Structural Aspects of [2.2]Heterophanes. Part II.[1] Molecular Structure of [2.2](2,5)Thiophenophane and [2.2](2,5)Furanophane

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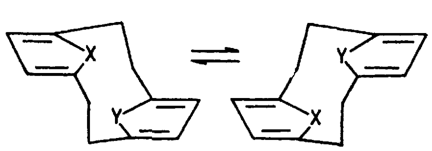
The crystal and molecular structure of the title compounds has been determined from the three-dimensional *X*-ray data by conventional Patterson and Fourier methods for (I) and by direct methods for (II). Crystals of (I) are monoclinic, space group $P2_1/c$, with $a = 6.052(6)$, $b = 12.63(1)$, $c = 7.111(7)$ Å, $\beta = 101.34(9)°$, $Z = 2$. Crystals of (II) are orthorhombic, space group *Pbca*, with $a = 13.60(1)$, $b = 7.507(7)$, $c = 9.725(7)$ Å, $Z = 4$. The structures were refined by least squares techniques to R 0.030 (I) and 0.041 (II) on the basis of 1215 and 421 independent reflections. The molecules of both compounds are centrosymmetric and well approximate to C_{2h} symmetry. The heteroatoms are displaced (S 0.196, O 0.082 Å) from the planes of the aromatic rings which are parallel and separated by 2.63 (I) and 2.34 Å (II). The CH_2-CH_2 bond lengths are significantly stretched [1.592(2) (I), and 1.569(6) Å (II)]. The differently stepped structures are related to the different steric hindrance of oxygen and sulphur which determines the considerably different conformational mobility of such phanes.

In the preceding paper[1] we discussed reasons for determining the molecular geometries of [2.2]heterophanes, particularly in the study of conformational mobility in ring inversion.[2,3] On this basis we can roughly divide them into two groups: (i) those being rigid on the n.m.r. time-scale ($E_{act} > 27$ kcal mol^{-1}) and (ii) those having a measurable E_{act}.

Such different behaviour, both in six- and five-membered phanes, has been mainly attributed to the nature and the size of the X and Y groups (Scheme).[2]

When X (and/or Y) is a group of atoms (*e.g.* CH, NH) or a large atom (*e.g.* S) $E_{act} > 27$ kcal mol^{-1}. On the other hand if both X and Y are small atoms, such as N or O, then inversion takes place.

Thus [2.2](2,5)thiophenophane (thph) (I; X = Y = S) belongs to group (i) whereas [2.2](2,5)furanophane (fuph) (II; X = Y = O) falls into the second group (ii). The accurate structural analysis of both these compounds and a comparison of their geometries should contribute to an understanding of their solution behaviour.[4] The structure of (I) has been already reported in its 1 : 1 π complex with benzotrifuroxan.[5] The accuracy of the



Scheme

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[1] Part I, N. Bresciani Pahor, M. Calligaris, and L. Randaccio, preceding paper.

[2] J. R. Fletcher and I. O. Sutherland, *Chem. Comm.*, 1969, 1504.

[3] S. M. Rosenfeld and P. M. Kechn, *J.C.S. Chem. Comm.*, 1974, 119.

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

[5] B. Kamenar and C. K. Prout, *J. Chem. Soc.*, 1965, 4838.

structure analysis, however, is too low for a useful comparison.

EXPERIMENTAL

Crystal Data.—(*a*) $C_{12}H_{12}S_2$, (I), $M = 220.4$. Monoclinic, $a = 6.052(6)$, $b = 12.63(1)$, $c = 7.111(7)$ Å, $\beta = 101.34(9)°$, $U = 532.9$ Å^3, $D_m = 1.38$ (by flotation), $Z = 2$, $D_c = 1.37$. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 4.41 cm^{-1}. Space group $P2_1/c$.

(*b*) $C_{12}H_{12}O_2$, (II), $M = 188.2$. Orthorhombic, $a = 13.60(1)$, $b = 7.507(7)$, $c = 9.725(7)$ Å, $U = 992.9$ Å^3, $D_m = 1.28$ (by flotation), $Z = 4$, $D_c = 1.26$. μ(Mo-K_α) = 0.92 cm^{-1}. Space group *Pbca*.

Cell parameters were determined from Weissenberg and precession photographs taken with Co-K_α radiation and refined with an on-line automated single-crystal Siemens diffractometer (Mo-K_α).

Intensity Measurements.—Three-dimensional intensity data were collected on a Siemens diffractometer by the θ—2θ scan technique with Mo-K_α radiation to $2\theta_{max.}$ 60° for (I) and 54° for (II). Reflections having $I_o < 3\sigma(I_o)$ for (I) and $I_o < 2\sigma(I_o)$ for (II) were rejected and the remainder corrected for Lorentz-polarization factors. A total of 1 215 reflections for (I) and 421 for (II) were used in the subsequent calculations. No absorption correction was applied [μR 0.062 for (I) and 0.013 for (II)].

Structure Determination and Refinement.—The structure of (I) was determined by conventional Patterson and Fourier methods, and that of (II) by direct methods using the Multan program.[6] An *E* map based on the phases obtained for the 62 reflections with $|E| > 1.90$ revealed the seven crystallographically independent non-hydrogen atom positions. Final anisotropic least-squares refinement, including the hydrogen atoms (with isotropic temperature factors), gave *R* 0.030 for (I) and 0.041 for (II). Final weighting schemes were: $w = 1/(A + B|F_o| + C|F_o|^2)$ where $A = 1.0$, $B = 1.0$, $C = 0.018$, for (I), and $A = 4.0$, $B = 1.0$, $C = 0.009$ for (II), chosen so to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of $|F_o|$ and $(\sin \theta/\lambda)^2$.

TABLE 1

Atomic positional parameters ($\times 10^4$, H $\times 10^3$) for thph, 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 B/Å^2

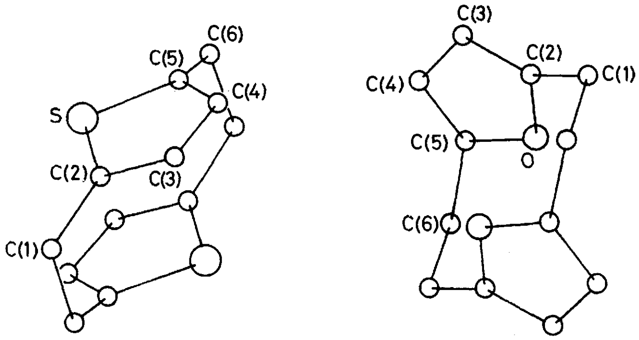
	x	y	z	B/Å^2
S	−1 223(1)	276(0)	1 760(0)	
C(1)	−2 934(3)	1 553(1)	−1 377(2)	
C(2)	−1 074(2)	1 386(1)	358(2)	
C(3)	1 063(3)	1 787(1)	758(2)	
C(4)	2 617(3)	1 128(1)	2 028(2)	
C(5)	1 650(3)	227(1)	2 577(2)	
C(6)	2 666(3)	−845(1)	3171(2)	
H(1,1)	−433(4)	137(2)	−99(3)	2.9(4)
H(1,2)	−292(4)	235(2)	−177(3)	3.5(5)
H(3)	149(4)	244(2)	11(3)	2.6(4)
H(4)	429(4)	126(2)	235(3)	2.5(4)
H(6,1)	163(4)	−121(2)	391(3)	2.9(4)
H(6,2)	411(3)	−75(2)	405(3)	2.8(4)

Final atomic positional parameters are listed in Tables 1 and 2, together with their estimated standard deviations. The numbering scheme used for the atoms is shown in Figure 1. Observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 22071 (9 pp., 1 microfiche).* Atomic scattering factors were calculated according to ref. 7.

TABLE 2

Atomic positional parameters ($\times 10^4$, H $\times 10^3$) for fuph, 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 B/Å^2

	x	y	z	B/Å^2
O	525(2)	−1 183(3)	542(2)	
C(1)	1 261(3)	1 565(6)	1 428(4)	
C(2)	1 307(3)	3(6)	448(4)	
C(3)	1 801(3)	−326(6)	−734(4)	
C(4)	1 266(3)	−1 701(6)	−1 468(4)	
C(5)	486(3)	−2 133(5)	−682(4)	
C(6)	−486(3)	−2 995(5)	−970(4)	
H(1,1)	109(3)	112(5)	240(4)	3.4(8)
H(1,2)	190(3)	218(5)	145(4)	2.5(9)
H(3)	239(3)	26(6)	−106(5)	3.9(1.0)
H(4)	141(3)	−224(5)	−235(4)	2.1(9)
H(6,1)	−39(3)	−395(6)	−170(4)	4.0(9)
H(6,2)	−74(3)	−364(5)	−18(4)	3.5(9)



(a) (b)

FIGURE 1 A view of the molecules (a) thph (I), and (b) fuph (II) together with the atom numbering scheme used in the analysis

Calculations.—All calculations were carried out on a CDC 6200 computer with programs described in ref. 8.

RESULTS AND DISCUSSION

Structure of (I) *thph*.—The structure of (I) consists of discrete molecules held together by weak van der Waals forces. The shape of a single molecule is shown in Figure 1(a) together with the numbering scheme for its atoms. The molecule has exact C_i symmetry and approximates well to C_{2h} symmetry. The thiophen rings are envelope-shaped, the sulphur atom being displaced 0.196 Å out of the plane of the other atoms which in turns are coplanar within ±0.001 Å. Such a distortion is very similar to that reported for thph in its 1 : 1 π-adduct with benzotrifuroxan (thph–bztx), but it is

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

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

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

[8] V. Albano, A. Domenicano, and A. Vaciago, *Gazzetta*, 1966, **96**, 922.

larger than that reported for thiophen-2-carboxylic acid (0.028 Å).[9] On the other hand free thiophen has been found to be planar.[10] Bond lengths and angles are reported in Figure 2(a) together with some non-bonded distances.

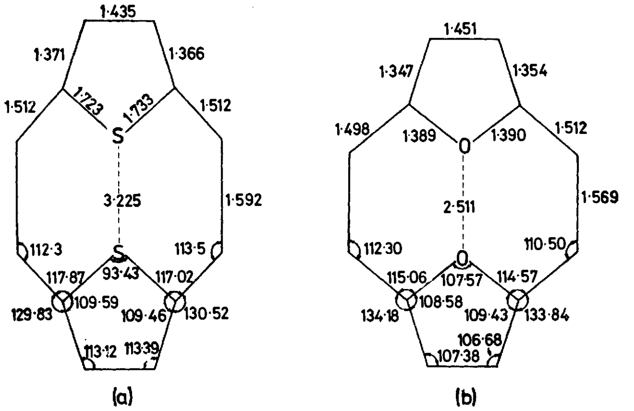

FIGURE 2 Bond lengths (Å) and angles (°) for (a) thph and (b) fuph. Estimated standard deviations are 0.001—0.002 Å and 0.1—0.2° for thph, and 0.004—0.006 Å and 0.3—0.4° for fuph

Chemically inequivalent bond lengths and angles in the thiophen ring are compared in Table 3 with those of thiophen[10] and thiophen-2-carboxylic acid.[9] The corresponding values for thph in its 1 : 1 adduct were excluded owing to their large estimated standard deviations. As far as bond lengths are concerned there are slight differences among the three compounds. An increase in the S–C(2) and C(3)–(4) bond lengths is in the order thiophen-2-carboxylic acid < thiophen < thph. However, the bond angles are nearly equal in thiophen and in its acid-derivative, whereas in thph an increase of the angles at S and C(3) corresponds to a decrease of the angle at the bridgehead C(2) atom. The contraction of *ca.* 2° of the S–C(2)–C(3) angle is consistent with the analogous effect observed in pyph [*] and in [2.2]phanes,[1] where the angles at the bridgehead atoms are significantly smaller than the others.

TABLE 3

Chemically inequivalent bond lengths (Å) and angles (°) in rings of thph, thiophen, and thiophen-2-carboxylic acid. For numbering scheme see Figure 1(a)

	thph [a]	Thiophen [b]	Thiophen-2-carboxylic acid [c]
S–C(2)	1.728(2)	1.714(1)	1.698(10)
C(2)–C(3)	1.369(2)	1.370(2)	1.362(11)
C(3)–C(4)	1.435(2)	1.423(2)	1.414(11)
S–C(2)–C(3)	109.5(1)	111.5(2)	111.8(5)
C(2)–C(3)–C(4)	113.3(2)	112.4(2)	112.2(7)
C(2)–S–C(5)	93.43(6)	92.2(1)	92.1(4)

[a] Present work. [b] Ref. 10. [c] Ref. 9.

A side view of the molecule projected along the direction passing through the mid-points of the CH_2–CH_2 bonds is shown in Figure 3(a). The least-squares planes through the ring carbon atoms of each thiophen ring are exactly parallel and separated by 2.63 Å. The geometry of the ethylene bridges is characterized by a strained C–C bond length of 1.592(2) Å and by angles of 112.3(1) and 113.5(1)°. Their conformation is intermediate between the gauche and the eclipsed, the torsion angle being 34.4°. The ' inclination ' (as defined in the preceding paper[1]) is 115°, whereas the direction of the H_2C–CH_2 bonds is nearly perpendicular to the thiophen rings (102°). The sulphur–sulphur distance [3.225(1) Å] [Figure 2(a)] is similar to that [3.19(1) Å] in thph–bztx, and *ca.* 0.5 Å shorter than the expected van der Waals distance. The sulphur atoms also make short contacts with the carbon atoms of the opposite rings. Two of these, *i.e.* S · · · C(2′) and S · · · C(5′), are 3.071(1) and 3.109(1) Å, whereas S · · · C(3′) and S · · · C(4′) are 3.174(1) and 3.197(1) Å. Thus each sulphur atom lies nearly above the midpoint of the opposite ring.

Structure of (II), *fuph*.—Crystals of (II) are built up by discrete molecules held together by weak non-bonded interactions. Figure 1(b) shows a drawing of a single molecule, together with the atom numbering scheme.

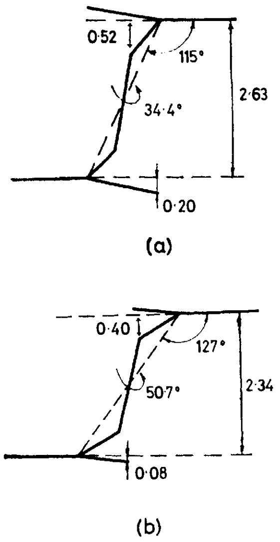

FIGURE 3 A view of the molecules (a) thph and (b) fuph along the direction passing through the mid-points of the ethylene bridges. Some distances (Å) and angles (°) of interest are also reported

The molecule, which possesses a crystallographic symmetry centre, has approximate C_{2h} symmetry. The furan rings are envelope-shaped, the oxygen atom being displaced 0.085 Å out of the plane of the carbon atoms, which are coplanar to within ±0.002 Å. A less-strained ring has been found in [2.2](2,5)furano(2,5)pyridinophane[11] (fpyph) where the O atom is displaced 0.057 Å

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[*] [2.2](2,6)Pyridinophane; see preceding paper.

[9] M. Nardelli, G. Fava, and G. Giraldi, *Acta Cryst.*, 1962, **15**, 737.

[10] B. Bak, D. Cristensen, L. Hansen-Nygaard, and J. Rostrup-Andersen, *J. Mol. Spectroscopy*, 1961, **7**, 58.

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

out of the plane of the carbon atoms. The ring of furan [12] itself and of its 2,5-derivatives [13] has however been found planar. Bond lengths and angles are reported in Figure 2(b) together with some non-bonded distances. The ethylene bridge is characterized by a strained CH_2–CH_2 bond [1.569(6) Å] and angles of 112.3(3) and 110.5(3)°. Chemically inequivalent bond lengths and angles in the furan ring are reported in Table 4 together with those of furan [12] and *syn*-5-nitro-2-furaldehyde oxime.[13] The difference between the two phane derivatives is slight, but the bond lengths for fuph appear significantly longer. Bond angles do however differ slightly among the four compounds, but, the observed differences show the same trends found for other phane derivatives.

TABLE 4

Chemically inequivalent bond lengths (Å) and angles (°) in the rings of fuph, fpyph, furan, and *syn*-5-nitro-2-furaldehyde oxime (nfuo). For numbering scheme see Figure 1(b)

		fuph [a]	fpyph [b]	Furan [c]	nfuo [d]
O–C(2)	(Å)	1.392(5)	1.380(3)	1.368(6)	1.364(4)
C(2)–C(3)		1.351(6)	1.344(3)	1.322(6)	1.342(5)
C(3)–C(4)		1.451(6)	1.434(4)	1.428(7)	1.404(6)
O–C(2)–C(3)	(°)	109.0(3)	108.9(3)	110.1(4)	110.5(3) 113.2(3)
C(2)–C(3)–C(4)		107.0(4)	107.2(3)	106.8(2)	107.0(3) 105.3(3)
C(2)–O–C(5)		107.6(3)	107.7(2)	106.2(6)	104.0(2)

[a] Present work. [b] Ref. 11. [c] Ref. 12. [d] Ref. 13.

A side-view of the fuph molecule is shown in Figure 3(b). The planes through the carbon atoms of each ring are exactly parallel and separated by 2.34 Å. The conformation of the ethylene bridges is close to gauche, the torsion angle being 50.7°. The ' inclination ' is 127° and the direction of the CH_2–CH_2 bond is nearly perpendicular to the furan ring (93°). The $O \cdots O$ distance [2.511(3) Å] is less than the sum of the van der Waals radii. Finally the oxygen atoms make short contacts with only two carbon atoms of the opposite ring (2.81 and 2.85 Å) *i.e.* C(2′) and C(5′), whereas they are separated by normal van der Waals distances from the other two [C(3′) 3.37, C(4′) 3.38 Å].

Discussion of the Structures.—The main difference between the structures of the two compounds, besides some obvious differences in bond lengths and angles, appears to be the different nature of the ' step '. In fact, in the thph structure the two aromatic rings are more ' face-to-face ' than in fuph, as shown by the lower inclination angle (115 *vs.* 127°). In turn, the structure of the latter compound is close to that of [2.2](2.5)pyridinophane [1] and some [2.2]carbophanes.[4] Furthermore in thph the inter-ring distance (2.63 Å) is significantly larger than that in the other phanes where it ranges from 2.22 to 2.42 Å.[1]

It seems likely that such differences, as well as the marked out-of-plane displacement of the sulphur atom, result from the greater bulkiness of sulphur as compared with oxygen or nitrogen.

Similarly, the different conformation of the ethylene bridges in the two compounds seems to be due to a compromise between inter-ring steric interactions and bond-angle strains at the bridge-head atoms. In fact a torsion angle greater than 34.4° in thph should imply a decrease in the S–C(5)–C(6) and S–C(2)–C(1) angles if the two rings cannot get closer.

Therefore the high conformational rigidity of the thph molecules ($\Delta G^\ddagger > 27$ kcal mol^{-1}) seems to be attributable to the steric hindrance of the sulphur atoms, which would have to take part in any intermediate state of the inversion process. The more extended stepped structure of fuph, together with the lesser bulk of oxygen, should allow the transition between the two conformations, even if at the expense of a noticeable energy ($\Delta G^\ddagger$ 16.8 kcal mol^{-1}).[2]

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[12] R. Fourme, *Acta Cryst.*, 1972, **B28**, 2984.

[13] M. Mathew and G. J. Palenik, *J.C.S. Perkin II*, 1972, 1033.