3552 © *1984 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *57*, *3552—3556 (1984)* [Vol. 57, No. 12

Molecular Structure of [2]Paracyclo[2](2,5)furanophane[†]

Fumio Hama,[††] Yasushi Kai, Noritake Yasuoka,[†††] and Nobutami Kasai*
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565

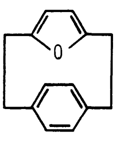
(Received June 30,1984)

The molecular structures of [2]paracyclo[2](2,5)furanophane (**1**) at 20 °C and −150 °C have been determined by means of X-ray diffraction. The crystal is tetragonal, with a=15.996(1), c=8.374(1) Å (at 20 °C), and a=15.823(3), c=8.330(3) Å (at −150 °C), space group $P\bar{4}2_1c$, and Z=8. The structures were solved by the direct method, and refined anisotropically by the block-diagonal least-squares procedure: R=0.069 and 0.075 for the structures at 20 °C and −150 °C, respectively. The furan ring has an envelope form, and the benzene ring boat-shape.

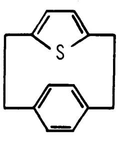
Many multi-layered paracyclofuranophanes have been synthesized by Misumi and his co-workers[1] in order to investigate the trans-annular π-electron interaction between benzene and heteroaromatic rings. They observed the ring inversion phenomena of furan rings in double-, triple-, and quadruple-layered paracyclofuranophanes by variable temperature NMR spectroscopy. The flipping of furan ring in triple- and quadruple-layered paracyclofuranophanes were found to be easier than that in double-layered one. On the other hand, no ring inversion of the thiophene ring was observed in the multi-layered paracyclothiophenophanes.

In a series of structural studies on layered cyclophanes, the molecular sturctures of double- and triple-layered paracycloheterophane containing furan and thiophene rings have been determined by means of X-ray diffraction in order to obtain structural informations about the ring inversion. The molecular structures of triple-layered paracyclofuranophane (**3**) and dimethyl triple-layered paracyclothiopheneophane (**4**) have been reported.[2] This paper deals with the molecular structure of double-layered paracyclofuranophane (**1**) ([2]paracyclo[2](2,5)furanophane) at 20 °C and −150 °C, temperatures above and below the coalescence (−39 °C) of NMR signals of aromatic protons of benzene ring faced to the furan ring.[1]

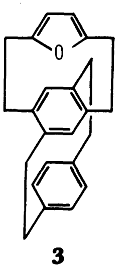
The structure analysis of double-layered paracyclothiophenophane ([2]paracyclo[2](2,5)thiophenophane) was also tried; however, due to the reason mentioned later the intensity data collection has been discontinued.



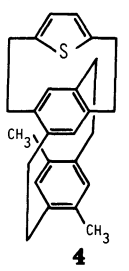
1



2



3



4

1: [2]Paracyclo[2](2,5)furanophane
2: [2]Paracyclo[2](2,5)thiophenophane
3: Triple-layered paracyclofuranophane
4: Dimethyl triple-layered paracyclothiophenophane

Experimental

[2]Paracyclo[2](2,5)furanophane (1). Crystals of double-layered paracyclofuranophane are colorless tetragonal prisms. Preliminary oscillation and Weissenberg photographs showed that the crystal belongs to the tetragonal system, and the systematic absence of reflections (hhl; $l=2n+1$ and $h00$; $h=2n+1$) determined the space group as $P\bar{4}2_1c$.

For the measurements of the unit-cell dimensions and integrated intensities, a Rigaku automated, four-circle diffractometer was used. A crystal with approximate dimensions of 0.2×0.2×0.2 mm was selected for the X-ray work. The unit-cell parameters were precisely determied by the least-squares fit of 2θ values of high angle reflections.

Crystal Data. $C_{14}H_{14}O$, M 198.3, tetragonal, space group $P\bar{4}2_1c$, (20 °C) a=15.996(1), c=8.374(1) Å, V=2142.5(4) Å^3, Z=8, D_m=1.23 g cm^{-3}, D_c=1.229 g cm^{-3}, $\mu(\mathrm{Cu}\,K\alpha)$=5.97 cm^{-1}; (−150 °C) a=15.823(3), c=8.330(3) Å, V=2085.4(10) Å^3, Z=8, D_c=1.263 g cm^{-3}, $\mu(\mathrm{Mo}\,K\alpha)$=0.84 cm^{-1}.

Intensity measurements were carried out by the θ—2θ scan technique at a 2θ scan rate of 4° min^{-1}. For the room temperature (20 °C) experiment nickel-filtered Cu$K\alpha$ radiation was used. The scan width was $\Delta 2\theta=(2.0+0.3\tan\theta)°$. The backgrounds were counted for 7.5 s at both ends of a scan. For the low temperature experiment the crystal was kept at −150 °C with the liquid nitrogen gas flow method. Graphite monochromatized Mo$K\alpha$ radiation was used. The scan width was $\Delta 2\theta=(2.0+0.7\tan\theta)°$. The backgrounds were counted for 5 s. The scans were repeated up to three times when the structure factor magnitude $|F_o|$ was less than $3\sigma(F_o)$, where $\sigma(F_o)$ is the standard deviation estimated from the counting statistics. Totals of 922 (at 20 °C; Cu$K\alpha$, $2\theta \leqq 120°$) and 1728 (at −150 °C; Mo$K\alpha$, $2\theta \leqq 60°$) reflections were collected, among which 106 and 267 reflections less than $3\sigma(F_o)$ were considered as unobserved. No intensity decrease of standard reflections was observed during the experiment. Corrections for the usual Lorentz and polarization effects were carried out, but no absorption correction was made [$\mu(\mathrm{Cu}\,K\alpha)$=5.97 and $\mu(\mathrm{Mo}\,K\alpha)$=0.84 cm^{-1}].

[2]Paracyclo[2](2,5)thiophenophane (2). *Crystal Data.* $C_{14}H_{14}S$, M 214.3, tetragonal, space group $P4_2nm$, $P\bar{4}n2$, or $P4_2/mnm$, a=7.762, c=9.159 Å, V=551.9 Å^3, Z=2, D_m=1.27 g cm^{-3}, D_c=1.29 g cm^{-3}.

The systematic absence of reflections showed the space group to be $P4_2nm$ (No. 102), $P\bar{4}n2$ (No. 118), or $P4_2/mnm$ (No. 136). Since two molecules are contained per unit-cell, the molecular symmetry in the crystal should be mm for the

---

[†] Structural Chemistry of Layered Cyclophanes. X.

[††] Present address: Research Laboratory, Kanzaki Paper Mfg. Co. Ltd., Jokoji-motomachi, Amagasaki 680.

[†††] Present address: Institute for Protein Research, Osaka University, Yamadaoka, Suita, Osaka 565.

space group $P4_2nm$, 222 or $\bar{4}$ for $P\bar{4}n2$, or mmm for $P4_2/mnm$. However, the possible highest symmetry of the present molecule is m, the crystal may include some disordered structure. For this reason the further X-ray experiment was given up.

Structure Solution and Refinement

The room temperautre structure was first solved by the direct method (*MULTAN* 74).[3] 18 peaks on the E map, synthesized with the set of phases with the highest figure of merit, gave an approximate structure of the molecule, but three peaks among them were later excluded as spurious. The refinement was carried out by the block-diagonal least-squares procedure with unit weight (*HBLS* V).[4] Six cycles of isotropic refinement gave the R index of 0.123. After an anisotropic refinement of non-hydrogen atoms (4 cycles, R=0.105) hydrogen atoms located on their calculated positions with isotropic temperature factors were included in the refinement. The final R value was 0.069 for the observed reflections. Atomic paramters are given in Table 1.*

The refinement of the low temperature structure started from the positional paramters for the 15 non-hydrogen atoms determined with the room temperature data: the isotropic temperature factor of B=2.0 Å^2 being assumed for each atom. Successive anisotropic refinement (four cycles) gave the R value of 0.105. Hydrogen atoms were located at the calculated positions and refined isotropically. The weighting scheme used was $w=\{\sigma^2(F_o)+a|F_o|+b|F_o|^2\}^{-1}$ for $|F_o|>0$ and w=c for $|F_o|=0$. The final R value was 0.076 (R_w=0.078) with a=−0.0893, b=0.0018, and c=0. The final atomic parameters with equivalent temperature facors are given in Table 1.*

The atomic scattering factors for non-hydrogen atoms were taken from International Tables for X-ray Crystallography, Vol. IV[5] and those for hydrogen atoms from Stewart, Davidson, and Simpson.[6] Computations were done on an ACOS 700S computer at the Crystallographic Research Center, Institute for Protein Reserach, Osaka University.

Results and Discussion

Molecular Structure. A perspective view of the molecular structure of double-layered paracyclofuranophane at −150 °C is drawn (ORTEP II)[7] in Fig. 1, with the atomic labelling. The molecular structure projected onto the plane defined by the C(10), C(11), C(13), and C(14) atoms is shown in Fig. 2(a), that onto the plane formed by the C(1), C(2), C(7), and C(8) in Fig. 2(b), and that along the plane made by the C(10), C(11), C(13), and C(14) in Fig. 2(c). Interatomic bond distances and bond angles at −150 °C are also given in Fig. 2 with estimated standard deviations, together with the parameters to describe the out-of-plane deformation of the benzene ring. No essential difference has been observed between the structures at 20 °C and −150 °C; therefore, the discussion will be limited hereafter on the low temperature structure otherwise stated.

The coincidence of structural parameters of chemically equivalent parts of the molecule is good: the molecule has an approximate mirror symmetry. The furan ring takes an envelope form with the oxygen atom away from the benzene ring: the dihedral angle between the planes made by the O, C(3), and C(6) atoms and the C(3), C(4), C(5), and C(6) being 3.3°. This is similar to the corresponding angle in the triple-layered paracyclofuranophane[3.8°].

Two CH_2–CH_2 bridge bonds also have a similar structure as those in the triple-layered paracyclophane: C–C distances being 1.589(6) and 1.582(6) Å, and the torsion angles around the C–C bond 34.8 and 30.3°. The C(1)–C(2)–C(3) and C(6)–C(7)–C(8) angles are 113.4(3) and 114.6(3)°, respectively, which are larger than the C(2)–C(1)–C(12) [108.3(3)°] and C(7)–C(8)–C(9) [108.3(3)°] angles.

The benzene ring adopts a symmetrical boat form as in the case of many other cyclophanes. The C(9) and C(12) atoms deviate from the plane defined by the C(10), C(11), C(13), and C(14) atoms by 13.8 and 14.2°, respectively. The C(1)–C(12) vector makes an anlge of 15.6° to the plane made by the C(11), C(12), and C(13), and the corresponding angle of the C(8)–C(9) vector is 15.1°. The C(1)–C(12)–C(13) and C(8)–C(9)–C(14) angles [117.8(3) and 117.7(3)°, respectively] are smaller than the C(1)–C(12)–C(11) and C(8)–C(9)–C(10) [122.3(4) and 122.0(4)°, respectively], which are also smaller than the corresponding angles in the triple-layered paracyclofuranophane. These facts may be explained by the fact that the C(1) and C(8) atoms are shifted back to the C(13) and C(14) atoms, respectively, so that the nonbonded atomic interactions between the furan and benzene rings is minimized.

Table 2 summarizes the structural parameters to

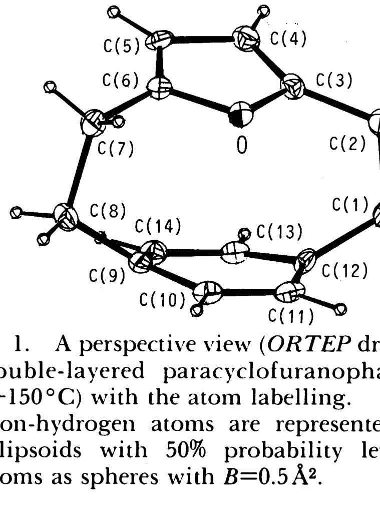


Fig. 1. A perspective view (*ORTEP* drawing)[7] of the double-layered paracyclofuranophane molecule (−150 °C) with the atom labelling.
Non-hydrogen atoms are represented by thermal ellipsoids with 50% probability level, hydrogen atoms as spheres with B=0.5 Å^2.

---

*Tables of observed and calculated structure factors and anisotropic temperature factors of both structures 20 °C and −150 °C are kept at the Chemical Society of Japan, Document No. 8433.

TABLE 1. FINAL ATOMIC POSITIONAL PARAMETERS OF [2]PARACYCLO[2](2,5)FURANOPHANE WITH EATIMATED STANDARD DEVIATIONS IN PARENTHESES

Room temperature structure(20°C)

a) Non-hydrogen atoms

Atom	x	y	z	B_{eq}[8]/Å^2
O	0.2627(3)	0.9515(2)	0.8712(5)	3.7
C(1)	0.2378(5)	0.9342(4)	0.4905(8)	5.1
C(2)	0.2804(4)	0.8773(4)	0.6214(9)	5.0
C(3)	0.3187(4)	0.9254(4)	0.7557(8)	3.9
C(4)	0.3938(4)	0.9580(4)	0.7890(8)	4.6
C(5)	0.3845(4)	1.0097(4)	0.9293(8)	5.0
C(6)	0.3038(4)	1.0055(4)	0.9732(7)	4.0
C(7)	0.2476(5)	1.0485(4)	1.0895(8)	5.0
C(8)	0.1958(4)	1.1245(4)	1.0158(9)	5.2
C(9)	0.1790(4)	1.1075(4)	0.8451(8)	4.4
C(10)	0.1161(4)	1.0513(4)	0.7978(9)	4.9
C(11)	0.1265(4)	1.0035(5)	0.6610(7)	4.5
C(12)	0.2001(4)	1.0089(4)	0.5698(7)	4.4
C(13)	0.2518(4)	1.0792(4)	0.5981(8)	4.9
C(14)	0.2399(4)	1.1274(4)	0.7347(9)	4.5

b) Hydrogen atoms

Atom	x	y	z	B/Å^2
H(1A)	0.191(4)	0.897(4)	0.420(7)	4.3(16)
H(1B)	0.281(5)	0.952(4)	0.405(9)	6.6(21)
H(2A)	0.326(4)	0.846(4)	0.568(8)	5.3(18)
H(2B)	0.235(5)	0.840(4)	0.671(8)	5.9(19)
H(4)	0.441(4)	0.955(4)	0.726(8)	4.2(16)
H(5)	0.425(4)	1.045(4)	0.987(8)	5.0(18)
H(7A)	0.288(5)	1.065(4)	1.189(8)	5.9(20)
H(7B)	0.209(5)	1.015(5)	1.149(8)	7.6(23)
H(8A)	0.233(5)	1.174(5)	1.022(10)	7.0(22)
H(8B)	0.150(4)	1.131(4)	1.087(7)	4.7(17)
H(10)	0.070(5)	1.040(5)	0.873(8)	6.2(21)
H(11)	0.088(4)	0.956(4)	0.627(7)	4.0(16)
H(13)	0.300(4)	1.092(4)	0.518(8)	4.3(17)
H(14)	0.286(4)	1.173(4)	0.753(8)	3.3(15)

Low temperature structure(−150°C)

a) Non-hydrogen atoms

Atom	x	y	z	B_{eq}[8]/Å^2
O	0.26235(16)	0.95118(16)	0.8727(3)	1.20
C(1)	0.2371(3)	0.9356(3)	0.4887(5)	1.67
C(2)	0.2797(3)	0.8765(3)	0.6201(5)	1.47
C(3)	0.3184(3)	0.9246(3)	0.7568(5)	1.39
C(4)	0.3962(3)	0.9572(3)	0.7888(5)	1.57
C(5)	0.3866(3)	1.0102(3)	0.9297(5)	1.48
C(6)	0.3045(3)	1.0055(3)	0.9742(5)	1.36
C(7)	0.2483(3)	1.0490(3)	1.0945(5)	1.55
C(8)	0.1960(3)	1.1259(3)	1.0246(5)	1.65
C(9)	0.1782(3)	1.1087(3)	0.8496(5)	1.37
C(10)	0.1144(3)	1.0535(3)	0.8006(5)	1.45
C(11)	0.1250(3)	1.0053(3)	0.6631(5)	1.50
C(12)	0.1989(3)	1.0110(3)	0.5732(5)	1.36
C(13)	0.2513(3)	1.0817(3)	0.6005(5)	1.41
C(14)	0.2413(3)	1.1299(3)	0.7377(5)	1.53

b) Hydrogen atoms

Atom	x	y	z	B/Å^2
H(1A)	0.192(4)	0.901(4)	0.428(6)	1.3(12)
H(1B)	0.280(4)	0.949(4)	0.423(6)	0.9(11)
H(2A)	0.323(3)	0.845(4)	0.565(6)	0.7(11)
H(2B)	0.235(4)	0.838(4)	0.664(6)	1.5(12)
H(4)	0.446(4)	0.950(4)	0.734(6)	1.1(11)
H(5)	0.431(4)	1.041(3)	0.978(6)	1.0(12)
H(7A)	0.281(4)	1.063(4)	1.178(6)	1.4(12)
H(7B)	0.208(4)	1.006(4)	1.135(6)	1.5(12)
H(8A)	0.230(4)	1.175(4)	1.046(6)	0.8(11)
H(8B)	0.150(4)	1.134(4)	1.092(6)	0.8(11)
H(10)	0.062(3)	1.046(3)	0.873(6)	0.8(11)
H(11)	0.079(4)	0.960(4)	0.633(6)	0.9(11)
H(13)	0.301(4)	1.089(4)	0.537(6)	0.9(11)
H(14)	0.284(4)	1.177(4)	0.771(7)	1.5(12)

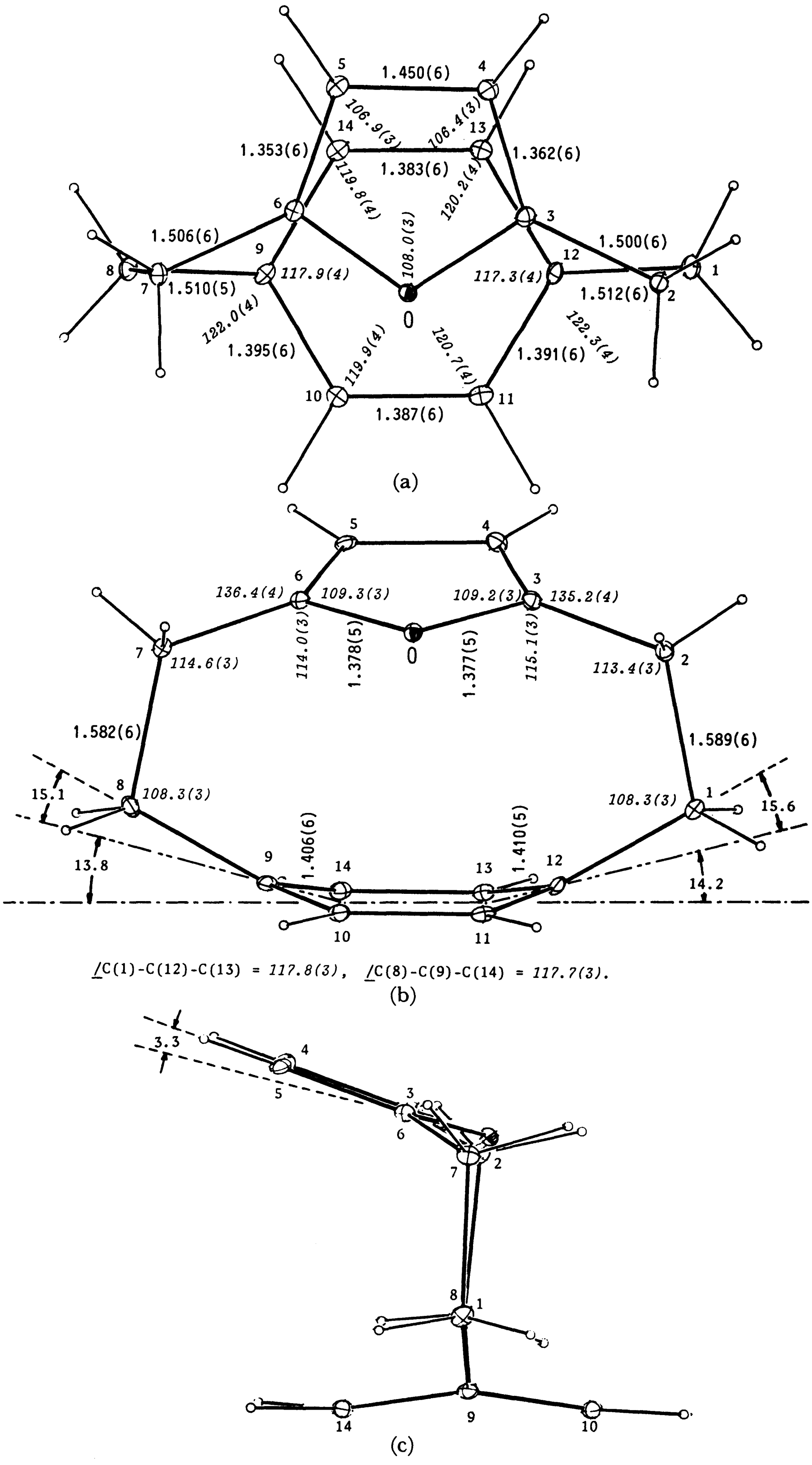


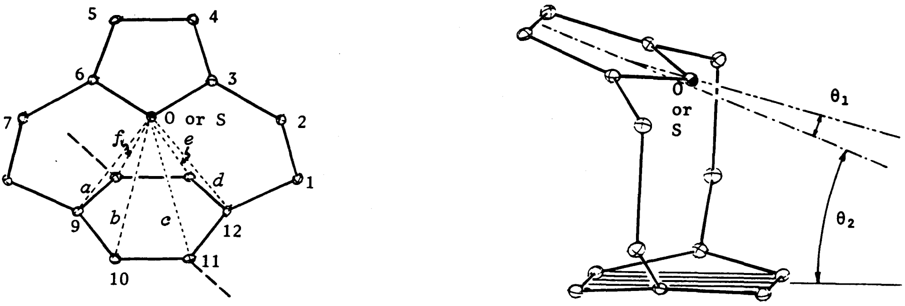
Fig. 2. Molecular structure (*ORTEP* drawing)[7] with bond distances, bond angles and other structural parameters at −150 °C. Estimated standard deviations in parentheses.

(a) Projection onto the plane defined by the C(10), C(11), C(13), and C(14) atoms.

(b) Projection onto the plane defined by the C(1), C(2), C(7), and C(8) atoms. Structural parameters given in Fig. 2(a) are omitted.

(C) Projection along the plane defined by the C(10), C(11), C(13), and C(14) atoms.

TABLE 2. COMPARISON OF SOME STRUCTURAL PARAMETERS OF DOUBLE- AND TRIPLE- LAYERED PARACYCLOFURANOPHANES (F-X AND F-D-X) AND DIMETHYL TRIPLE- LAYERED PARACYCLOTHIOPHENOPHANE(T-D-D)



	Dihedral angle (ϕ/°)		Intramolecular atomic contact (l/Å)					
	θ_1	θ_2	a	b	c	d	e	f
					(O····C)			
F-X^a (**1**) (−150°C)	3.3	20.6	2.833(5)	2.909(5)	2.916(5)	2.851(5)	3.072(4)	3.062(4)
(20°C)	3.4	20.9	2.840(7)	2.902(8)	2.921(7)	2.866(7)	3.070(7)	3.058(7)
F-D-X$^{b,c)}$ (**3**) (20°C)	3.8	18.6	2.860	2.927	3.054	2.820	3.012	3.174
					(S····C)			
T-D-D^b (**4**) (20°C)	8.3	6.8	3.123(3)	3.044(3)	3.196(3)	3.124(3)	3.438(3)	3.597(3)

a: present study; b: reference 2; c: average of three independent molecules

show the out-of-plane deformation of heteroaromatic ring (θ_1), relative position of the heteroaromatic ring to the benzene ring next to it(θ_2), and nonbonded distances between the heteroatom and benzene carbon atoms (a to f) in double- and triple-layered paracyclofuranophane and triple-layered paracyclothiophenophane molecules.

The marked difference between the molecular structures of double- and triple-layered paracyclofuranophanes is that c and f distances in the triple-layered one are much longer than those in the double-layered one. On the other hand, a, b, d, and e distances in these two molecules have respectively similar values. This feature is due to the structural difference of the benzene ring next to the furan ring in these molecules; boat form in the double-layered one and twisted form in the triple-layered one. This is probably the most important structural factor to lower the energy barrier of the ring inversion of the furan in triple- and quadruple-layered paracyclofuranophane compared with the double-layered one.

Crystal Structure. Figure 3 shows the crystal structure of double-layered paracyclofuranophane. Molecules are loosely packed in the crystal. Only one or two intermolecular atomic contacts are less than 3.8 Å: the closest one being C(5)(x,y,z)····C(4) (−0.5+y, 0.5+x, 0.5+z)[3.727(9)(20 °C) and 3.667(6) Å (−150 °C)].

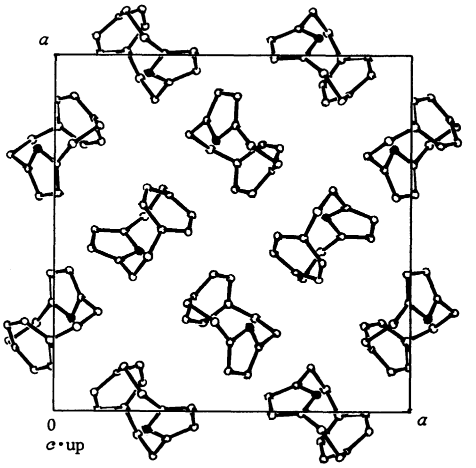


Fig. 3. Crystal structure viewed down along the c axis (*ORTEP* drawing).[7]
Carbon and oxygen atoms are respectively represented by white and black ellipsoids. Hydrogen atoms omitted.

The authors wish to express their deep thanks to Professor Soichi Misumi and co-workers, Institute for Scientific and Industrial Research, Osaka University for crystals and helpfull discussions.

References

1) T. Otsubo, S. Mizogami, N. Osaka, Y. Sakata, and S. Misumi, *Bull. Chem. Soc. Jpn.*, **50**, 1841 (1977).
2) Y. Kai, T. Watanabe, N. Yasuoka, and N. Kasai, *Acta Crystallogr., Sect. B*, **36**, 2276 (1980).
3) P. Main, M. M. Woolfson, L. Lessinger, G. Germain, and J. P. Declercq, *MULTAN* 74, "A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data," Univs. of York, England and Louvain, Belgium (1974).
4) T. Ashida, *HBLS* V, "The Universal Crystallographic Computing System-Osaka," The Computation Center, Osaka Univ. (1973), p. 55.
5) International Tables for X-Ray Crystallography, Vol. IV, Kynoch Press, Birmingham (1974), p. 71.
6) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
7) C. K. Johnson, *ORTEP* II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee (1976).
8) W. C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959).