The X-Ray Crystallographically Determined Conformation of [2.2](2,5)Furano(2,5)pyridinophane

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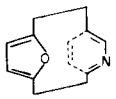
We have recently (1) described the synthesis and solution-conformation of [2.2](2,5)furano(2,5)pyridinophane (**1**). The pmr and ultraviolet spectral analyses of this compound established that the furan ring oxygen atom is inclined towards the pyridine ring nitrogen atom in a fashion as indicated by structure **1**. Because of the lack of availability of more detailed structural analyses of this compound and related ring systems, an X-ray crystallographic analysis of the mixed heterocyclophane **1** was undertaken.



It is the purpose of this paper to describe the results of this study and to compare these with the strucutral features of [2.2]paracyclophane (**2**) and of related molecules.

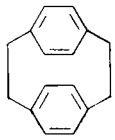
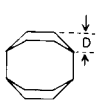


Table I.

Comparison of Structural Parameters for [2.2]cyclophanes

Compound	Ring-Ring Angle (α)	Bridging Group	Carbon-Carbon Bridge-Bond Length (Average)	D (a)	Ref.
[2.2]Paracyclophane	0°	$-CH_2CH_2-$	1.558	0.172	2
[2.2]Metacyclophane	0°	$-CH_2CH_2-$	1.56	--	3
4,12-Dimethyl[2.2]metacyclophane	0°	$-CH_2CH_2-$	1.573 (2)	--	4
4,12-Di(bromomethyl)[2.2]metacyclophane	0°	$-CH_2CH_2-$	1.568 (8)	--	5
[2.2]Di(2,5)thiafuranophane	0°	$-CH_2CH_2-$	1.67 (5) 1.55 (5)	--	6
[2.2](2,5)Furano)2,5)pyridinophane	23°	$-CH_2CH_2-$	1.574 (5)	0.172	this work
[2.2]Paracyclophane-1,9-diene	0°	$H\diagdown C = C\diagup H$	1.336 (6)	0.172	7
[2.2]Metaparacyclophane-1,9-diene	41°	$H\diagdown C = C\diagup H$	1.246 (4)	0.235	8
[2.2](2,6)Pyridinoparacyclophane-1,9-diene	90°	$H\diagdown C = C\diagup H$	1.324 (12)	0.222	9

(a) D is defined for the para-bridged ring systems as the distance the two bridge-bonded carbon atoms lie out of the plane of the remaining four.



F. N.

Table II

Crystal Data

Mol. Formula	$C_{13}H_{13}NO$
Mol. wt.	199.25
Linear abs. coeff. μ	0.87
Max. crystal dimensions	0.55 mm x 0.55 mm x 0.80 mm
Space group	Cc
Molecules/unit cell	4
Calcd. Density	1.30 g. cm^{-3}
Cell constants (a)	a = 10.187 (3); b = 12.618 (3); c = 8.311 (2) β = 107.64 (1)°
Cell vol.	1018.07 Å^3

(a) MoKα radiation, λ = 0.71069 Å. Ambient temperature of 23 ± 1°C.

Table III

Interatomic Distances (Å) and Angles (°) for [2.2](2,5)Furano(2,5)pyridinophane

O-C1	1.379 (3)	O-C4	1.382 (3)
C1-C2	1.346 (4)	C3-C4	1.341 (4)
C1-C13	1.490 (4)	C4-C5	1.501 (4)
C12-C13	1.577 (5)	C5-C6	1.572 (5)
C9-C12	1.408 (4)	C6-C7	1.505 (4)
N-C7	1.346 (4)	N-C8	1.336 (4)
C7-C11	1.385 (4)	C8-C9	1.392 (4)
C10-C11	1.380 (4)	C9-C10	1.385 (4)
C2-C3	1.434 (4)	C5-H3	0.97 (4)
C5-H4	1.00 (4)	C6-H5	1.00 (4)
C6-H6	1.07 (4)	C12-H10	0.93 (4)
C12-H11	1.13 (4)	C12-H12	1.02 (4)
C12-H13	1.05 (4)		
O-N	2.843 (3)	O-C8	2.812 (3)
O-C7	2.822 (3)	O-C9	2.795 (3)
O-C11	3.126 (3)	O-C10	3.085 (3)

Bond Angles

C1-O-C4	107.7 (2)	O-C1-C2	108.8 (2)
C1-C2-C3	107.2 (3)	C2-C3-C4	107.2 (3)
C3-C4-O	108.9 (2)		
C2-C1-C13	137.2 (3)	C3-C4-C5	136.6 (3)
O-C1-C13	113.7 (3)	O-C4-C5	114.1 (2)
C1-C13-C12	114.7 (2)	C4-C5-C6	113.4 (2)
C13-C12-C9	108.4 (2)	C5-C6-C7	108.5 (2)
C12-C9-C10	119.5 (3)	C6-C7-C11	118.7 (3)
C12-C9-C8	121.6 (3)	C6-C7-N	117.4 (3)
C9-C10-C11	119.4 (3)	C7-C11-C10	117.7 (3)
N-C8-C9	123.1 (3)	N-C7-C11	122.1 (3)
C8-C9-C10	116.7 (3)	C7-N-C8	116.9 (3)

The several [2.2]cyclophane structures thus far determined may be divided, as illustrated in Table I, into two groups: those bridged by -C=C- units and those bridged by -C-C- single bonds. One general difference of the two classes emerges: the carbon-carbon single bonds of the

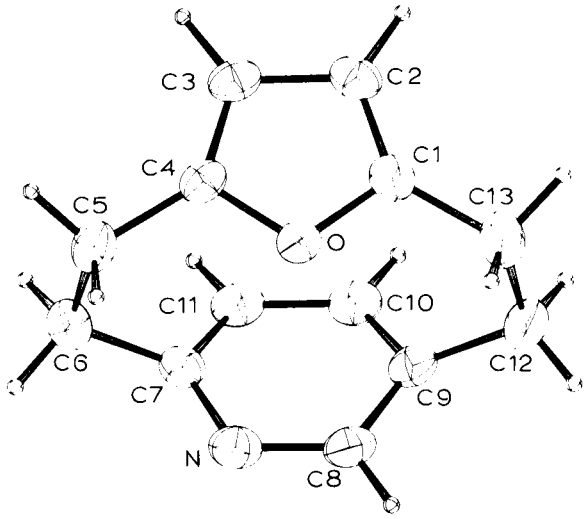


Figure I. Molecular Structure of [2.2](2,5)furano(2,5)pyridinophane with the Atoms Displayed as 50% Probability Ellipsoids for Thermal Motion.

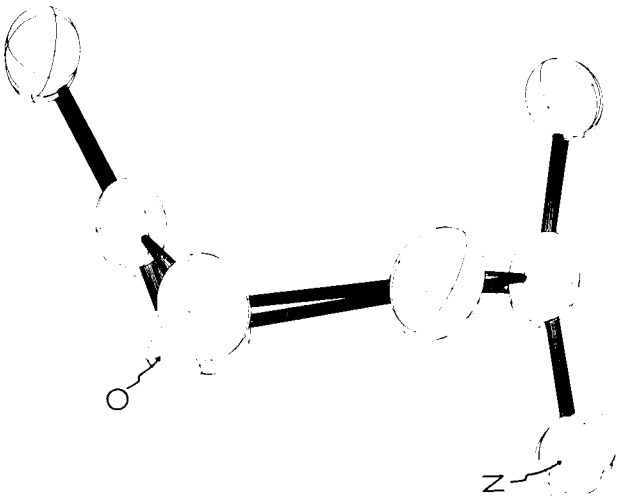


Figure II. Projection of [2.2](2,5)furano(2,5)pyridinophane Parallel to the Bridge-Carbon Bonds.

bridging atoms are quite significantly longer than normal in [2.2](2,5)furano(2,5)pyridinophane (**1**), 1.574Å average, as they are also in all related structures (see Table I). On the other hand, the carbon-carbon double bonds between the bridging atoms remain quite close to the expected ethylenic value of 1.334Å (10): 1.336Å in [2.2]paracyclophane-1,9-diene, 1.346Å in [2.2]metaparacyclophane-1,9-diene, and 1.324Å in [2.2](2,6)pyridinoparacyclophane-1,9-diene. Thus it appears that it requires less energy to effect the out-of-plane deformation of the aromatic ring systems than to lengthen the carbon-carbon double bond in the ethylenic bridges. Indeed, the one

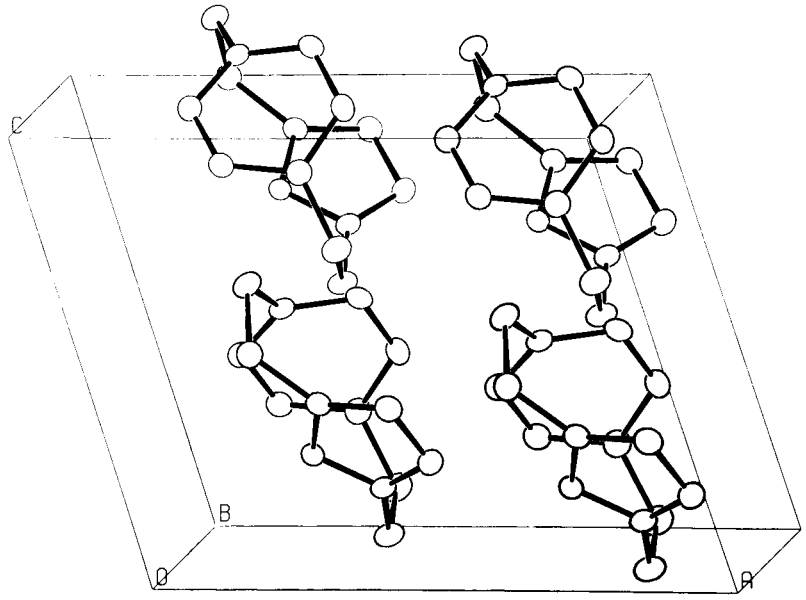


Figure III. The Crystal Packing of Four Molecules of [2.2]-(2,5)furano(2,5)pyridinophane with a Superimposed Unit Cell.

Table IV

Comparison of Bond Lengths (Å) in Furan (11) and Pyridine (12) With Those in [2.2](2,5)-Furano(2,5)pyridinophane

Bond	Furan	Pyridine	[2.2](2,5)Furano(2,5)-pyridinophane (a)
O-C1	1.371 (16)		1.380 (3)
C1-C2	1.354 (16)		1.344 (3)
C2-C3	1.440 (16)		1.434 (4)
N-C7		1.340 (5)	1.341 (4)
C7-C11		1.390 (5)	1.388 (4)
C10-C11		1.400 (5)	1.382 (4)

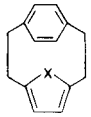
(a) Average values of the two independent distances given in Table III.

feature common to all [2.2]cyclophane structures is a boat-configured *para*-ring system, as is graphically illustrated in the footnote to Table I.

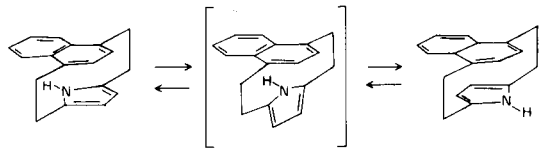
The two aromatic rings are parallel for the situation in which both are *para*-substituted, for [2.2]metacyclophane and for its 4,12-dimethyl derivative. Such is not the case, however, for the remaining three compounds given in Table I, where the ring-ring angles range from 23° to 90°.

The added rigidity imposed by the presence of olefinic rather than ethylenic bridges in the *meta*-cyclophanes may well account for these non-parallel ring conformations. On the other hand the two rings in [2.2](2,5)furano-(2,5)pyridinophane (**1**) are at an angle of 23° with respect to one another and represent the first X-ray crystallographically determined ethylenic-bridged cyclophane compound with a ring-to-ring angle of other than 0°.

This situation has, apparently, also been observed in cyclophanes of the following type:



It is of interest to note that, in these systems, variable temperature studies have suggested the existence of the following equilibrium:



Yet, we have not been able (1) to show the occurrence of this inversion process in the furanopyridine **1**. It is difficult to conceive that the nitrogen lone-pair of electrons would significantly inhibit this inversion process described for the benzenoid analog and one wonders whether an explanation other than that of the proposed equilibrium might not account for the observed variable temperature behavior in these benzenoid cyclophanes.

The various bond lengths and bond angles determined for the mixed heterophane **1** are listed in Table III (see Figure 1). A comparison of the bond parameters of furan itself with those of the furan ring in compound **1** point to only small differences in the bond lengths in these two

Table V

Final Fractional Coordinates and Thermal Parameters (a) for [2.2](2,5)Furano(2,5)pyridinophane

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O	0.3296 (4)	0.1770 (2)	0.2795 (5)	0.0074 (2)	0.0042 (1)	0.0104 (3)	-0.0001 (1)	0.0019 (2)	-0.0004 (2)
N	0.2394 (4)	0.3256 (2)	0.4802 (5)	0.0096 (3)	0.0057 (2)	0.0144 (5)	0.0014 (2)	0.0040 (2)	-0.0008 (2)
C1	0.4309 (5)	0.1962 (2)	0.2046 (6)	0.0099 (3)	0.0048 (2)	0.0102 (4)	-0.0005 (2)	0.0036 (3)	-0.0017 (2)
C2	0.5365 (5)	0.1295 (3)	0.2704 (6)	0.0096 (4)	0.0052 (2)	0.0145 (5)	-0.0000 (2)	0.0048 (4)	-0.0023
C3	0.5026	0.0681	0.3975	0.0101	0.0040	0.0146	0.0007	0.0026	-0.0013
C4	0.3786 (4)	0.1009 (2)	0.4026 (5)	0.0091 (3)	0.0031 (2)	0.0121 (5)	-0.0003 (2)	0.0020 (3)	-0.0008 (2)
C5	0.2898 (5)	0.0840 (3)	0.5152 (6)	0.0102 (4)	0.0048 (2)	0.0149 (6)	-0.0011 (2)	0.0039 (4)	0.0011 (3)
C6	0.3118 (5)	0.1697 (3)	0.6582 (6)	0.0127 (5)	0.0066 (3)	0.0141 (6)	0.0006 (3)	0.0067 (4)	0.0011 (3)
C7	0.3441 (4)	0.2739 (2)	0.5905 (5)	0.0102 (4)	0.0049 (2)	0.0101 (5)	0.0010 (2)	0.0042 (3)	-0.0009 (2)
C8	0.2702 (4)	0.3838 (2)	0.3624 (6)	0.0096 (4)	0.0045 (2)	0.0138 (5)	0.0018 (2)	0.0025 (3)	-0.0001 (3)
C9	0.4023 (5)	0.3896 (2)	0.3468 (6)	0.0105 (4)	0.0031 (2)	0.0155 (6)	0.0004 (2)	0.0040 (4)	-0.0003 (2)
C10	0.5093 (4)	0.3567 (2)	0.4846 (6)	0.0079 (3)	0.0040 (2)	0.0167 (6)	-0.0008 (2)	0.0027 (3)	-0.0018 (3)
C11	0.4803 (5)	0.2992 (2)	0.6109 (6)	0.0092 (4)	0.0048 (2)	0.0110 (4)	0.0006 (2)	0.0008 (3)	-0.0017 (2)
C12	0.4257 (6)	0.4002 (3)	0.1768 (6)	0.0146 (5)	0.0049 (2)	0.0177 (7)	0.0009 (3)	0.0070 (5)	0.0027 (3)
C13	0.4014 (5)	0.2886 (3)	0.0872 (6)	0.0143 (5)	0.0068 (3)	0.0122 (6)	-0.0006 (3)	0.0055 (4)	0.0005 (3)
H1 (C2)	0.623	0.124	0.237 (b,c)						
H2 (C3)	0.561	0.012	0.467						
H3 (C5)	0.189 (5)	0.089 (4)	0.446 (6)						
H4 (C5)	0.307 (5)	0.012 (5)	0.561 (6)						
H5 (C6)	0.224 (5)	0.173 (4)	0.692 (6)						
H6 (C6)	0.391 (5)	0.148 (4)	0.763 (7)						
H7 (C8)	0.198	0.425	0.281						
H8 (C10)	0.606	0.374	0.490						
H9 (C11)	0.556	0.277	0.712						
H10 (C12)	0.366 (5)	0.452 (4)	0.106 (7)						
H11 (C12)	0.533 (5)	0.425 (4)	0.203 (6)						
H12 (C13)	0.296 (5)	0.276 (4)	0.021 (6)						
H13 (C13)	0.468 (5)	0.279 (4)	0.014 (6)						

(a) Anisotropic thermal parameters defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell)]$. (b) Isotropic thermal parameters set at 5.0 for all hydrogen atoms. (c) Ring hydrogen atom positions were not varied.

Table VI

Least-Squares Plane Calculations for [2.2]-(2,5)Furano(2,5)pyridinophane

Plane	Equation of Plane
A (a)	0.1256X - 0.8285Y - 0.5457Z + 5.3362 = 0
B	-0.2261X - 0.6950Y - 0.6825Z + 3.6853 = 0

	Deviation of Atoms from Planes (Å)		
Atom	Plane A	Atom	Plane B
N	0.011	O	0.022
C8	-0.011	C1	-0.017
C10	0.011	C2	0.006
C11	-0.011	C3	0.008
C7	0.174	C4	-0.019
C9	0.169		
O	2.611		

(a) Plane defined by N, C8, C10, and C11.

compounds (Table IV). A similar comparison between pyridine and the pyridine ring in the mixed heterophane **1** shows again, no significant deviations.

The most intriguing feature of the structure of compound **1** is revealed when a projection along the methylene group axis is examined (Figure II). The projection not only confirms our earlier description of the pyridine to furan ring configuration (1), but further establishes that neither the pyridine nor the furan rings are planar. The pyridine is bent in such a fashion that C8, C10, C11 and the nitrogen atom are situated away from the center of the molecule. In fact, the distortion from planarity corresponds to 0.17Å (Table I), if one looks down the pyridine ring from C7 towards C9. A similar, but considerably less pronounced (0.02Å), distortion from planarity is noted for the furan ring when one looks down the C1 to C4 atoms in this part of the molecule.

There now remains to examine the location of the furan oxygen atom with respect to the C8-N bond. In other words, is it located closer to the nitrogen atom than to C8 or is the oxygen equidistant from both of these atoms? Since the N to O distance is 2.843Å (Table III) while the C8 to O distance is 2.812Å, the oxygen is situated only somewhat closer to C8 than the pyridine nitrogen, and for all intents and purposes the oxygen atom is essentially equidistant from C8 and N. This observation leads to the interesting conclusion that there appears to be very little, if any, replusion between the lone-pair electrons on nitrogen and those on oxygen at these distances.

Finally, the X-ray parameters of compound **1**, and the earlier spectral analyses of the substance, seem to support Wynberg's recent suggestion that benzene, and presumably all related aromatic systems, can be bent out of planarity to a substantial extent without significantly altering their aromatic character.

EXPERIMENTAL

X-ray Data Collection.

Single crystals of the compound were prepared by the literature method (1), and sealed in thin-walled glass capillaries. The final lattice parameters given in Table II were determined from a least-squares refinement of the angular settings of 15 accurately centered reflections ($\theta > 20°$).

Data were taken on an Enraf-Nonius CAD-4 diffractometer with graphite crystal monochromated molybdenum radiation. The diffracted intensities were collected by the ω-2θ scan technique with a takeoff angle of 3.0°. The scan rate was variable and was determined by a fast (20° min^{-1}) prescan. Calculated speeds based on the net intensity gathered in the prescan ranged from 7 to 0.8° min^{-1}. Moving-crystal moving-counter backgrounds were collected for 25% of the total scan width at each end of the scan range. For each intensity the scan width was determined by the equation

$$\text{scan range} = A + B \tan \theta$$

where A = 1.00° and B = 0.27°. Aperture settings were determined in a like manner with A = 4 mm and B = 4 mm. Other diffractometer parameters and the method of estimation of the standard deviations have been described previously (13). As a check on the stability of the instrument and the crystal, two reflections, the (221) and ($\bar{4}$00), were measured after every 25 reflections; no significant variation was noted.

One independent quadrant of data was measured out to 2θ = 54°, a slow scan was performed on a total of 965 unique reflections. Since these data were scanned at a speed which would yield a net count of 4000, the calculated standard deviations were all very nearly equal. No reflection was subjected to a slow scan unless a net count of 30 was obtained in the prescan. Based on these considerations, the data set of 965 reflections (used in the subsequent structure determination and refinement) was considered observed, and consisted in the main of those for which $I > 3\sigma(I)$. The intensities were corrected for Lorentz and polarization effects.

Fourier calculations were made with the ALFF program (14). The full-matrix, least-squares refinement was carried out using the Busing and Levy program ORFLS (15). The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction. Atomic scattering factors for O, N, and C were taken from Cromer and Waber (16). Scattering factors for hydrogen were from "International Tables for X-ray Crystallography" (17). Final bond distances, angles, and errors were computed with the aid of the Busing, Martin, and Levy ORFFE program (18). Crystal structure illustrations were obtained with the program ORTEP (19).

Structure Solution and Refinement.

Statistical tests verified the space group as the acentric Cc; the structure was nonetheless solved by the straightforward application of the direct methods program MULTAN (20). Anisotropic refinement with unit weights of the fifteen non-hydrogen atoms in the asymmetric unit gave agreement indices of $R_1 = 0.054$ $R_2 = 0.062$ where

$$R_1 = \Sigma \, |F_o| - |F_c| / \Sigma \, |F_o|$$

$$R_2 = \left\{ \Sigma \, w (|F_o| - |F_c|)^2 / \Sigma \, w |F_o|^2 \right\}^{1/2}$$

Location of the bridgecarbon-hydrogen atoms on a difference Fourier map, inclusion of the hydrogen atoms bonded to the

ring systems at calculated positions (C-H bond length assumed to be 1.00 Å), and further anisotropic refinement of the non-hydrogen atoms led to final values of $R_1 = 0.032$ and $R_2 = 0.032$. Unobserved reflections were not included. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviations. The value of the standard deviation of an observaiton of unit weight was 1.00. A final difference Fourier map showed no unaccounted electron density. The final values of the positional and thermal parameters are given in Table V.

The unit cell packing, illustrated in Figure III, is normal for a molecular compound of this type. The only major atom intermolecular distances less than 3.50 Å are O-C10′ (21), 3.46 Å, and O-C11′, 3.42 Å.

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