit on crystallographic centers of symmetry so there is only one half molecule per asymmetric unit. Bond lengths and bond angles are within the normal ranges; average C—C, C—N, C—O and C—Cl bonds for the three compounds are 1.379 (13), 1.325 (15), 1.381 (22) and 1.726 (11) Å respectively. The major packing forces for all three structures are stacking interactions between the aromatic rings (phenyl—phenyl and pyridyl—pyridyl only). Stacking distances are between about 3.3 and 3.7 Å.

The conformations are best described in terms of the conventions adopted for diphenyl ether compounds (see Fig. 3a), in which the orientations of the aromatic rings are defined by the swing angle, φ_1 , and the twist angle, φ_2 , about the two C—O bonds of the ether (Cody, 1974). In the past φ_1 and φ_2 have been specified either by the torsion angles about the ether bonds or by the dihedral angles between the ring planes and the ether plane. In Table 3 we provide both measures. For all three structures the φ_1 and φ_2 values fall within the ranges defining the so-called skew conformation, in which one ring is more or less coplanar with the

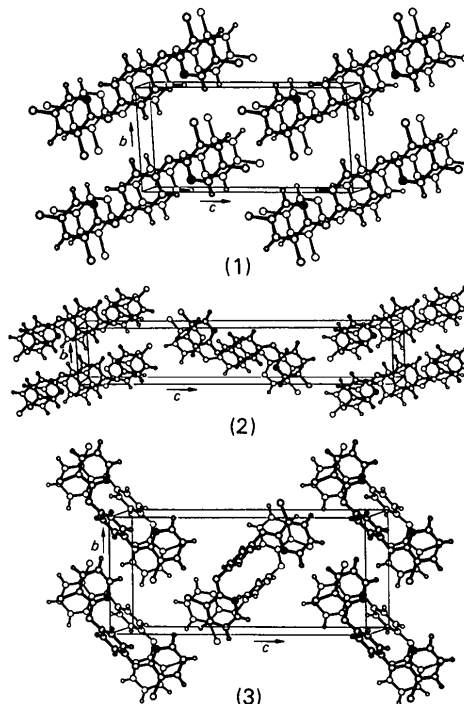


Fig. 2. The crystal-packing diagrams. N atoms are darkened.

C—O—C plane of the ether and the other ring is more or less perpendicular to this plane (van der Heijden, Griffith, Chandler & Robertson, 1975). In diphenyl ethers there is a correlation between φ_1 and φ_2 . A φ_2 value of 0° allows maximum conjugation between ring B (Fig. 3a) and the ether O, but this is opposed by the steric interaction between the *ortho* substituent, X, and ring A. φ_1 and φ_2 may make mutual adjustments to mitigate steric problems and optimize electronic influences. It has generally been observed that the steric factors dominate over the electronic component and that φ_1 and φ_2 often deviate considerably from their ideal skew values of 90° and 0° , respectively.

In the pyridyloxybenzenes, the phenyl ring B of Fig. 3(a) is replaced by a pyridyl ring (Fig. 3b), in which the N atom is *ortho* to the ether bond. This appears to have

a significant influence on the behavior of φ_1 and φ_2 . Specifically, these structures seem to favor a φ_2 value near 0° , with notable twist occurring only for quite extreme (acute) values of φ_1 . This indicates both a strong preference for conjugation between the ether O atoms and the pyridyl rings (note in Table 3 the relative shortening of the pyridyl—O bonds *versus* the phenyl—O bonds) and a less sensitive interplay between φ_1 and φ_2 . In (3), for example, φ_1 and φ_2 are quite close to their ideal skew values (see Table 4). A φ_2 value so near to 0° is not usually observed in diphenyl ethers except when bulky di-*ortho* substituents (*Y* and *Z* in Fig. 3a) on one ring constrain the other ring to the ether plane (Griffith, Chandler & Robertson, 1972). In thyronine.HCl ethyl ester, where all of the *ortho* substituents are H atoms and steric constraints are minimal, φ_2 is -37° (Camerman & Camerman, 1974). In (2), φ_2 remains near 0° even though φ_1 is nearly 60° . Only in (1), where φ_1 is most acute [$52.7(3)^\circ$], does a correlation between φ_1 and φ_2 become apparent, as the pyridyl ring twists out of the ether plane and away from the phenyl ring, through a φ_2 dihedral angle of about 9° .

Although the electron-withdrawing substituents on the pyridyl rings promote conjugation with the ether O, their influence is not alone sufficient to account for the very low φ_2 values observed. Compare, for example, the somewhat analogous diphenyl ether (4-methoxycarbonyl-2-nitrophenoxy)benzene (Gopal, Chandler & Robertson, 1980), which, like (1), has electron-withdrawing substituents *ortho* and *para* to the ether C on one ring. In this compound a φ_1 of 54.6° [similar to that of (1)] is accompanied by a φ_2 of 16.5° , almost twice that of (1) and significantly larger than the φ_2 values for (2) and (3). In light of this comparison, it is interesting to note that 1,4-bis(2,4-dichlorophenoxy)benzene, the diphenyl ether analog of (1), lacks biological activity (Poland, 1982).

The modified φ_1 - φ_2 interactions of the pyridyl-phenyl ether moiety can be attributed largely to the unique electronic and steric properties of the pyridyl N. Because of its electronegativity, the N adds additional weight to the electronic component of the interaction, favoring conjugation between the ether O and the pyridyl ring. At the same time, the N provides an optimal steric environment for this conjugation; in all

three structures the N is found to be proximal to the phenyl ring, where, lacking a substituent, it presents little steric conflict with the phenyl ring; hence φ_1 can vary considerably while φ_2 remains near 0° .

Elucidation of the conformational properties of these compounds contributes to a conformational rationale for their biological activities. Two factors seem to be of primary significance. One is the conjugation (discussed above) between the ether O atoms and the lateral (pyridyl) rings. This is an important determinant of the overall conformation and its occurrence in both the active and inactive compounds suggests that it is probably a necessary though not sufficient condition for activity. The other major factor is the relative placement of the two lateral rings. In both of the active compounds [(1) and (2)] these pyridyl rings are *anti* (with respect to the central ring) while in the inactive compound (3) they are *syn*. The reason for the choice of *syn* or *anti* is not clear and it is possible that in solution the two conformers exist in equilibrium. It is interesting, though perhaps only fortuitous, that the active and inactive compounds exhibit different conformers in the crystal. Further biological and physical studies should clarify the importance of the *syn* and *anti* conformers. In addition to their biological significance, these structures offer further insight into the conformational properties of diphenyl ethers and bridged diaromatic compounds in general. Our data will also be of value in the design of conformationally rigid analogs of biologically active bis(pyridyloxy)benzenes.

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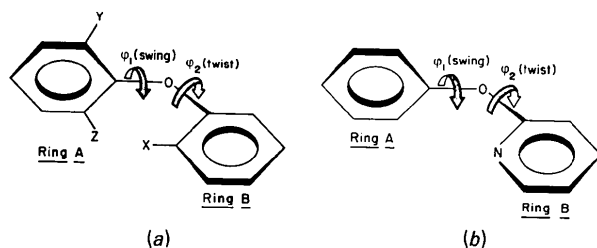


Fig. 3. φ_1 and φ_2 angles defined for (a) diphenyl ethers and (b) the pyridyl-phenyl ether moiety of the bis(pyridyloxy)benzenes.