

isomerization reaction (Furukawa & Itaka, 1974). The other point of difference in the structures of (I) and (II) is found at ring C. As can be seen in Fig. 2, the presence of the geminal methoxy and acetoxy groups at C(12), which lie at the *peri* position with respect to the hydroxyl group at C(11), indicates that the methanolysis reaction of triacetylkidamycin bis(trimethylammonium) iodide (III) [in which one of the acetoxy groups was at C(11)] takes place at C(12) by methoxylation; thereby the migration of the acetyl group from C(11) to C(12) is accomplished.

Comparison of the structures of (I) and (II), along with much chemical and spectroscopic evidence, has led to the structure of kidamycin as shown in Fig. 1, which constitutes a new class of polycyclic microbial metabolites.

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## Structural Chemistry of Layered Cyclophanes.

### VI. Molecular Structures of Triple-Layered [2.2]Paracyclophane Containing Furan and Thiophene Rings

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#### Abstract

The molecular structures of [2.2](2,5)furano(4,7)[2.2]-paracyclophane and 12,15-dimethyl[2.2](2,5)thiopheno(4,7)[2.2]paracyclophane have been determined by means of X-ray diffraction. The former is monoclinic, with  $a = 28.066$  (2),  $b = 16.018$  (1),  $c = 26.753$  (2) Å,  $\beta = 116.43$  (1)°, space group  $C2/c$ , and  $Z = 24$ ; the latter is also monoclinic, with  $a = 15.126$  (1),  $b = 10.342$  (1),  $c = 13.321$  (1) Å,  $\beta = 101.87$  (1)°, space group  $P2_1/c$ , and  $Z = 4$ . Both structures were solved by the direct method, and refined anisotropically by the least-squares procedure;  $R = 0.055$  for non-zero reflexions for the former and 0.066 for the latter. In both molecules, the furan or thiophene ring has an envelope shape, the outer

benzene ring is boat-shaped, and the inner benzene ring is twisted by two upper and two lower methylene bridges.

#### Introduction

Misumi and co-workers synthesized [2.2]paracyclophanes containing (2,5)-bridged five-membered heterocycles. By means of NMR studies at elevated temperature they found inversion of the furan ring but not of the thiophene ring, and they determined energy barriers for the furan-ring inversion. As part of a series of structural studies on layered cyclophanes and in order to obtain information on the ring inversion and the molecular structure, the X-ray structure determination of double- and triple-layered [2.2]paracyclophanes containing five-membered heterocycles has been carried out. This paper deals with the molecular structures of triple-layered [2.2]paracyclophanes containing furan and thiophene rings.

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## Experimental

### Crystal data

[2.2](2,5)Furano(4,7)[2.2]paracyclophane (triple-layered paracyclofuranophane hereafter),  $C_{24}H_{24}O$ ,  $M_r = 328.46$ , monoclinic, space group  $C2/c$ ,  $a = 28.066$  (2),  $b = 16.018$  (1),  $c = 26.753$  (2) Å,  $\beta = 116.43$  (1)°,  $V = 10\,769.9$  (16) Å<sup>3</sup>,  $D_m = 1.20$ ,  $Z = 24$ ,  $D_c = 1.21$  Mg m<sup>-3</sup>. 12,15-Dimethyl[2.2](2,5)-thiopheno(4,7)[2.2]paracyclophane (dimethyl triple-layered paracyclothiophenophane hereafter),  $C_{26}H_{28}S$ ,  $M_r = 372.58$ , monoclinic, space group  $P2_1/c$ ,  $a = 15.126$  (1),  $b = 10.342$  (1),  $c = 13.321$  (1) Å,  $\beta = 101.87$  (1)°,  $V = 2039.3$  (3) Å<sup>3</sup>,  $D_c = 1.213$  Mg m<sup>-3</sup>,  $Z = 4$ .

Unit-cell dimensions and reflexion intensities were measured on a Rigaku automated four-circle diffractometer with graphite-monochromatized Cu K $\alpha$  radiation. Intensities were collected by the  $\theta$ - $2\theta$  scan technique at a rate of 4° min<sup>-1</sup> in the range  $\Delta 2\theta = (1.6 + 0.3 \tan \theta)$ °. Backgrounds were counted for 5 s before and after the scan of each peak. Totals of 8204 (6529 non-zero) and 3030 (2815 non-zero) unique data were collected up to  $2\theta = 120^\circ$  respectively for  $C_{24}H_{24}O$  and  $C_{26}H_{28}S$ ; these were corrected for the Lp effect but not for absorption [ $\mu$ (Cu K $\alpha$ ) = 0.556 and 1.40 mm<sup>-1</sup>].

### Structure solution and refinement

Both structures were solved by the direct method (*MULTAN*, Germain, Main & Woolfson, 1971), and refined by the block-diagonal least-squares procedure (*HBL5* V, Ashida, 1973) with anisotropic temperature factors for non-hydrogen atoms and isotropic for H.

### Triple-layered paracyclofuranophane

Of the two possible space groups  $C2/c$  and  $Cc$  determined by the systematic absences of the reflexions,  $C2/c$  was assumed to be correct; this was later confirmed by the structure determination. Since the space group is  $C2/c$  and the number of molecules per unit cell is 24, three independent molecules are contained in an asymmetric unit. From the  $E$  map calculated using 498  $|E|$  values greater than 1.8, 75 non-hydrogen atoms were located. Six cycles of isotropic refinement with 2916 reflexions gave an  $R$  index of 0.139. After four cycles of anisotropic refinement with 3435 reflexions a difference Fourier map revealed all the H atoms. The H atoms with isotropic temperature factors were then included in the refinement, 6344 reflexions being used. The final  $R$  was 0.055 for non-zero (0.081 for all) reflexions, and

$R_w = 0.073$ . The weighting schemes used were  $w = 1$  for  $|F_o| < F_{max}$ ,  $w = F_{max}/|F_o|$  for  $|F_o| > F_{max}$ , and  $w = F_{wt}$  for  $|F_o| = 0$ , where  $F_{max} = 7.0$  and  $F_{wt} = 0.2$ . The atomic scattering factors used for O and C atoms were taken from *International Tables for X-ray Crystallography* (1974) and those of H from Stewart, Davidson & Simpson (1965). The final atomic parameters are listed in Table 1.\*

### Dimethyl triple-layered paracyclothiophenophane

The weighting schemes used in the refinement were:  $w = [\sigma^2(F_o) + a|F_o| + b|F_o|^2]^{-1}$  for  $|F_o| > 0$  and  $w = c$  for  $|F_o| = 0$ . The final  $R$  value was 0.066 for 3030

\* Lists of structure factors and anisotropic thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35273 (51 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

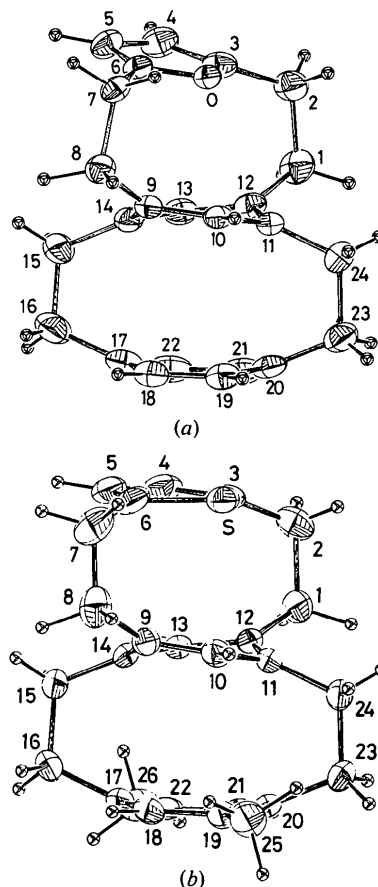


Fig. 1. Molecular structures with the numbering schemes of the atoms. Thermal ellipsoids for non-hydrogen atoms are drawn at the 50% probability level. H atoms are shown as spheres with radii of 0.1 Å. (a) Triple-layered paracyclofuranophane. In the numbering, the last digits (which indicate independent molecules 1, 2 or 3) are omitted for clarity. (b) Dimethyl triple-layered paracyclothiophenophane.

non-zero (0.071 for all) reflexions, and  $R_w = 0.103$  with  $a = -0.0982$ ,  $b = 0.0080$ ,  $c = 1.2520$ . Atomic scattering factors for S and C were taken from Hanson, Herman, Lea & Skillman (1964), and for H from Stewart, Davidson & Simpson (1965). The final atomic parameters are listed in Table 2.\*

\* See previous footnote.

## Results and discussion

### Triple-layered paracyclofuranophane

Interatomic bond distances and bond angles are listed in Table 3. Almost all the corresponding bond distances and bond angles in the three independent molecules, except C(4)–C(5) and C(17)–C(22), and

Table 1. Fractional atomic coordinates ( $\times 10^4$ , for H  $\times 10^3$ ) and isotropic thermal parameters of triple-layered paracyclofuranophane with e.s.d.'s in parentheses

$B_{eq}$  is as defined in Hamilton (1959).

Molecule (1)				Molecule (2)					
x	y	z	$B_{eq}/B$ ( $\text{\AA}^2$ )	x	y	z	$B_{eq}/B$ ( $\text{\AA}^2$ )		
O(1)	2972 (1)	2471 (1)	1981 (1)	3.8	O(2)	1392 (1)	3128 (1)	3025 (1)	4.0
C(11)	1732 (1)	2627 (3)	1679 (2)	5.9	C(12)	1039 (1)	4633 (2)	3574 (2)	5.2
C(21)	2172 (1)	1948 (2)	1999 (2)	5.6	C(22)	1308 (1)	4590 (2)	3171 (2)	4.8
C(31)	2581 (1)	1871 (2)	1785 (2)	4.7	C(32)	1660 (1)	3850 (2)	3271 (1)	4.1
C(41)	2650 (2)	1409 (2)	1397 (2)	5.8	C(42)	2174 (1)	3663 (2)	3590 (2)	4.8
C(51)	3088 (1)	1769 (2)	1331 (2)	4.9	C(52)	2228 (1)	2786 (2)	3561 (2)	5.0
C(61)	3265 (1)	2422 (2)	1684 (1)	4.1	C(62)	1745 (1)	2474 (2)	3223 (1)	4.3
C(71)	3649 (1)	3124 (2)	1797 (1)	4.2	C(72)	1488 (1)	1632 (2)	3066 (2)	4.7
C(81)	3400 (1)	3940 (2)	1461 (1)	4.6	C(82)	1239 (1)	1311 (2)	3449 (2)	5.1
C(91)	2836 (1)	3993 (2)	1380 (1)	3.7	C(92)	1045 (1)	2048 (2)	3651 (1)	3.7
C(101)	2724 (1)	4253 (2)	1810 (1)	3.7	C(102)	570 (1)	2445 (2)	3304 (1)	3.6
C(111)	2269 (1)	3989 (2)	1854 (1)	4.0	C(112)	483 (1)	3292 (2)	3358 (1)	3.5
C(121)	1988 (1)	3325 (2)	1505 (1)	4.3	C(122)	935 (1)	3757 (2)	3702 (1)	3.8
C(131)	2034 (1)	3229 (2)	1014 (1)	4.4	C(132)	1347 (1)	3325 (2)	4129 (1)	4.1
C(141)	2421 (1)	3622 (2)	913 (1)	4.0	C(142)	1381 (1)	2464 (2)	4144 (1)	4.0
C(151)	2354 (2)	3723 (2)	327 (1)	5.6	C(152)	1719 (1)	2029 (3)	4694 (2)	5.8
C(161)	2123 (2)	4602 (3)	80 (2)	7.2	C(162)	1383 (2)	1781 (3)	5005 (2)	6.2
C(171)	1856 (1)	5027 (2)	394 (1)	5.3	C(172)	861 (1)	2243 (2)	4799 (1)	4.7
C(181)	2132 (1)	5622 (2)	798 (1)	4.8	C(182)	400 (1)	1872 (2)	4399 (1)	4.5
C(191)	2009 (1)	5761 (2)	1239 (1)	4.6	C(192)	-18 (1)	2359 (2)	4037 (1)	4.3
C(201)	1612 (1)	5302 (2)	1289 (2)	4.7	C(202)	14 (1)	3221 (2)	4066 (1)	4.3
C(211)	1266 (1)	4867 (2)	818 (2)	5.6	C(212)	421 (1)	3565 (2)	4538 (1)	4.7
C(221)	1384 (1)	4730 (2)	377 (2)	6.0	C(222)	837 (1)	3084 (2)	4905 (1)	5.0
C(231)	1633 (1)	5141 (2)	1851 (2)	5.7	C(232)	-290 (1)	3741 (2)	3556 (2)	5.0
C(241)	2067 (2)	4477 (2)	2203 (2)	5.7	C(242)	-73 (1)	3649 (2)	3109 (1)	4.8
H(11A)	143 (2)	234 (3)	134 (2)	6.4 (11)	H(12A)	129 (2)	494 (3)	395 (2)	5.4 (10)
H(11B)	158 (1)	286 (2)	194 (1)	4.0 (8)	H(12B)	71 (1)	495 (2)	338 (1)	4.6 (9)
H(21A)	239 (1)	214 (2)	244 (2)	5.0 (9)	H(22A)	100 (1)	458 (2)	274 (2)	4.8 (9)
H(21B)	200 (1)	134 (2)	198 (1)	4.0 (8)	H(22B)	152 (1)	512 (2)	323 (1)	2.7 (7)
H(41)	242 (2)	90 (3)	116 (2)	6.4 (11)	H(42)	247 (1)	413 (2)	384 (2)	5.2 (10)
H(51)	322 (1)	160 (2)	105 (1)	4.5 (9)	H(52)	256 (1)	242 (2)	377 (2)	5.0 (10)
H(71A)	396 (1)	295 (2)	172 (1)	2.3 (7)	H(72A)	175 (1)	121 (2)	307 (2)	5.2 (10)
H(71B)	382 (1)	329 (2)	223 (1)	3.3 (8)	H(72B)	116 (1)	165 (2)	264 (1)	4.4 (9)
H(81A)	361 (1)	442 (2)	170 (2)	5.2 (10)	H(82A)	92 (1)	92 (2)	320 (1)	3.9 (8)
H(81B)	342 (1)	392 (2)	105 (1)	2.3 (7)	H(82B)	153 (1)	98 (2)	378 (1)	4.1 (9)
H(101)	299 (1)	465 (2)	214 (1)	2.8 (7)	H(102)	27 (1)	209 (2)	296 (1)	3.4 (8)
H(131)	176 (1)	284 (2)	69 (1)	4.2 (9)	H(132)	166 (1)	365 (2)	447 (1)	3.4 (8)
H(151A)	212 (2)	327 (3)	8 (2)	6.6 (11)	H(152A)	202 (2)	242 (2)	494 (2)	5.2 (10)
H(151B)	271 (1)	363 (2)	31 (2)	5.0 (10)	H(152B)	190 (2)	147 (3)	462 (2)	6.4 (11)
H(161A)	244 (2)	499 (3)	11 (2)	8.6 (14)	H(162A)	132 (2)	114 (3)	492 (2)	6.1 (11)
H(161B)	185 (2)	449 (3)	-33 (2)	7.0 (12)	H(162B)	162 (2)	190 (3)	545 (2)	5.7 (10)
H(181)	246 (1)	590 (2)	80 (1)	3.6 (8)	H(182)	38 (1)	124 (2)	434 (1)	4.0 (8)
H(191)	225 (1)	613 (2)	156 (1)	3.5 (8)	H(192)	-34 (1)	208 (2)	370 (1)	3.8 (8)
H(211)	94 (1)	458 (2)	83 (2)	4.5 (9)	H(212)	43 (1)	422 (2)	458 (2)	5.0 (10)
H(221)	116 (1)	435 (2)	5 (1)	4.1 (9)	H(222)	117 (1)	338 (2)	523 (2)	4.6 (9)
H(231A)	127 (1)	490 (2)	180 (1)	3.7 (8)	H(232A)	-26 (1)	439 (2)	368 (1)	4.0 (8)
H(231B)	175 (1)	569 (2)	212 (2)	4.9 (9)	H(232B)	-69 (2)	359 (3)	336 (2)	5.8 (10)
H(241A)	240 (1)	482 (2)	252 (1)	3.8 (8)	H(242A)	-32 (1)	326 (2)	279 (1)	4.3 (9)
H(241B)	189 (1)	411 (2)	237 (1)	4.4 (9)	H(242B)	-9 (1)	424 (2)	292 (1)	3.3 (8)

Table 1 (cont.)

Molecule (3)	x	y	z	$B_{eq}/B$ (Å <sup>2</sup> )
O(3)	3995 (1)	4376 (1)	3095 (1)	3.6
C(13)	3741 (1)	2677 (2)	3559 (1)	4.7
C(23)	3387 (1)	3441 (2)	3233 (1)	4.2
C(33)	3676 (1)	4256 (2)	3359 (1)	3.8
C(43)	3748 (1)	4898 (2)	3709 (2)	4.9
C(53)	4146 (1)	5429 (2)	3682 (2)	4.9
C(63)	4295 (1)	5078 (2)	3315 (1)	3.9
C(73)	4726 (1)	5215 (2)	3138 (1)	4.5
C(83)	5245 (1)	4690 (2)	3470 (1)	4.3
C(93)	5090 (1)	3873 (2)	3635 (1)	3.7
C(103)	4864 (1)	3239 (2)	3249 (1)	3.5
C(113)	4510 (1)	2659 (2)	3282 (1)	3.6
C(123)	4307 (1)	2852 (2)	3662 (1)	3.7
C(133)	4621 (1)	3344 (2)	4115 (1)	3.7
C(143)	5048 (1)	3805 (2)	4140 (1)	3.8
C(153)	5474 (1)	4098 (2)	4702 (1)	5.4
C(163)	5924 (2)	3441 (3)	4989 (2)	6.4
C(173)	5783 (1)	2587 (2)	4720 (1)	5.0
C(183)	5926 (1)	2368 (2)	4298 (1)	4.4
C(193)	5638 (1)	1790 (2)	3899 (1)	4.4
C(203)	5195 (1)	1408 (2)	3902 (2)	4.8
C(213)	5136 (1)	1488 (2)	4392 (2)	5.7
C(223)	5429 (1)	2073 (3)	4798 (2)	5.8
C(233)	4740 (2)	1105 (2)	3369 (2)	6.2
C(243)	4408 (1)	1834 (2)	2976 (1)	4.7
H(13A)	374 (2)	264 (3)	396 (2)	6.0 (11)
H(13B)	358 (1)	217 (2)	332 (1)	3.3 (8)
H(23A)	324 (1)	332 (2)	280 (1)	3.7 (8)
H(23B)	309 (1)	350 (2)	334 (1)	4.2 (9)
H(43)	355 (1)	497 (2)	395 (1)	3.2 (8)
H(53)	429 (1)	593 (2)	392 (1)	3.2 (8)
H(73A)	482 (1)	581 (2)	316 (1)	4.4 (9)
H(73B)	456 (1)	505 (2)	270 (1)	3.5 (8)
H(83A)	541 (1)	456 (2)	320 (1)	3.1 (7)
H(83B)	550 (1)	504 (2)	384 (1)	3.8 (8)
H(103)	496 (1)	323 (2)	291 (2)	3.6 (8)
H(133)	453 (1)	341 (2)	446 (1)	3.0 (7)
H(153A)	529 (1)	421 (2)	498 (2)	5.3 (10)
H(153B)	563 (2)	464 (2)	468 (2)	5.4 (10)
H(163A)	626 (2)	373 (3)	496 (2)	6.6 (11)
H(163B)	601 (2)	343 (3)	539 (2)	7.7 (13)
H(183)	619 (1)	270 (2)	425 (1)	4.4 (9)
H(193)	573 (1)	167 (2)	356 (1)	2.9 (7)
H(213)	482 (1)	114 (2)	441 (2)	4.6 (9)
H(223)	536 (2)	216 (3)	515 (1)	7.7 (13)
H(233A)	449 (1)	78 (2)	348 (2)	4.6 (9)
H(233B)	486 (1)	73 (2)	315 (2)	4.7 (9)
H(243A)	451 (2)	191 (3)	264 (2)	6.3 (11)
H(243B)	401 (1)	164 (2)	280 (1)	4.0 (9)

C(10)–C(11)–C(24), C(14)–C(15)–C(16), and C(15)–C(16)–C(17), are equal within the limits of error. There are no essential differences between these three molecules; the discussion, therefore, will be of the average structure (Table 3) unless otherwise stated. A perspective view of the molecule with the numbering scheme of the atoms is shown in Fig. 1 (ORTEP II, Johnson, 1976). A remarkable distortion of the benzene rings from a regular hexagon is observed. The outer benzene ring is boat-shaped as in the case of many other cyclophanes. The C(18)–C(19)–C(20) and

Table 2. Fractional atomic coordinates ( $\times 10^4$ , for H  $\times 10^3$ ) and isotropic thermal parameters of dimethyl triple-layered paracyclothiophenophane with e.s.d.'s in parentheses

$B_{eq}$ is as defined in Hamilton (1959).				
	x	y	z	$B_{eq}/B$ (Å <sup>2</sup> )
S	8586.6 (5)	3698.5 (8)	2374.8 (6)	5.2
C(1)	6764 (2)	3805 (3)	3624 (3)	5.3
C(2)	7484 (3)	4894 (3)	3503 (3)	7.0
C(3)	8400 (2)	4365 (3)	3497 (3)	5.5
C(4)	9077 (2)	3994 (4)	4276 (3)	6.5
C(5)	9680 (2)	3100 (4)	3989 (3)	6.4
C(6)	9475 (2)	2764 (4)	2983 (3)	5.9
C(7)	9741 (2)	1611 (5)	2444 (4)	8.4
C(8)	9088 (2)	434 (4)	2353 (3)	6.8
C(9)	8216 (2)	770 (3)	2681 (2)	4.3
C(10)	7467 (2)	1234 (2)	2004 (2)	4.0
C(11)	6812 (2)	1997 (2)	2310 (2)	4.0
C(12)	7044 (2)	2499 (3)	3317 (2)	3.8
C(13)	7667 (2)	1789 (3)	4009 (2)	3.7
C(14)	8189 (2)	820 (3)	3733 (2)	3.9
C(15)	8619 (2)	–184 (3)	4504 (2)	5.1
C(16)	8048 (2)	–1483 (3)	4389 (3)	5.8
C(17)	7074 (2)	–1254 (3)	3855 (3)	5.0
C(18)	6824 (2)	–1520 (3)	2817 (3)	5.4
C(19)	6114 (2)	–910 (3)	2166 (3)	5.0
C(20)	5650 (2)	47 (3)	2598 (2)	5.0
C(21)	5791 (2)	109 (3)	3652 (2)	5.1
C(22)	6481 (2)	–548 (3)	4293 (3)	5.1
C(23)	5187 (2)	1159 (3)	1954 (2)	5.8
C(24)	5888 (2)	2137 (3)	1640 (2)	4.9
C(25)	5935 (3)	–1159 (3)	1023 (3)	6.6
C(26)	6646 (3)	–300 (4)	5452 (3)	7.1
H(1A)	672 (1)	380 (2)	441 (2)	4.4 (7)
H(1B)	614 (2)	405 (3)	320 (2)	5.8 (7)
H(2A)	754 (2)	554 (3)	414 (2)	6.5 (8)
H(2B)	725 (2)	538 (3)	281 (2)	6.8 (8)
H(4)	912 (2)	431 (3)	503 (2)	6.3 (8)
H(5)	1021 (2)	274 (3)	451 (2)	6.8 (8)
H(7A)	1037 (2)	130 (3)	283 (2)	7.5 (9)
H(7B)	975 (2)	186 (3)	170 (2)	6.9 (8)
H(8A)	945 (2)	–35 (3)	287 (2)	7.1 (8)
H(8B)	893 (2)	11 (3)	155 (2)	6.2 (8)
H(10)	742 (1)	101 (2)	123 (2)	4.0 (6)
H(13)	775 (1)	204 (2)	480 (2)	4.5 (6)
H(15A)	866 (2)	20 (3)	525 (2)	5.6 (7)
H(15B)	929 (2)	–400 (3)	441 (2)	5.3 (7)
H(16A)	810 (2)	–186 (3)	512 (2)	6.2 (8)
H(16B)	834 (2)	–215 (3)	398 (2)	5.4 (7)
H(18)	726 (2)	–219 (2)	251 (2)	4.7 (8)
H(21)	537 (2)	76 (3)	399 (2)	5.5 (7)
H(23A)	481 (2)	170 (3)	244 (2)	6.9 (8)
H(23B)	476 (2)	85 (3)	131 (2)	5.6 (7)
H(24A)	595 (2)	200 (3)	89 (2)	5.6 (7)
H(24B)	564 (2)	305 (3)	166 (2)	4.9 (7)
H(25A)	650 (2)	–153 (3)	82 (2)	6.5 (8)
H(25B)	540 (2)	–183 (3)	83 (2)	6.5 (8)
H(25C)	575 (2)	–320 (3)	61 (2)	6.6 (8)
H(26A)	719 (2)	37 (3)	567 (2)	6.1 (7)
H(26B)	607 (2)	10 (3)	567 (2)	6.2 (8)
H(26C)	681 (2)	–117 (3)	586 (2)	6.8 (8)

C(17)–C(22)–C(21) angles in the triple-layered paracyclofuranophane have normal values. The inner benzene ring is twisted by two upper and two lower

Table 3. *Interatomic bond distances (Å) and bond angles (°) with e.s.d.'s in parentheses*

	Triple-layered paracyclofuranophane				Average	Dimethyl triple-layered paracyclothiophenophane
	Molecule (1)	Molecule (2)	Molecule (3)			
O—C(3)	1.375 (5)	1.378 (4)	1.377 (4)	1.377		
O—C(6)	1.374 (4)	1.376 (4)	1.370 (4)	1.373		
S—C(3)					1.722 (4)	
S—C(6)					1.717 (4)	
C(3)—C(4)	1.357 (6)	1.344 (5)	1.346 (5)	1.349	1.355 (5)	
C(5)—C(6)	1.348 (5)	1.346 (6)	1.349 (5)	1.348	1.356 (6)	
C(4)—C(5)	1.439 (6)	1.418 (6)	1.433 (6)	1.430	1.406 (5)	
C(1)—C(2)	1.581 (7)	1.571 (6)	1.573 (5)	1.575	1.598 (5)	
C(7)—C(8)	1.565 (5)	1.560 (6)	1.570 (5)	1.565	1.557 (6)	
C(15)—C(16)	1.568 (7)	1.561 (6)	1.560 (6)	1.563	1.588 (5)	
C(23)—C(24)	1.577 (6)	1.573 (6)	1.570 (6)	1.573	1.583 (5)	
C(2)—C(3)	1.500 (6)	1.488 (5)	1.495 (5)	1.494	1.491 (5)	
C(6)—C(7)	1.494 (5)	1.499 (6)	1.498 (5)	1.497	1.489 (6)	
C(1)—C(12)	1.510 (6)	1.503 (5)	1.512 (5)	1.508	1.497 (4)	
C(8)—C(9)	1.500 (5)	1.500 (5)	1.506 (5)	1.502	1.513 (5)	
C(11)—C(24)	1.506 (6)	1.511 (5)	1.512 (5)	1.510	1.502 (4)	
C(14)—C(15)	1.502 (6)	1.521 (6)	1.520 (5)	1.514	1.511 (4)	
C(16)—C(17)	1.514 (7)	1.503 (6)	1.514 (6)	1.510	1.517 (5)	
C(20)—C(23)	1.499 (6)	1.498 (6)	1.509 (7)	1.502	1.517 (5)	
C(9)—C(10)	1.385 (5)	1.392 (5)	1.385 (5)	1.387	1.381 (4)	
C(10)—C(11)	1.399 (5)	1.398 (5)	1.391 (5)	1.396	1.393 (4)	
C(11)—C(12)	1.404 (5)	1.404 (5)	1.405 (5)	1.404	1.414 (4)	
C(12)—C(13)	1.385 (5)	1.395 (5)	1.385 (5)	1.388	1.385 (4)	
C(13)—C(14)	1.383 (5)	1.381 (5)	1.384 (5)	1.383	1.373 (4)	
C(9)—C(14)	1.406 (5)	1.403 (5)	1.409 (5)	1.406	1.410 (4)	
C(17)—C(18)	1.392 (6)	1.387 (5)	1.401 (5)	1.393	1.385 (5)	
C(18)—C(19)	1.385 (6)	1.383 (5)	1.372 (5)	1.380	1.385 (5)	
C(19)—C(20)	1.390 (6)	1.383 (5)	1.388 (6)	1.387	1.404 (5)	
C(20)—C(21)	1.388 (6)	1.386 (6)	1.399 (6)	1.391	1.378 (5)	
C(21)—C(22)	1.378 (6)	1.378 (6)	1.393 (6)	1.383	1.383 (5)	
C(17)—C(22)	1.389 (6)	1.399 (6)	1.378 (6)	1.389	1.376 (5)	
C(19)—C(25)					1.512 (5)	
C(22)—C(26)					1.534 (5)	
C(3)—O—C(6)	108.7 (3)	108.0 (3)	108.1 (3)	108.3	93.89 (18)	
C(3)—S—C(6)					111.8 (3)	
C(2)—C(1)—C(12)	108.3 (4)	108.5 (3)	108.1 (3)	108.3	113.3 (3)	
C(1)—C(2)—C(3)	113.3 (4)	113.2 (3)	114.1 (3)	113.5		
O—C(3)—C(2)	114.5 (3)	114.0 (3)	114.7 (3)	114.4		
O—C(3)—C(4)	108.2 (4)	108.6 (3)	108.7 (3)	108.5		
S—C(3)—C(2)					118.1 (3)	
S—C(3)—C(4)					108.5 (3)	
C(2)—C(3)—C(4)	136.9 (4)	137.0 (4)	136.3 (3)	136.7	131.1 (3)	
C(3)—C(4)—C(5)	107.2 (4)	107.3 (4)	107.2 (3)	107.2	114.2 (4)	
C(4)—C(5)—C(6)	107.0 (4)	107.7 (4)	106.9 (4)	107.2	114.4 (4)	
O—C(6)—C(5)	108.8 (3)	108.3 (3)	108.9 (3)	108.7		
O—C(6)—C(7)	113.9 (3)	113.7 (3)	114.3 (3)	114.0		
S—C(6)—C(5)					108.7 (3)	
S—C(6)—C(7)					119.1 (3)	
C(5)—C(6)—C(7)	137.1 (4)	137.5 (4)	136.4 (4)	137.0	130.6 (4)	
C(6)—C(7)—C(8)	114.5 (3)	114.3 (3)	114.7 (3)	114.5	115.7 (4)	
C(7)—C(8)—C(9)	107.7 (3)	108.6 (3)	108.4 (3)	108.2	112.0 (3)	
C(8)—C(9)—C(10)	120.9 (3)	120.9 (3)	120.9 (3)	120.9	122.5 (3)	
C(8)—C(9)—C(14)	120.4 (3)	120.8 (3)	120.4 (3)	120.5	120.0 (2)	
C(10)—C(9)—C(14)	117.4 (3)	117.0 (3)	116.9 (3)	117.1	116.7 (3)	
C(9)—C(10)—C(11)	122.2 (3)	122.2 (3)	123.0 (3)	122.5	122.9 (3)	
C(10)—C(11)—C(12)	115.8 (3)	115.8 (3)	115.5 (3)	115.6	115.6 (3)	
C(10)—C(11)—C(24)	120.2 (3)	121.0 (3)	121.2 (3)	120.8	120.8 (3)	
C(12)—C(11)—C(24)	123.5 (3)	122.9 (3)	122.9 (3)	123.3	123.3 (3)	
C(11)—C(12)—C(13)	117.1 (3)	116.9 (3)	116.9 (3)	117.0	116.1 (3)	
C(1)—C(12)—C(11)	123.9 (4)	123.8 (3)	124.1 (3)	123.9	124.1 (3)	
C(1)—C(12)—C(13)	117.9 (4)	118.3 (3)	118.2 (3)	118.1	119.2 (3)	
C(12)—C(13)—C(14)	123.2 (3)	122.7 (3)	123.2 (3)	123.0	123.9 (3)	
C(13)—C(14)—C(15)	120.5 (3)	119.4 (3)	119.6 (3)	119.8	120.7 (3)	
C(9)—C(14)—C(13)	115.6 (3)	116.0 (3)	115.8 (3)	115.8	115.4 (3)	
C(9)—C(14)—C(15)	123.6 (3)	124.2 (3)	124.0 (3)	123.9	123.7 (3)	
C(14)—C(15)—C(16)	111.9 (4)	111.6 (3)	112.8 (3)	112.1	111.5 (3)	
C(15)—C(16)—C(17)	112.5 (4)	113.8 (4)	113.1 (3)	113.1	111.7 (3)	
C(16)—C(17)—C(18)	120.0 (4)	120.2 (4)	120.1 (3)	120.2	118.4 (4)	
C(16)—C(17)—C(22)	121.9 (4)	121.6 (4)	121.5 (4)	121.7	122.6 (4)	
C(18)—C(17)—C(22)	116.9 (4)	116.8 (4)	117.3 (4)	117.0	117.5 (4)	
C(17)—C(18)—C(19)	120.6 (4)	120.9 (4)	121.0 (4)	120.8	123.5 (4)	
C(18)—C(19)—C(20)	120.7 (4)	120.7 (4)	120.8 (4)	120.8	116.9 (3)	
C(19)—C(20)—C(21)	116.4 (4)	117.0 (4)	116.4 (4)	116.8	117.8 (3)	
C(19)—C(20)—C(23)	120.8 (4)	120.6 (4)	121.4 (4)	120.9	121.0 (3)	
C(21)—C(20)—C(23)	121.5 (4)	120.9 (4)	120.7 (4)	121.0	119.8 (3)	
C(20)—C(21)—C(22)	121.4 (4)	121.4 (4)	121.2 (4)	121.3	123.0 (4)	
C(17)—C(22)—C(21)	120.4 (4)	120.1 (4)	120.0 (4)	120.2	118.3 (3)	
C(20)—C(23)—C(24)	113.0 (4)	112.6 (3)	113.2 (4)	112.9	112.2 (3)	
C(11)—C(24)—C(23)	112.6 (4)	112.0 (3)	112.0 (3)	112.2	111.9 (3)	

Table 3 (cont.)

	Dimethyl triple-layered paracyclothiophenophane
C(18)—C(19)—C(25)	120.5 (4)
C(20)—C(19)—C(25)	122.1 (3)
C(17)—C(22)—C(26)	122.0 (3)
C(21)—C(22)—C(26)	119.0 (3)

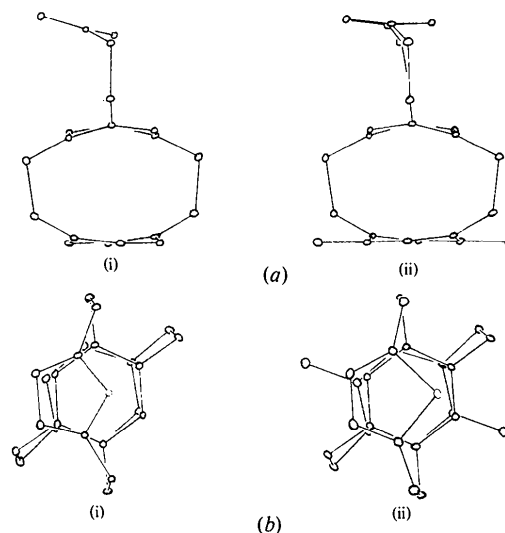


Fig. 2. Projections of the molecules. H atoms are omitted. Molecules projected (a) along the C(9)→C(12) vector, and (b) onto the plane containing the C(9)→C(12) and C(10)→C(14) vectors. (i) Triple-layered paracyclofuranophane. (ii) Dimethyl triple-layered paracyclothiophenophane.

methylene bridges (Fig. 2a), interatomic distances and bond angles being the same as those in the inner benzene rings in centrosymmetric tetramethyl quadruple-layered cyclophane (Mizuno, Nishiguchi, Toyoda, Otsubo, Misumi & Morimoto, 1977).

Although it seems that the corresponding bond distances and bond angles in the furan moiety differ only little from those in the furan molecule (Fourme, 1972) within the limits of error, the C(3)—C(4) and C(5)—C(6) distances (1.349 and 1.348 Å) and the O—C(3)—C(4) and O—C(6)—C(5) angles (108.5 and 108.7°) show a tendency to deviate from those in furan [1.322 (6) Å and 110.14 (40)°]. The deviation of the O atom from the best plane of the furan ring is 0.05–0.06 Å, which is more than 20 times larger than the deviations of the other atoms. It can be said that the furan ring is no longer planar. The furan ring is envelope-shaped and the O atom bent away from the inner benzene ring. The dihedral angle between the planes defined by O, C(3) and C(6) and C(3), C(4), C(5) and C(6) is 3.8°. The same structure has been found in the furan moiety in double-layered paracyclofuranophane (Hama, Kai, Yasuoka & Kasai, 1979).

*Dimethyl triple-layered paracyclothiophenophane*

An *ORTEP* (Johnson, 1976) drawing of the molecule with the atom numbering is given in Fig. 1. Interatomic distances and bond angles are given in Table 3.

In this molecule the distortion of the benzene rings from the regular hexagon is also remarkable, and is similar to that of the triple-layered paracyclofuranophane. Bond distances and bond angles in the outer and inner benzene rings are very similar to those in the outer *p*-dimethylbenzene and inner benzene rings in centrosymmetric tetramethyl quadruple-layered cyclophane (Mizuno *et al.*, 1977).

The thiophene ring has an envelope form, the S atom being bent away and the dihedral angle between the planes defined by S, C(3) and C(6), and C(3), C(4), C(5) and C(6) being  $8.0^\circ$  (Fig. 2). Four non-bonded S...C distances [S...C(9) 3.123 (3), S...C(10) 3.044 (3), S...C(11) 3.196 (3), and S...C(12) 3.124 (3) Å] are too short to allow the inversion of the thiophene ring. In the thiophene ring two S—C [1.722 (4) and 1.717 (4) Å] and two C—C distances [1.355 (5) and 1.356 (5) Å] are respectively equal to, but C(4)—C(5) [1.406 (5) Å] is shorter than, the corresponding distances in the free thiophene molecule (Bak, Christensen, Rastrup-Andersen & Tannenbaum, 1956). On the other hand, all the bond angles deviate from those in the free molecule.

*Crystal structure*

The crystal structures of triple-layered paracyclofuranophane and dimethyl triple-layered paracyclothiophenophane are shown in Fig. 3. In crystals of triple-layered paracyclofuranophane, 24 molecules (which comprise three kinds of independent molecules) are packed. Rather close intermolecular atomic contacts were observed between molecules 2, the closest being between those related by a twofold axis: C(242)(*x*, *y*, *z*)...C(24)(-*x*, *y*, 0.5 - *z*) = 3.462 (6) Å; and C(242)(*x*, *y*, *z*)...C(112)(-*x*, *y*, 0.5 - *z*) and C(112)(*x*, *y*, *z*)...C(242)(-*x*, *y*, 0.5 - *z*) = 3.611 (6) Å. In crystals of dimethyl triple-layered paracyclothiophenophane the closest atomic contacts were C(6)(*x*, *y*, *z*)...C(8)(2 - *x*, 0.5 + *y*, 0.5 - *z*) and C(8)(*x*, *y*, *z*)...C(6)(2 - *x*, 0.5 + *y*, 0.5 - *z*) [both 3.599 (6) Å].

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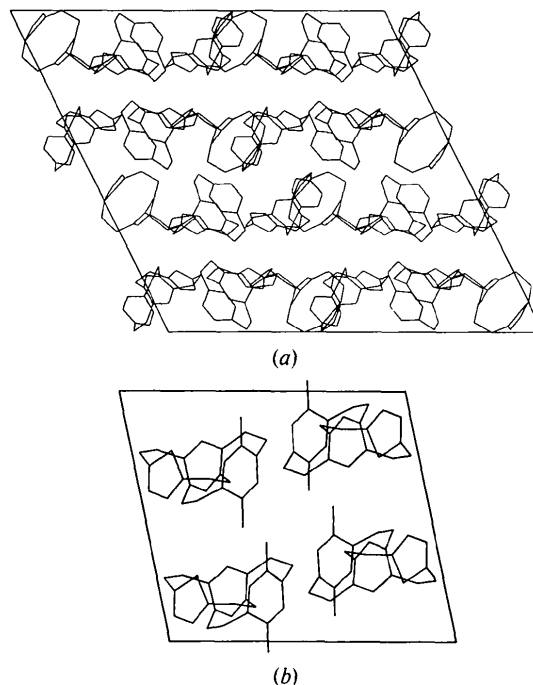


Fig. 3. Crystal structures projected along the *b* axis. (a) Triple-layered paracyclofuranophane. (b) Dimethyl triple-layered paracyclothiophenophane.

with the *ORTEP* drawings. Computations were carried out on an ACOS series 77 NEAC System 700 computer at Osaka University.

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