Structural Aspects of [2.2]Heterophanes. Part I. Molecular Structure of [2.2](2,6)Pyridinophane

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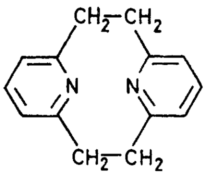
The crystal and molecular structure of the title compound has been determined from three-dimensional *X*-ray diffractometer data. Crystals are orthorhombic with a = 13.49(8), b = 7.525(7), c = 11.24(8) Å, space group *Pbca*. The structure was solved by direct methods and refined by least squares techniques to *R* 0.047 for 616 independent reflections. The crystals are built up by discrete centrosymmetric molecules approaching C_{2h} symmetry. The pyridine rings are distorted towards an asymmetric boat conformation and are so arranged as to get a stepped geometry (N · · · N 2.54, inter-ring distance 2.22 Å). A significant stretching of the C–C bond length of the ethylene bridges, in a gauche conformation (63°), is observed (1.581 Å). The geometrical features are compared with those of free pyridine and other [2.2]phanes.

THE stereochemistry of [2.2]phanes and related systems was reviewed a few years ago by Vögtle and Neumann,[1] who concluded that investigations on systems such as [2.2]heterophanes are far from being considered complete; since then very few structural studies have been reported.[2,3] In order partially to fill this gap in [2.2]phane chemistry we have undertaken a structural study of a series of [2.2]heterophanes. We report here the crystal and molecular structure of [2.2](2,6)pyridinophane (pyph), (I)



(I) pyph

EXPERIMENTAL

Crystal Data.—$C_{14}H_{14}N_2$, M = 210.3. Orthorhombic, a = 13.49(8) b = 7.525(7), c = 11.24(8) Å, U = 1 141.0 Å^3, D_m = 1.23, Z = 4, D_c = 1.22. Mo-K_α radiation, λ = 0.7107

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[1] F. Vögtle and P. Neumann, *Angew. Chem. Internat. Edn.*, 1972, **11**, 73.

[2] L. H. Weaver and B. W. Matthews, *J. Amer. Chem. Soc.*, 1974, **96**, 1581.

[3] J. L. Atwood, W. E. Hunter, C. Wong, and W. W. Paudler, *J. Heterocyclic Chem.*, 1975, **12**, 433.

Å; μ(Mo-K_α) = 0.79 cm^{-1}. Space group *Pbca*. Cell parameters were determined from Weissenberg and precession photographs taken with Co-K_α radiation and refined with an online automated Siemens diffractometer.

Intensity Measurements.—Three-dimensional intensity data were collected on a Siemens diffractometer by the θ—2θ scan technique with Mo-K_α radiation for a maximum 2θ angle of 54°. All reflections having $I_0 < 3\sigma(I_0)$ were rejected, the remainder being corrected for Lorentz-polarization factors. A total of 616 independent reflections were used in the subsequent calculations. No correction for absorption (μR 0.02) was applied.

Structure Determination and Refinement.—The structure was determined by direct methods by use of the Multan program.[4] The E map based on the phases obtained for the 88 reflections with $|E| > 1.9$ revealed all eight crystallographically independent non hydrogen atoms. Least-squares isotropic refinement reduced R to 0.12. After anisotropic refinement (R 0.089) a three-dimensional difference-Fourier synthesis was calculated to locate the hydrogen atoms. The estimated positions of these all occured in regions of positive electron density. Final anisotropic refinement including the hydrogen atoms (with isotropic temperature factors) gave R 0.047. The final weighting scheme was $w = 1/(A + B|F_o| + C|F_o|^2)$, where $A = 3.0$, $B = 1.0$, and $C = 0.007$ were chosen so to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of $|F_o|$ and ($\sin \theta/\lambda$). Final atomic positional parameters are listed in Table 1, together with their estimated standard deviations.

TABLE 1

Atomic positional parameters of ($\times 10^4$, H $\times 10^3$) with estimated standard deviations in parentheses. H atoms are numbered according to the atom to which they are bonded and their isotropic temperature factors are also listed

	x	y	z	B/Å^2
N	623(2)	1 264(3)	−83(2)	
C(1)	−883(3)	2 931(4)	229(3)	
C(2)	121(2)	2 352(4)	664(2)	
C(3)	447(2)	2 691(4)	1 819(3)	
C(4)	1 273(2)	1 798(4)	2 225(2)	
C(5)	1 716(2)	518(5)	1 512(3)	
C(6)	1 357(2)	250(4)	361(2)	
C(7)	1 641(2)	−1 347(5)	−388(3)	
H(1,1)	−114(2)	402(5)	76(3)	3.3(7)
H(1,2)	−87(2)	329(4)	−66(3)	3.1(8)
H(3)	4(3)	353(5)	233(3)	3.9(8)
H(4)	149(3)	199(4)	306(3)	3.4(8)
H(5)	226(2)	−36(5)	177(3)	3.7(8)
H(7,1)	166(2)	−101(4)	−131(3)	3.0(7)
H(7,2)	231(2)	−170(4)	−13(2)	2.9(6)

Observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 22070 (4 pp., 1 microfiche).* Atomic scattering factors were calculated according to ref. 5.

RESULTS AND DISCUSSION

Description of the Structure.—The crystals are built up of discrete molecules held together by van der Waals forces. Figure 1 shows a drawing of the molecule together with the numbering scheme used for the atoms. Each molecule possesses a crystallographic symmetry centre and fairly approaches C_{2h} symmetry. Bond lengths and angles are given in Figure 2 together with some intramolecular non-bonded distances. Observed differences between chemically equivalent bond lengths and angles do not appear to be significant.

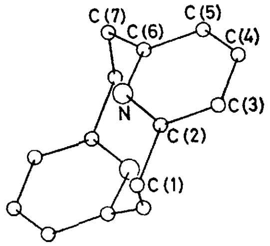

FIGURE 1 A view of the molecule of (I) together with the numbering scheme for the atoms used in the crystallographic analysis

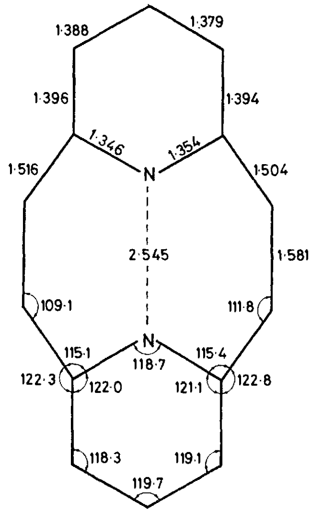

FIGURE 2 Bond lengths (Å) and angles (°). Estimated standard deviations are 0.004—0.005 Å for distances and 0.2—0.3° for angles

The aromatic rings are distorted from planarity towards an asymmetric boat conformation, the N and C(4) atoms being displaced above the plane of the other ring atoms (coplanar within ±0.002) of 0.115 and 0.046 Å respectively. Such a distortion has already been observed in other metacyclophanes.[3] The ethylene bridges have a nearly *gauche* conformation with a torsion angle around the CH$_2$–CH$_2$ bonds of 63.0°. The aliphatic bond is significantly stretched to 1.581(5) Å, a value in the range of those reported for other cyclophanes.[3] A side view of the molecule is shown in Figure 3 together with some distances of interest.

The stepped structure is characterized by an inter-ring distance of 2.22 Å, the nitrogen atom of one ring being displaced from the pyridine ring by 2.33 Å [N · · · N

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1977, Index issue.

[4] G. Germain, P. Main, and M. N. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

[5] F. H. Moore, *Acta Cryst.*, 1963, **16**, 1169.

2.54 Å]. The 'inclination' of the step may be expressed by the dihedral angle (134°) between the planes passing through the coplanar carbon atoms of the pyridine ring (at positions 2,3,5, and 6) and the plane through the four bridgehead atoms (at positions 2, 6, and their centrosymmetric ones). Finally we observe that the direction of the H_2C-CH_2 bond is nearly parallel to that bisecting the angle between the planes defined by N, C(2), C(6) and C(2), C(3), C(5), C(6).

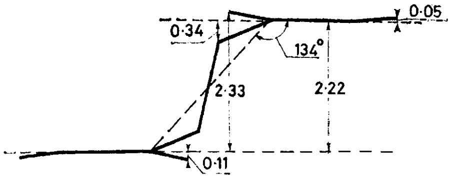


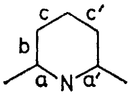
FIGURE 3 A view of (I) along the mid-points of the ethylene bridges. Some relevant distances (Å) and angles (°) are shown

Discussion of the Structure.—Chemically inequivalent bond lengths and angles in (I) are compared in Table 2 with those of other pyridine rings contained in a phane structure, (II) and (III) {(II), [2.2] (2,6)-pyridinoparacyclophane, (III), [2.2](2,5)furanopyridinophane}, and pyridine itself, (IV). While bond lengths are nearly the same in all four compounds, bond angles differ significantly in the (2,6)- and (2,5)-derivatives when compared with pyridine. In fact, values for compounds (I) and (II) show a marked decrease of the (*a*,*b*) angle, at the bridgehead atoms, together with an increase of the (*a*,*a*′) and (*c*,*c*′) angles. On the other hand (III) has values much closer to those for pyridine, particularly for the angle at nitrogen, and only small differences, though with the same trend as for (2,6)-derivatives, are observable for the other angles.

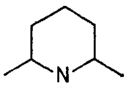
TABLE 2

Structural parameters of the pyridine ring in pyph (I) and related systems

	Bond lengths (Å)			Bond angles (°)			
	a	*b*	*c*	(*a*,*a*′)	(*a*,*b*)	(*b*,*c*)	(*c*,*c*′)
(I) [a]	1.350(4)	1.395(5)	1.384(5)	118.7(2)	121.6(3)	118.7(3)	119.7(3)
(II) [b]	1.340(6)	1.405(8)	1.361(9)	121.1(3)	120.2(5)	118.7(5)	121.1(5)
(III) [c]	1.341(4)	1.388(4)	1.382(4)	116.9(3)	122.6(3)	117.2(3)	119.4(3)
(IV) [d]	1.340(1)	1.394(1)	1.395(1)	116.8	123.9	118.5	118.3



(I)



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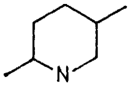
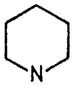


(III)



(IV)

[a] Present work. [b] Ref. 2. [c] Ref. 3. [d] B. Bak, L. Hansen-Nygaard, and J. Rostrup-Andersen, *J. Mol. Spectroscopy*, 1958, **2**, 361.

TABLE 3

Mean values of bond angles (°) at bridgehead (α) and at non-bridgehead (β) atoms for some cyclophanes

(*a*) *meta*-Bridged compounds *

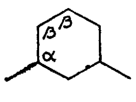
	[2.2]Metacyclophane [a]	4,12-Dimethyl[2.2]-metacyclophane [b]	4,12-Bisbromomethyl-[2.2]metacyclophane [c]	[2.2]Metacyclophane-1,9-diene [d]	[2.2]Metaparacyclophanediene [e]
α	117.3	118.9	118.5	117.7	116.9
β	121.0	120.1	120.1	120.1	121.2

(*b*) *para*-Bridged compounds

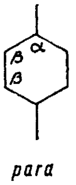
	[3.3]Paracyclophane [f]	[3.3]Paracyclophane-tetracyanoethylene [g]	[2.2]Paracyclophane [h]	[2.2]Paracyclophane-1,9-diene [i]	
α	116.9	117.2	118.4	117.4	116.0
β	121.4	121.2	119.8	120.3	119.7

[a] C. J. Brown, *J. Chem. Soc.*, 1953, 3278. [b] A. W. Hanson, *Acta Cryst.*, 1962, **15**, 956. [c] M. Mathew, *ibid.*, 1968, *B*,**24**, 530. [d] A. W, Hanson and M. Röhrl, *ibid.*, 1972, *B*,**28**, 2032. [e] A. W. Hanson, *ibid.*, 1971, *B*,**27**, 197. [f] P. K. Gantzel and K. N. Trueblood, *ibid.*, 1965, **18**, 958. [g] J. Bernstein and K. N. Trueblood, *ibid.*, 1971, *B*,**27**, 2078. [h] K. Lonsdale, H. J. Milledge, and K. V. K. Rao, *Proc. Roy. Soc.*, 1960, *A*,**225**, 82. [i] C. L. Coulter and K. N. Trueblood, *Acta Cryst.*, 1953, **16**, 667.

* Key to angles:



meta



para

A similar effect at the bridgehead atoms is found in meta- and para-carbophanes (Table 3). In both types of compounds the α angles are significantly smaller than the others, which have values approaching those expected for an undistorted benzene ring.

Table 4 reports structural data for CH$_2$·CH$_2$ bridges connecting the aromatic rings in some carbophanes and heterophanes; for comparison phanes with olefinic bridges are also listed. As already observed,[3] the CH$_2$–CH$_2$ distances are stretched (1.56—1.59 Å) compared with CH=CH distances (1.32—1.34 Å) which remain quite close to the standard C=C bond length. However, the bridge bond angles in the latter case appear much more strained (126—128°) than in the former (110—114°). These features may be due either to steric or electronic (*vide infra*) effects, but it is still difficult to discriminate between them.

The boat distortion of the pyridine ring is similar to that of [2.2]metacyclophane and similar systems,[1] as shown in Table 5 where structural data for several phanes are summarized for comparison. The geometrical features reported are depicted in Figure 4. The stepped structure of the thiophen derivative appears much less pronounced than that of the others, and that of the diene derivative is much more enhanced. Furthermore the deformation of the six-membered rings, expressed by d_1, d_2, and d_3 values, increases with the increasing bulkiness of the group A as expressed by the distance d.

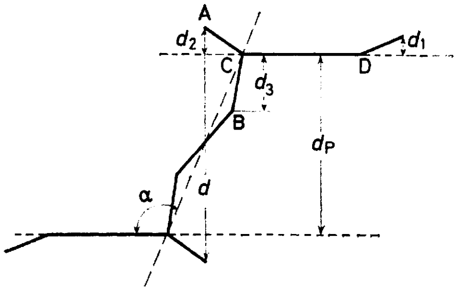


FIGURE 4 Key for interpreting Table 5

Finally atom C, hybridized sp^2, undergoes a deformation from planarity in the five-membered ring derivatives which is about twice that found in the six-membered ones (Table 5).

TABLE 4

Bridge geometry [distances (Å), angles (°)] in some metacyclophanes and metacyclophane-1,9-dienes. Compounds marked by an asterisk have five-membered rings

(*a*) Metacyclophanes *

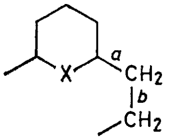
X	CH[a]	C–CH$_2$Br[b]	C–CH$_3$[c]	N[d]	O*[e]	O*[f]	S*[e]
a	1.54(1)	1.519(8)	1.517(3)	1.510(5)	1.507(6)	1.496(4)	1.512(2)
b	1.56(1)	1.568(8)	1.573(3)	1.581(5)	1.569(6)	1.575(4)	1.592(2)
a,b	110.3	112.5(5)	111.5(3)	110.4(3)	111.4(3)	114.1(3)	112.9(1)

(*b*) Metacyclophane-1,9-dienes

X	CH[g]	CH[h]	N[i]
a	1.484(3)	1.484(4)	1.490(8)
b	1.341(3)	1.346(4)	1.324(6)
a,b	126.0(2)	125.7(3)	128.2(5)

[a] Footnote *a* of Table 3. [b] Footnote *c* of Table 3. [c] Footnote *b* of Table 3. [d] Present work. [e] N. Bresciani-Pahor, M. Calligaris, and L. Randaccio, following paper. [f] Ref. 3. [g] Footnote *i* of Table 3. [h] Footnote *e* of Table 3. [i] Ref. 2.

* Key to labels:



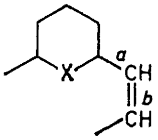


TABLE 5

Comparison of distortions in pyph and similar systems; distances (Å), angles (°)

	d_1	d_2	d_3	d	d_P	α	OP[a]	A
pyph[b]	0.046	0.115	0.350 0.333	2.54	2.22	134	0.066	N
[2.2]Metacyclophane[c]	0.042	0.143	0.368 0.444	2.69	2.35	128	0.079	CH
4,12-Bisbromomethyl[2.2]-metacyclophane[d]	0.080	0.178	0.367 0.481	2.77	2.38	128	0.065	C·CH$_2$Br
4,12-Dimethyl[2.2]metacyclophane[e]	0.088	0.187	0.417 0.453	2.82	2.42	126	0.072	CMe
[2.2](2,5)Furanophane[f]		0.085	0.413 0.395	2.51	2.34	127	0.120	O
[2.2](2,5)Thiophenophane[f]		0.196	0.514 0.536	3.23	2.63	115	0.144	S
[2.2]Metacyclophane-1,9-diene[g]	0.079	0.227	0.479 0.498	2.57	1.85	143	0.091	CH

[a] OP = Mean displacement of atom C above the plane passing through atoms A,B,D of Figure 4. [b] Present work. [c] Footnote *a* of Table 3. [d] Footnote *c* of Table 3. [e] Footnote *b* of Table 3. [f] Following paper. [g] Footnote *d* of Table 3.

Recently the u.v. photoelectron spectrum of (I) has been interpreted assuming ' through space ' and ' through bond ' interactions.[6] The most peculiar ' through space ' interactions, which appear particularly strong, are those between the nitrogen lone pairs and the aromatic ring π systems, which overlap [Figure 5(a)]. ' Through bond ' interactions arise from the overlap of the $\sigma(CH_2{-}CH_2)$ bonds and the π systems of pyridine [Figure 5(b)]. Such interactions are consistent with the observed structure since they would imply a lengthening of the $CH_2{-}CH_2$ bonds and their orthogonality to the aromatic rings as well as a proper ' inclination ' of the step so as to produce better overlap of the nitrogen and pyridine orbitals.

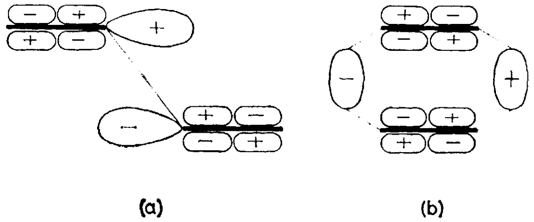


FIGURE 5 MO assumed to be responsible for (a) ' through space ' and (b) ' through bond ' interactions in (I)

These features may also be interpreted in terms of a ' classical ' force field, and this has, in fact, already been attempted for some carbophanes.[7]

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[7/142 *Received, 27th January, 1977*]

[6] F. Bernardi, F. P. Colonna, P. Dembech, G. Distefano, and P. Vivarelli, *Chem. Phys. Letters*, 1975, **36**, 539.

[7] R. H. Boyd, *J. Chem. Phys.*, 1968, **49**, 2574.