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Structure of Tris(2,4,6-trimethoxyphenyl)phosphine. Resolution of Space-Group Ambiguity by Solid-State NMR

BY G. NEMETH AND A. A. PINKERTON

Department of Chemistry, University of Toledo, Toledo, Ohio 43606, *USA*

AND J. A. STOWE AND C. A. OGLE

Department of Chemistry, University of North Carolina at Charlotte, Charlotte, North Carolina 28223, *USA*

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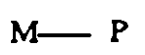
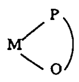
Abstract. $C_{27}H_{33}O_9P$, $M_r = 532.53$, monoclinic, Pn, $a = 8.0903$ (4), $b = 24.865$ (1), $c = 13.442$ (1) Å, $\beta = 96.79$ (1)°, $V = 2685$ (1) Å^3, $Z = 4$, $D_x = 1.32$ g cm^{-3}, λ(Mo $K\alpha$) = 0.70930 Å, $\mu = 1.5$ cm^{-1}, $F(000) = 1128$, $T = 294$ (1) K, $R = 0.036$ for 3368 unique observed reflections of 8609 total data. The observation of two ^{31}P signals in the cross-polarization magic-angle spinning (CP-MAS) NMR spectrum indicates that there are two molecules in the asymmetric unit and thus confirms the choice of space group. The two molecules are related by a pseudo-2_1 operation which leads to all $0k0$ with k odd reflections being only weakly observed. The molecules have the characteristic propeller shape of triarylphosphines.

Introduction. Tris(2,4,6-trimethoxyphenyl)phosphine (TMPP) has been reported to be an extremely basic and bulky phosphine (Wada & Higashizaki, 1984). Recent reports of the coordination chemistry of TMPP with transition-metal ions have demonstrated a number of different ligating modes: (1) monodentate (Wada & Higashizaki, 1984; Bowmaker, Cotton, Healy, Kildea, Silong, Skelton & White, 1989); (2) bidentate with one methoxy group also bound to the metal (Dunbar, Haefner & Swepston, 1991); (3) tridentate with the incorporation of two methoxy groups into the metal coordination sphere (Dunbar, Haefner & Pence, 1989; Dunbar, Haefner & Burzynski, 1990); (4) tridentate and bridging (Chen & Dunbar, 1991), but in this case the bridging methoxy group has been demethylated. Although the coordination chemistry of TMPP is well developed, there is no report of the structure of the parent phosphine.



(1)



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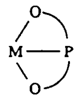

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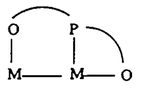

(4)

Experimental. TMPP was prepared from PCl_3 by a modification of the method in the literature (Wada & Higashizaki, 1984), and crystallized from tetrahydrofuran. Colorless plate, 0.30 × 0.26 × 0.18 mm, mounted on a glass fiber; Enraf–Nonius CAD-4 diffractometer; graphite monochromator; ω–2θ scan technique, backgrounds obtained from analysis of the scan profile (Blessing, Coppens & Becker, 1974); unit-cell constants from the setting angles of 25 reflections in the range $12 < \theta < 14°$; empirical absorption correction (from 0.973 to 0.999 on I); maximum $2\theta = 52.0°$; $0 < h < 9$, $-23 < k < 30$, $-16 < l < 16$; anisotropic decay (from 0.980 to 1.092 on I); reflection averaging gave $R_{\text{int}} = 1.9\%$; 8609 total reflections measured, 4761 unique, 3368 reflections with $F_o^2 > 3.0\sigma(F_o^2)$; solution by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); refinement by full-matrix least squares, function minimized $\sum w(|F_o| - |F_c|)^2$, weight w defined as $4F_o^2/\sigma^2(F_o^2)$; non-H atoms refined anisotropically, H atoms refined as riding atoms in calculated positions; 665 refined parameters; $R = 0.036$, $wR = 0.050$, $S = 1.59$; largest shift = 0.05σ; highest peak in final difference map 0.18 (4), lowest peak −0.06 (4) e Å^{-3}. Scattering factors for neutral atoms and the values for f' and f'' were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV); computer programs from *MolEN* (Fair, 1990).

Final atomic coordinates are reported in Table 1;* selected bond lengths, bond angles and torsion angles in Table 2. Fig. 1 prepared by *ORTEP* (Johnson, 1976). Chemagnetics CMC-200 NMR spectrometer, observation frequency 80.745842 MHz,

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, all bond lengths and angles and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55400 (46 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0412]

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Table 1. *Positional parameters and equivalent isotropic thermal parameters* ($Å^2$) *for tris(2,4,6-trimethoxyphenyl)phosphine with e.s.d.'s in parentheses*

$$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Molecule *A*				
P1*A*	0.000	0.58257 (4)	0.500	3.05 (2)
O1*A*	−0.1103 (4)	0.6845 (1)	0.5475 (2)	3.89 (7)
O2*A*	0.0928 (4)	0.7029 (1)	0.8903 (2)	4.24 (8)
O3*A*	0.2084 (4)	0.5439 (1)	0.7022 (2)	4.16 (7)
O4*A*	−0.1479 (5)	0.5035 (1)	0.6060 (2)	4.60 (8)
O5*A*	0.1006 (5)	0.3438 (1)	0.5005 (3)	5.54 (9)
O6*A*	0.2858 (5)	0.5189 (1)	0.4079 (3)	6.02 (9)
O7*A*	0.3702 (5)	0.6115 (1)	0.5557 (2)	4.83 (8)
O8*A*	0.4345 (6)	0.7027 (2)	0.2433 (3)	8.9 (1)
O9*A*	−0.0710 (6)	0.6177 (1)	0.2972 (2)	6.7 (1)
C1*A*	0.0480 (6)	0.6137 (1)	0.6241 (3)	2.93 (9)
C2*A*	−0.0254 (6)	0.6640 (1)	0.6338 (3)	2.93 (9)
C3*A*	−0.0083 (6)	0.6930 (1)	0.7225 (3)	3.39 (9)
C4*A*	0.0828 (6)	0.6710 (1)	0.8050 (3)	3.15 (9)
C5*A*	0.1554 (6)	0.6216 (1)	0.8020 (3)	3.21 (9)
C6*A*	0.1385 (6)	0.5931 (1)	0.7103 (3)	3.09 (9)
C7*A*	0.0690 (6)	0.5118 (1)	0.5090 (3)	2.89 (8)
C8*A*	−0.0332 (6)	0.4778 (2)	0.5576 (3)	3.5 (1)
C9*A*	−0.0177 (7)	0.4224 (2)	0.5554 (3)	4.1 (1)
C10*A*	0.0968 (7)	0.3998 (2)	0.5010 (3)	4.1 (1)
C11*A*	0.2005 (7)	0.4309 (2)	0.4535 (3)	3.9 (1)
C12*A*	0.1882 (7)	0.4865 (2)	0.4584 (3)	3.8 (1)
C13*A*	0.1444 (7)	0.6176 (1)	0.4289 (3)	3.4 (1)
C14*A*	0.3099 (7)	0.6301 (2)	0.4622 (3)	3.8 (1)
C15*A*	0.4151 (7)	0.6589 (2)	0.4046 (3)	4.6 (1)
C16*A*	0.3436 (8)	0.6736 (2)	0.3085 (3)	5.5 (1)
C17*A*	0.1827 (8)	0.6614 (2)	0.2721 (3)	5.5 (1)
C18*A*	0.0884 (7)	0.6335 (2)	0.3308 (3)	4.4 (1)
C19*A*	−0.1842 (8)	0.7367 (2)	0.5523 (3)	5.4 (1)
C20*A*	0.1865 (7)	0.6827 (2)	0.9778 (3)	5.2 (1)
C21*A*	0.3225 (7)	0.5239 (2)	0.7816 (3)	4.7 (1)
C22*A*	−0.2693 (8)	0.4723 (2)	0.6476 (4)	7.8 (2)
C23*A*	0.1915 (9)	0.3182 (2)	0.4327 (4)	8.1 (2)
C24*A*	0.4359 (8)	0.4996 (3)	0.3837 (5)	8.3 (2)
C25*A*	0.5359 (7)	0.6197 (2)	0.5956 (4)	6.7 (2)
C26*A*	0.579 (1)	0.7262 (3)	0.2838 (6)	11.4 (3)
C27*A*	−0.135 (1)	0.6271 (3)	0.1988 (4)	10.4 (2)
Molecule *B*				
*P*1*B*	0.5048 (2)	0.08351 (4)	0.06242 (7)	2.92 (2)
O1*B*	0.6153 (4)	0.1809 (1)	−0.0138 (2)	4.00 (7)
O2*B*	0.3937 (5)	0.1631 (1)	−0.3631 (2)	6.2 (1)
O3*B*	0.2886 (4)	0.0324 (1)	−0.1259 (2)	3.99 (7)
O4*B*	0.6689 (5)	−0.0006 (1)	−0.0261 (2)	5.35 (8)
O5*B*	0.3693 (6)	−0.1540 (1)	0.0801 (3)	6.3 (1)
O6*B*	0.2234 (5)	0.0227 (1)	0.1608 (3)	6.9 (1)
O7*B*	0.1351 (5)	0.1079 (1)	−0.0035 (2)	5.09 (8)
O8*B*	0.0398 (5)	0.2086 (1)	0.2903 (2)	5.89 (9)
O9*B*	0.5587 (5)	0.1274 (1)	0.2616 (2)	4.71 (8)
C1*B*	0.4582 (6)	0.1059 (1)	−0.0693 (2)	2.66 (8)
C2*B*	0.5275 (6)	0.1547 (1)	−0.0929 (3)	3.35 (9)
C3*B*	0.5112 (7)	0.1751 (2)	−0.1902 (3)	4.1 (1)
C4*B*	0.4169 (7)	0.1474 (2)	−0.2635 (3)	4.3 (1)
C5*B*	0.3379 (6)	0.1003 (2)	−0.2442 (3)	3.9 (1)
C6*B*	0.3605 (6)	0.0796 (1)	−0.1482 (3)	3.13 (9)
C7*B*	0.4432 (6)	0.0118 (1)	0.0646 (3)	3.32 (9)
C8*B*	0.5482 (6)	−0.0240 (2)	0.0211 (3)	3.8 (1)
C9*B*	0.5256 (7)	−0.0793 (2)	0.0238 (3)	4.3 (1)
C10*B*	0.4000 (7)	−0.1002 (2)	0.0716 (3)	4.4 (1)
C11*B*	0.2977 (8)	−0.0670 (2)	0.1182 (4)	5.1 (1)
C12*B*	0.3206 (7)	−0.0114 (2)	0.1143 (3)	3.9 (1)
C13*B*	0.3484 (6)	0.1200 (1)	0.1253 (3)	2.84 (8)
C14*B*	0.1860 (6)	0.1309 (2)	0.0869 (3)	3.20 (9)
C15*B*	0.0758 (7)	0.1601 (2)	0.1380 (3)	4.3 (1)
C16*B*	0.1341 (6)	0.1794 (2)	0.2324 (3)	4.0 (1)
C17*B*	0.2932 (7)	0.1690 (2)	0.2753 (3)	4.0 (1)
C18*B*	0.3989 (6)	0.1392 (1)	0.2238 (3)	3.4 (1)
C19*B*	0.6879 (8)	0.2320 (2)	−0.0329 (4)	5.9 (1)
C20*B*	0.4800 (8)	0.2080 (2)	−0.3912 (3)	6.3 (2)
C21*B*	0.1811 (7)	0.0053 (2)	−0.2002 (3)	5.0 (1)
C22*B*	0.7907 (8)	−0.0340 (2)	−0.0621 (5)	8.5 (2)
C23*B*	0.4823 (9)	−0.1901 (2)	0.0420 (5)	7.9 (2)
C24*B*	0.0762 (8)	0.0048 (3)	0.1969 (5)	9.8 (2)
C25*B*	−0.0291 (8)	0.1147 (2)	−0.0486 (4)	7.2 (2)
C26*B*	−0.1173 (8)	0.2290 (2)	0.2461 (4)	6.8 (2)
C27*B*	0.6141 (8)	0.1418 (2)	0.3625 (3)	5.5 (1)

Table 2. *Selected bond distances* (Å), *bond angles* (°) *and torsion angles* (°)

	Molecule *A*	Molecule *B*		Molecule *A*	Molecule *B*
P1—C1	1.838 (3)	1.852 (3)	C7—C8	1.398 (6)	1.405 (6)
P1—C7	1.846 (4)	1.852 (4)	C7—C12	1.394 (6)	1.385 (7)
P1—C13	1.817 (5)	1.842 (4)	C13—C14	1.396 (7)	1.381 (6)
C1—C2	1.399 (5)	1.388 (5)	C13—C18	1.400 (5)	1.421 (5)
C1—C6	1.393 (5)	1.407 (5)			
C1—P1—C7	108.2 (2)	106.3 (2)	P1—C7—C8	114.6 (3)	115.2 (3)
C1—P1—C13	101.3 (2)	102.6 (2)	P1—C7—C12	128.3 (3)	128.2 (3)
C7—P1—C13	106.5 (2)	105.4 (2)	C8—C7—C12	115.9 (3)	116.0 (3)
P1—C1—C2	114.5 (3)	116.1 (3)	P1—C13—C14	126.2 (3)	126.9 (3)
P1—C1—C6	129.4 (3)	127.8 (3)	P1—C13—C18	118.3 (4)	117.1 (3)
C2—C1—C6	116.0 (3)	116.1 (3)	C14—C13—C18	115.5 (4)	116.0 (4)

	Molecule *A*	Molecule *B*
C7—P1—C1—C2	−168.3 (2)	−166.3 (3)
C7—P1—C1—C6	7.8 (5)	14.0 (5)
C13—P1—C1—C2	80.0 (4)	83.3 (4)
C13—P1—C1—C6	−103.9 (4)	−96.5 (4)
C1—P1—C7—C8	74.9 (3)	72.4 (4)
C1—P1—C7—C12	−118.4 (4)	−116.5 (4)
C13—P1—C7—C8	−177.0 (3)	−179.2 (3)
C13—P1—C7—C12	−10.3 (4)	−8.0 (4)
C1—P1—C13—C14	41.7 (4)	36.9 (4)
C1—P1—C13—C18	−139.2 (3)	−142.9 (3)
C7—P1—C13—C14	−71.3 (4)	−74.2 (4)
C7—P1—C13—C18	107.8 (3)	106.0 (3)
C19—O1—C2—C1	−178.3 (4)	−179.0 (4)
C19—O1—C2—C3	−1.2 (6)	1.9 (7)
C20—O2—C4—C3	−179.4 (4)	4.2 (8)
C20—O2—C4—C5	1.2 (7)	−174.9 (5)
C21—O3—C6—C1	170.4 (4)	176.4 (4)
C21—O3—C6—C5	−10.3 (6)	−3.7 (6)
C22—O4—C8—C7	172.9 (4)	173.0 (4)
C22—O4—C8—C9	−6.9 (6)	−8.9 (6)
C23—O5—C10—C9	168.5 (5)	4.2 (7)
C23—O5—C10—C11	−13.0 (7)	−173.8 (5)
C24—O6—C12—C7	159.7 (5)	167.8 (5)
C24—O6—C12—C11	−24.6 (7)	−13.0 (7)
C25—O7—C14—C13	177.6 (4)	178.0 (4)
C25—O7—C14—C15	−1.0 (6)	2.0 (6)
C26—O8—C16—C15	−14.4 (8)	−11.6 (6)
C26—O8—C16—C17	165.2 (6)	169.7 (4)
C27—O9—C18—C13	−174.6 (5)	−175.4 (4)
C27—O9—C18—C17	4.3 (7)	6.3 (6)

decoupler frequency 199.485306 MHz; CP-MAS, time domain size 1024, contact time 5 ms.

Discussion. From the volume of the unit cell, it was clear that it comprised four molecules. The presence of an *n* glide was evident from the systematic absences and the 0*k*0, *k* = odd, reflections (Table 3) were either weak or absent; hence, a first choice for the space group was $P2_1/n$. Although a solution was obtained for the structure, the refinement was very poor ($R = 0.21$, unreasonable thermal parameters). Closer examination of the 0*k*0 reflections suggested that there was no screw axis, giving $P2/n$ or Pn as possible space groups. At this point, a ^{31}P CP-MAS NMR spectrum was obtained (Fig. 2) which clearly shows two signals indicating that there are either two independent molecules in the asymmetric unit (Davies, Dutremez & Pinkerton, 1991) or that the structure is disordered. Disorder was not considered to be likely due to the number of observable reflections at high angle, thus the space group was most likely to be Pn with $Z = 4$. It is probable that another polymorph exists for this compound as there is a literature report of a singlet for the ^{31}P CP-MAS spectrum (Bowmaker *et al.*, 1989). The structure was thus solved in the non-centrosymmetric space group and cleanly refined. There were only four correlation coefficients greater than 0.6, the maximum being 0.74, thus clearly confirming the choice of space group.

A perspective view of one of the molecules in the asymmetric unit is shown in Fig. 1, the other molecule being essentially identical. The P atoms are pyramidal with the P—C bonds folded back from the lone-pair position. The C—P—C angles are less than ideal tetrahedral with one of the three angles significantly smaller than the other two. A similar observation has been made for triphenylphosphine (Dunne & Orpen, 1991; Daly, 1964) and for the 2,6-dimethoxy analog of the present compound (Livant, Sun & Webb, 1991). The average P—C bond length is 1.84 (1) Å, almost identical to that found in the 2,6-dimethoxy compound, and is one of the longer values for P—C bonds as expected from the steric bulk of the substituents (Dunne, Morris & Orpen, 1991). The characteristic left- or right-handed propeller arrangement (both are present in the unit cell due to the *n* glide) formed by the aromatic groups, implies that the two P—C—C angles at the *ipso* C atoms are not the same. The average angle *syn* to the P-atom lone pair is 116 (1)° compared to a value of 128 (1)° for the *anti* angle. This difference is attributed to steric interactions of the *ortho* substituents of the aromatic rings. The ideal threefold symmetry of the molecule is not observed due to different amounts of rotation about the P—C bonds; the dihedral angles between the plane formed by the *ipso* C atoms and the planes of the phenyl rings range from 33.2 (2) to 74.0 (1)°. The phenyl groups are planar and the O atoms of the methoxy groups lie in the same plane, with the methyl groups also tending to lie in this plane (Table 3).

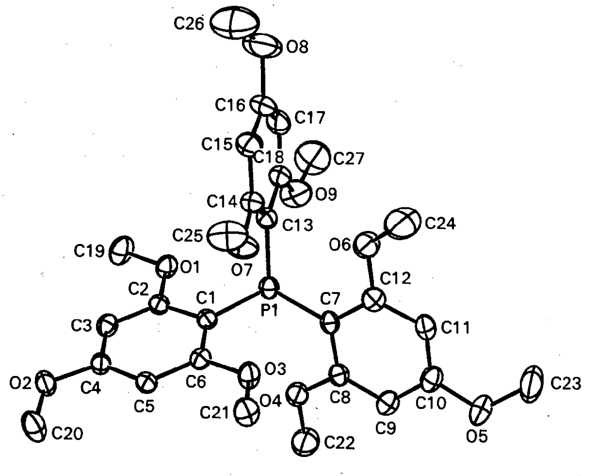

Fig. 1. *ORTEP* plot of one of the molecules viewed down the pseudo-threefold axis and including the atomic numbering scheme.

Table 3. 0*k*0 *reflections showing pseudo-screw extinctions*

h	k	l	$F_{obs} \times 10$	$F_{calc} \times 10$	$\sigma(F) \times 10$
0	2	0	706	726	2
0	3	0	85	83	2
0	4	0	931	936	3
0	5	0	18*	14	7
0	6	0	1481	1461	3
0	7	0	93	97	2
0	8	0	670	672	4
0	9	0	−63*	39	10
0	10	0	944	928	4
0	11	0	84	89	3
0	12	0	671	655	5
0	13	0	356	349	5
0	14	0	134	124	3
0	15	0	39	47	4
0	16	0	53	51	3
0	17	0	174	162	4
0	18	0	94	102	3
0	19	0	−40*	15	14
0	20	0	225	237	5
0	21	0	63	69	5
0	22	0	−46*	19	15
0	23	0	−18*	30	22
0	24	0	119	126	4
0	25	0	78	70	5
0	26	0	125	120	4
0	27	0	15*	76	57
0	28	0	66	62	7
0	29	0	43*	46	10
0	30	0	83	76	5

* Reflection considered unobserved, negative F_{obs} indicates negative measured intensity.

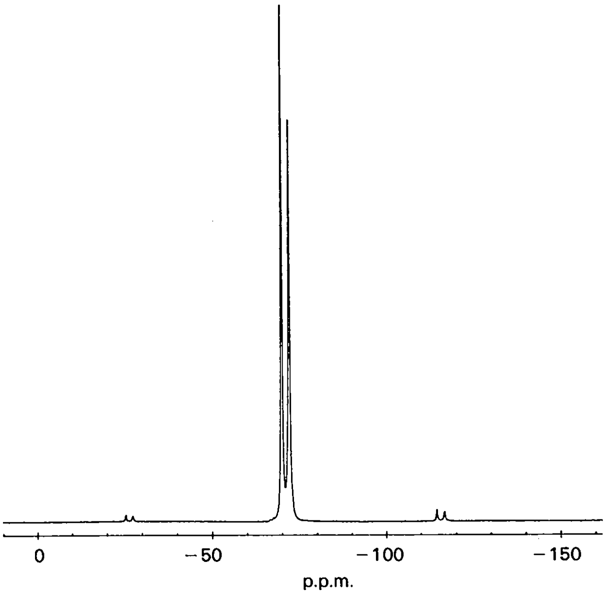

Fig. 2. CP-MAS ^{31}P NMR spectrum of TMPP.

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Structures of Three Derivatives of 5,12-Methano[2.2.2]paracyclophane*

By Peter G. Jones

Institut für Anorganische und Analytische Chemie der Technischen Universität, Hagenring 30, *W*-3300 *Braunschweig, Germany*

Dietmar Schomburg

Gesellschaft für Biotechnologische Forschung mbH, Mascheroder Weg 1, *W*-3300 *Braunschweig, Germany*

and Henning Hopf and Verena Lehne

Institut für Organische Chemie der Technischen Universität, Hagenring 30, *W*-3300 *Braunschweig, Germany*

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Abstract. 5,12-Methano[2.2.2]paracyclophan-25-one (1), $C_{25}H_{22}O$, $M_r = 338.4$, monoclinic, $P2_1/c$, $a = 10.677\,(2)$, $b = 26.122\,(3)$, $c = 13.053\,(2)$ Å, $\beta = 92.96\,(2)°$, $V = 3635.7\,(10)$ Å^3, $Z = 8$, $D_x = 1.237$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.54178 Å, $\mu = 0.57$ mm^{-1}, $F(000) = 1440$, $T = 293$ K, $R = 0.051$ for 5400 reflections. There are two independent molecules in the asymmetric unit which differ only in slight relative ring rotations. The approximate threefold symmetry of the parent [2.2.2]paracyclophane is lost on formation of the methano bridge. No disorder of the ethano bridges is observed. *endo*-5,12-Methano[2.2.2]paracyclophan-25-ol (2), $C_{25}H_{24}O$, $M_r = 340.4$, monoclinic, Cc, $a = 15.714\,(2)$, $b = 31.126\,(5)$, $c = 11.476\,(2)$ Å, $\beta = 96.51\,(2)°$, $V = 5577\,(3)$ Å^3, $Z = 12$, $D_x = 1.216$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.07$ mm^{-1}, $F(000) = 2184$, $T = 293$ K, $R = 0.071$ for 5288 reflections. There are three independent molecules in the asymmetric unit. The conformation of the seven-membered ring differs but otherwise the molecules are similar in conformation to each other and to compound (1). Two of the molecules are linked by a hydrogen bond of 2.97 Å between the hydroxyl O atoms. *endo*-25-Methyl-5,12-methano[2.2.2]paracyclophan-25-ol (3), $C_{26}H_{26}O$, $M_r = 354.5$, rhombohedral, $R3$, $a = 23.978\,(4)$, $c = 8.918\,(2)$ Å (hexagonal axes), $V = 4440\,(3)$ Å^3, $Z = 9$, $D_x = 1.193$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.07$ mm^{-1}, $F(000) = 1710$, $T = 293$ K, $R = 0.034$ for 2819 reflections. The molecule exhibits a conformation very similar to molecule 2 of compound (2) and has close to (non-crystallographic) mirror symmetry. Hydrogen bonds of 3.09 Å link the molecules around the threefold axes.

Introduction. [2.2.2]Paracyclophane was discovered by Baker, McOmie & Norman (1951). Its synthetic yield was markedly improved by Schmidbaur, Hager, Huber & Müller (1988). Its crystal structure was determined by Cohen–Addad, Baret, Chautemps & Pierre (1983). A recent study (Lehne, 1989) of the

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[*] Pentacyclo[14.3.2.2^{7,10}.1^{4,19}.1^{13,17}]pentacosa-1,3,7,9,13,15,-17(25),19(24),22-nonaene; substituents at C-atom number 18 (IUPAC).

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