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

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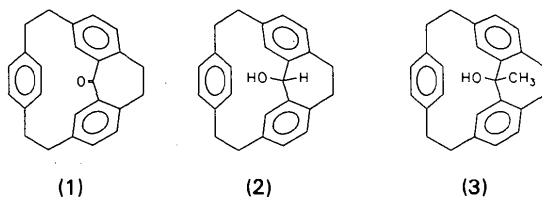
Abstract. 5,12-Methano[2.2.2]paracyclophan-25-one (1), $C_{25}H_{22}O$, $M_r = 338.4$, monoclinic, $P2_1/c$, $a = 10.677$ (2), $b = 26.122$ (3), $c = 13.053$ (2) Å, $\beta = 92.96$ (2)°, $V = 3635.7$ (10) Å³, $Z = 8$, $D_x = 1.237$ Mg m⁻³, $\lambda(Cu K\alpha) = 1.54178$ Å, $\mu = 0.57$ mm⁻¹, $F(000) = 1440$, $T = 293$ 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) Å³, $Z = 12$, $D_x = 1.216$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ 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) Å³, $Z = 9$, $D_x = 1.193$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ 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

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

chemical properties of [2.2.2]paracyclophane involved, among other aspects, detailed investigations of the chemistry of the bridged system 5,12-methano[2.2.2]paracyclophan-25-one (1). An attempted McMurry coupling of (1) with TiCl₄/Zn led to *endo*-5,12-methano[2.2.2]paracyclophan-25-ol (2). (1) can also be reacted with methyl lithium to give *endo*-25-methyl-5,12-methano[2.2.2]paracyclophan-25-ol (3). In order to establish the stereochemical course of these latter reactions, crystal-structure determinations of (2) and (3), as well as the starting material (1), were carried out. The structure determinations are reported here.



Experimental. Compound (1): A colourless prism 0.8 × 0.5 × 0.4 mm was mounted on a glass fibre. Intensities were registered to $2\theta_{\max}$ of 135° using monochromated Cu K α radiation and $\omega/2\theta$ scans (Syntex P₂, diffractometer). Of 6376 unique measured reflections ($\pm h + k + l$, index ranges $h - 12$ to 12, $k 0$ to 31, $l 0$ to 15), $5400 > 4\sigma(F)$ were considered observed. The orientation matrix was refined from setting angles of 15 reflections in the 2θ range 25–40°. Three check reflections showed no significant intensity variation. No absorption correction. The structure was solved by direct methods and subjected to anisotropic full-matrix least-squares refinement on F . H atoms were included using a riding model. The weighting scheme was $w^{-1} = \sigma^2(F) + gF^2$, with $g = 0.0002$; final $R = 0.051$, $wR = 0.064$, 469 parameters, $S = 2.9$, maximum $\Delta/\sigma = 0.002$, $-0.48 \leq \Delta\rho \leq 0.19 \text{ e \AA}^{-3}$. Final atom coordinates are given in Table 1; * derived bond lengths and angles fall within normally expected ranges.

Compound (2): As for (1) with the following differences. Colourless prism 0.6 × 0.4 × 0.25 mm, intensities to $2\theta_{\max}$ of 55° using monochromated Mo K α radiation and ω/θ scans (Stoe Stadi-4 diffractometer), 7243 unique measured reflections ($\pm h + k + l$, index ranges $h - 20$ to 20, $k 0$ to 40, $l 0$ to 14), $5288 > 2\sigma(F)$ considered observed. Cell constants refined from $\pm \omega$ angles of 50 reflections in

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for compound (1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
C(1)	6070 (2)	2878 (1)	9005 (2)	66 (1)
C(2)	5901 (2)	3445 (1)	8723 (2)	63 (1)
C(3)	7087 (2)	3745 (1)	8920 (1)	51 (1)
C(4)	7877 (2)	3832 (1)	8130 (1)	47 (1)
C(5)	9035 (2)	4045 (1)	8332 (1)	45 (1)
C(6)	9459 (2)	4194 (1)	9316 (1)	52 (1)
C(7)	8635 (2)	4134 (1)	10090 (2)	59 (1)
C(8)	7470 (2)	3907 (1)	9897 (1)	59 (1)
C(9)	10783 (2)	4389 (1)	9470 (2)	63 (1)
C(10)	11771 (2)	3966 (1)	9465 (2)	64 (1)
C(11)	11697 (2)	3575 (1)	8612 (1)	50 (1)
C(12)	10928 (2)	3614 (1)	7714 (1)	46 (1)
C(13)	10830 (2)	3209 (1)	7023 (1)	50 (1)
C(14)	11475 (2)	2754 (1)	7196 (2)	55 (1)
C(15)	12321 (2)	2737 (1)	8041 (2)	62 (1)
C(16)	12426 (2)	3138 (1)	8727 (2)	59 (1)
C(17)	11146 (2)	2282 (1)	6577 (2)	67 (1)
C(18)	10360 (2)	1902 (1)	7179 (2)	63 (1)
C(19)	9230 (2)	2142 (1)	7648 (1)	52 (1)
C(20)	8063 (2)	2160 (1)	7138 (2)	59 (1)
C(21)	7051 (2)	2391 (1)	7569 (2)	60 (1)
C(22)	7158 (2)	2617 (1)	8526 (2)	54 (1)
C(23)	8332 (2)	2594 (1)	9037 (2)	59 (1)
C(24)	9334 (2)	2361 (1)	8611 (2)	57 (1)
C(25)	9977 (2)	4027 (1)	7519 (1)	46 (1)
O(1)	9891 (1)	4270 (1)	6727 (1)	64 (1)
C(1')	8503 (2)	4549 (1)	4478 (2)	68 (1)
C(2')	8651 (2)	4496 (1)	3325 (2)	65 (1)
C(3')	7447 (2)	4609 (1)	2720 (1)	54 (1)
C(4')	6658 (2)	4209 (1)	2430 (1)	49 (1)
C(5')	5476 (2)	4305 (1)	1987 (1)	50 (1)
C(6')	5045 (2)	4801 (1)	1800 (2)	61 (1)
C(7')	5863 (2)	5196 (1)	2049 (2)	68 (1)
C(8')	7031 (2)	5104 (1)	2515 (2)	64 (1)
C(9')	3704 (2)	4865 (1)	1382 (2)	79 (1)
C(10')	2747 (2)	4787 (1)	2181 (2)	79 (1)
C(11')	2835 (2)	4317 (1)	2843 (2)	60 (1)
C(12')	3621 (2)	3897 (1)	2685 (1)	50 (1)
C(13')	3744 (2)	3513 (1)	3418 (1)	52 (1)
C(14')	3115 (2)	3522 (1)	4318 (2)	59 (1)
C(15')	2268 (2)	3914 (1)	4434 (2)	70 (1)
C(16')	2128 (2)	4296 (1)	3714 (2)	70 (1)
C(17')	3469 (2)	3150 (1)	5160 (2)	70 (1)
C(18')	4286 (2)	3401 (1)	6026 (2)	74 (1)
C(19')	5406 (2)	3692 (1)	5650 (1)	58 (1)
C(20')	6467 (2)	3444 (1)	5342 (2)	64 (1)
C(21')	7462 (2)	3718 (1)	4973 (2)	64 (1)
C(22')	7434 (2)	4244 (1)	4893 (1)	55 (1)
C(23')	6380 (2)	4487 (1)	5206 (2)	63 (1)
C(24')	5386 (2)	4218 (1)	5579 (2)	64 (1)
C(25')	4572 (2)	3872 (1)	1891 (1)	50 (1)
O(1')	4700 (1)	3501 (1)	1346 (1)	71 (1)

the 2θ range 20–22°. Solution and refinement: tentatively identified hydroxyl H atoms were fixed at the positions of the corresponding difference peaks. An extinction correction of the form $F_{\text{corr}} = F(1 + 0.002xF^2/\sin 2\theta)^{-0.25}$ was applied; the refined value of x was 0.00012 (5). $g = 0.0003$, $R = 0.071$, $wR = 0.051$, 702 parameters, $S = 1.4$, max. $\Delta/\sigma = 0.001$, $-0.29 \leq \Delta\rho \leq 0.27 \text{ e \AA}^{-3}$. The absolute structure was not determined. Final atom coordinates are given in Table 2.

Compound (3): As for (2) with the following differences. Colourless prism 0.7 × 0.4 × 0.44 mm, $2\theta_{\max}$ of 50°, ω scans (Siemens R3 diffractometer), 3624 measured reflections ($+h - k \pm l$), 3494 unique ($R_{\text{int}} = 0.018$, index ranges $h 0$ to 28, $k -28$ to 0, $l -10$ to 10), $2780 > 4\sigma(F)$ observed. The orienta-

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, libration-analysis results and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55377 (67 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0099]

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for compound (2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
O(1)	5762	5991 (1)	2849	51 (1)
C(1)	2028 (3)	5997 (2)	1000 (5)	62 (2)
C(2)	2524 (3)	6300 (2)	1889 (5)	60 (2)
C(3)	3327 (3)	6481 (1)	1462 (4)	48 (2)
C(4)	4130 (3)	6314 (1)	1876 (4)	44 (1)
C(5)	4865 (3)	6445 (1)	1422 (4)	42 (1)
C(6)	4819 (3)	6748 (1)	532 (4)	52 (2)
C(7)	4025 (3)	6924 (2)	151 (5)	63 (2)
C(8)	3293 (3)	6789 (2)	607 (5)	60 (2)
C(9)	5613 (3)	6884 (2)	8 (5)	72 (2)
C(10)	6137 (3)	6539 (2)	-533 (5)	65 (2)
C(11)	5971 (3)	6067 (2)	-312 (4)	47 (2)
C(12)	5791 (3)	5906 (1)	763 (4)	41 (1)
C(13)	5569 (3)	5480 (2)	867 (4)	43 (2)
C(14)	5538 (3)	5195 (1)	-65 (5)	47 (2)
C(15)	5777 (3)	5348 (2)	-1112 (5)	54 (2)
C(16)	5981 (3)	5776 (2)	-1231 (5)	56 (2)
C(17)	5213 (3)	4744 (1)	50 (5)	55 (2)
C(18)	4293 (3)	4690 (1)	-599 (4)	59 (2)
C(19)	3675 (3)	5015 (2)	-209 (4)	48 (2)
C(20)	3355 (3)	4979 (2)	857 (5)	59 (2)
C(21)	2811 (3)	5286 (2)	1237 (5)	59 (2)
C(22)	2578 (3)	5648 (2)	568 (5)	53 (2)
C(23)	2891 (4)	5680 (2)	-496 (5)	68 (2)
C(24)	3431 (4)	5374 (2)	-865 (5)	67 (2)
C(25)	5711 (3)	6220 (1)	1753 (4)	44 (1)
O(1')	7631 (2)	5856 (1)	3443 (3)	55 (1)
C(1')	9838 (4)	6918 (2)	6876 (5)	93 (3)
C(2')	8867 (4)	6945 (2)	6483 (5)	83 (2)
C(3')	8433 (3)	6520 (2)	6540 (5)	63 (2)
C(4')	8196 (3)	6278 (2)	5544 (4)	52 (2)
C(5')	7890 (3)	5865 (2)	5595 (4)	46 (2)
C(6')	7822 (3)	5665 (2)	6672 (4)	53 (2)
C(7')	8042 (3)	5914 (2)	7681 (5)	68 (2)
C(8')	8332 (4)	6327 (2)	7613 (5)	78 (2)
C(9')	7527 (4)	5211 (2)	6777 (5)	72 (2)
C(10')	7867 (3)	4859 (2)	6018 (5)	68 (2)
C(11')	8589 (3)	4968 (2)	5293 (4)	51 (2)
C(12')	8516 (3)	5314 (1)	4513 (4)	42 (1)
C(13')	9193 (3)	5421 (1)	3890 (4)	48 (1)
C(14')	9944 (3)	5185 (2)	3995 (4)	59 (2)
C(15')	9994 (3)	4834 (2)	4735 (5)	72 (2)
C(16')	9335 (3)	4731 (2)	5376 (5)	66 (2)
C(17')	10707 (3)	5337 (2)	3415 (5)	77 (2)
C(18')	11380 (3)	5558 (2)	4319 (5)	83 (2)
C(19')	11015 (3)	5914 (2)	4998 (5)	67 (2)
C(20')	10872 (3)	6320 (2)	4531 (5)	70 (2)
C(21')	10509 (4)	6638 (2)	5145 (5)	73 (2)
C(22')	10278 (3)	6574 (2)	6237 (5)	69 (2)
C(23')	10418 (4)	6167 (2)	6716 (5)	79 (2)
C(24')	10786 (3)	5845 (2)	6119 (5)	74 (2)
C(25')	7729 (3)	5598 (1)	4478 (4)	43 (1)
O(1'')	3059 (2)	7254 (1)	3492 (3)	66 (1)
C(1'')	4320 (3)	8536 (2)	6865 (5)	71 (2)
C(2'')	3407 (4)	8495 (2)	6253 (5)	70 (2)
C(3'')	3079 (3)	8040 (2)	6348 (5)	54 (2)
C(4'')	3098 (3)	7754 (1)	5416 (4)	47 (2)
C(5'')	2930 (3)	7321 (1)	5535 (5)	44 (1)
C(6'')	2753 (3)	7157 (2)	6623 (5)	52 (2)
C(7'')	2688 (3)	7452 (2)	7524 (5)	62 (2)
C(8'')	2846 (3)	7883 (2)	7385 (5)	63 (2)
C(9'')	2651 (4)	6685 (2)	6874 (5)	72 (2)
C(10'')	3144 (4)	6351 (2)	6300 (6)	86 (2)
C(11'')	3939 (3)	6478 (1)	5795 (5)	56 (2)
C(12'')	3907 (3)	6788 (1)	4912 (4)	47 (1)
C(13'')	4652 (3)	6919 (1)	4463 (4)	47 (2)
C(14'')	5445 (3)	6745 (2)	4878 (5)	53 (2)
C(15'')	5472 (3)	6431 (2)	5736 (5)	58 (2)
C(16'')	4732 (3)	6306 (1)	6188 (5)	61 (2)
C(17'')	6244 (3)	6936 (2)	4488 (5)	65 (2)
C(18'')	6682 (3)	7241 (2)	5427 (5)	63 (2)
C(19'')	6092 (3)	7587 (2)	5788 (5)	50 (2)
C(20'')	5861 (3)	7938 (2)	5097 (5)	60 (2)
C(21'')	5301 (3)	8246 (2)	5453 (5)	59 (2)
C(22'')	4943 (3)	8209 (2)	6479 (5)	56 (2)
C(23'')	5171 (4)	7851 (2)	7168 (4)	71 (2)
C(24'')	5738 (4)	7550 (2)	6828 (5)	66 (2)
C(25'')	3062 (3)	7017 (1)	4555 (4)	52 (2)

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for compound (3)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
O	804.6 (6)	140.4 (7)	4000	62 (1)
C(1)	3166 (1)	2604 (1)	4183 (3)	72 (1)
C(2)	2802 (1)	2172 (1)	2843 (3)	69 (1)
C(3)	2660 (1)	1490 (1)	3068 (3)	59 (1)
C(4)	2040 (1)	999 (1)	3390 (3)	51 (1)
C(5)	1903 (1)	383 (1)	3798 (3)	52 (1)
C(6)	2414 (1)	250 (1)	3903 (3)	65 (1)
C(7)	3025 (1)	740 (1)	3535 (4)	83 (1)
C(8)	3150 (1)	1344 (1)	3111 (4)	81 (1)
C(9)	2342 (1)	-381 (1)	4454 (4)	89 (1)
C(10)	1976 (1)	-662 (1)	5920 (4)	84 (1)
C(11)	1704 (1)	-306 (1)	6748 (3)	63 (1)
C(12)	1327 (1)	-76 (1)	6079 (3)	53 (1)
C(13)	1122 (1)	269 (1)	6955 (3)	55 (1)
C(14)	1263 (1)	391 (1)	8465 (3)	65 (1)
C(15)	1617 (1)	147 (1)	9130 (3)	77 (1)
C(16)	1831 (1)	-187 (1)	8286 (3)	78 (1)
C(17)	1098 (1)	831 (2)	9312 (3)	84 (1)
C(18)	1697 (1)	1489 (1)	9655 (3)	82 (2)
C(19)	2097 (1)	1807 (1)	8290 (3)	63 (1)
C(20)	1961 (1)	2180 (1)	7341 (3)	72 (1)
C(21)	2309 (1)	2444 (1)	6056 (3)	69 (1)
C(22)	2811 (1)	2347 (1)	5631 (3)	61 (1)
C(23)	2953 (1)	1979 (1)	6596 (3)	67 (1)
C(24)	2606 (1)	1720 (1)	7888 (3)	71 (1)
C(25)	1229 (1)	-99 (1)	4373 (3)	53 (1)
C(26)	927 (1)	-770 (1)	3672 (4)	78 (1)

tion matrix was refined from setting angles of 48 reflections in the 2θ range 20–23°. Solution and refinement: $x = 0.00048$ (5), $R = 0.034$, $wR = 0.041$, 247 parameters, $S = 1.4$, max. $\Delta/\sigma = 0.02$, $-0.17 \leq \Delta\rho \leq 0.18 \text{ e \AA}^{-3}$. Final atom coordinates are given in Table 3. A libration correction for a rigid body was applied ($R_{lib} = 9\%$) leading to bond-length corrections of 0.004–0.006 Å.

The Siemens program system *SHELXTL-Plus* was employed in the determinations (Sheldrick, 1989).

Discussion. The asymmetric unit of compound (1) consists of two molecules, one of which is depicted in Fig. 1. A least-squares fit* of the two molecules (one inverted) shows that the only significant differences are a rotation of the ring C(19–24) about the axis C(19)–C(22) which changes the positions of the other ring atoms by *ca* 0.33 Å [torsion angles: C(17)–C(18)–C(19)–C(20) 91 and -76°], and a change in position of the keto O atom (0.12 Å). The mean r.m.s. deviation of the other atoms is 0.025 Å. In the remainder of the discussion, only values for molecule 1 are given. In contrast to the parent [2.2.2]paracyclophane, no disorder of the ethano bridges is observed. The torsion angles about the bridges have similar absolute values: -53 about C(1)–C(2), 49 about C(9)–C(10) and 51° about C(17)–C(18). The

*Least-squares fits exclude H atoms; torsion angles throughout the discussion are given to the nearest degree; actual e.s.d.'s were in the range 0.2–0.4° for compounds (1) and (3), and up to 0.8° for compound (2).

non-crystallographic threefold symmetry of [2.2.2]-paracyclophane is destroyed by the addition of the methano bridge; indeed, the torsion angles of the seven-membered ring are such as to prevent even twofold or mirror symmetry [torsion angles: C(10)—C(11) 12, C(9)—C(10) 49, C(6)—C(9) -75°]. The six bridgehead atoms no longer lie in a plane with the aromatic rings perpendicular to it. The best plane through the six bridgehead atoms of (1) has a mean atomic deviation of 0.36 Å, and the aromatic rings make dihedral angles of 54 for C(3–8), 62 for C(11–16) and 49° for C(19–24) (tilted in the opposite sense) to this plane. As predicted by Tabushi, Yoshida & Imishiro (1975) on the basis of Dreiding models, the keto group cannot be coplanar with the neighbouring rings, which make dihedral angles of 71 and 63° with the plane defined by C(5), C(12),

C(25) and O(1). The additional bridge causes slight distortions of the bridged aromatic rings reminiscent of those in [2.2]paracyclophane (Vögtle, 1990). The bridgehead C(11) and C(14) atoms are displaced 0.06 Å out of the plane of the other four, C(12),

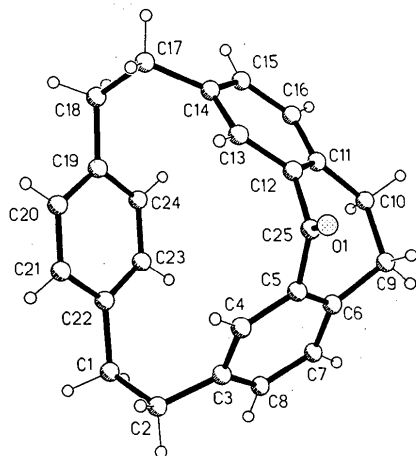


Fig. 1. One of the two independent molecules of compound (1) in the crystal. Radii are arbitrary and the view direction is perpendicular to the best plane through the six bridgehead atoms.

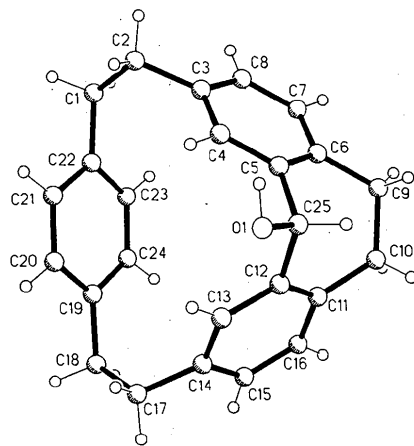


Fig. 2. One of the three independent molecules of compound (2) in the crystal. Radii are arbitrary.

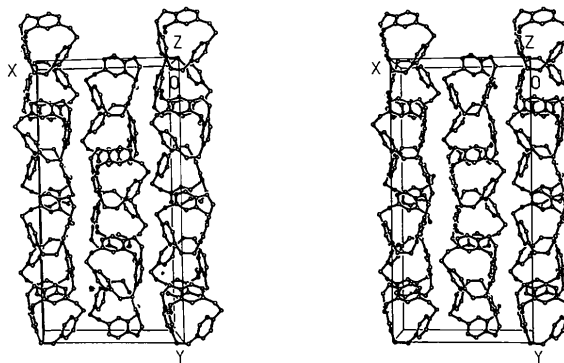


Fig. 3. Stereoscopic packing diagram of compound (2) viewed along the *z* axis with H atoms omitted.

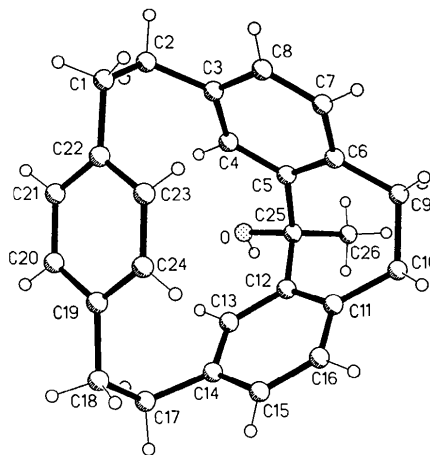


Fig. 4. The molecule of compound (3) in the crystal. Radii are arbitrary.

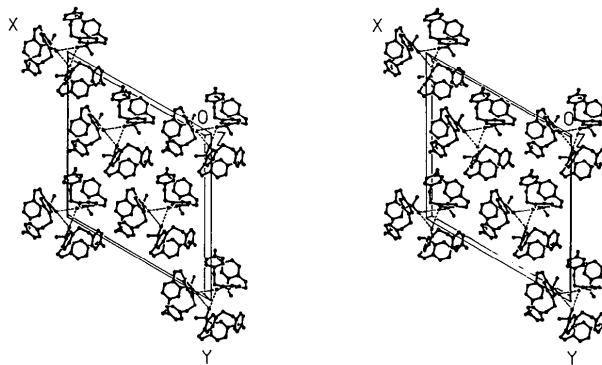


Fig. 5. Stereoscopic packing diagram of compound (3) viewed along the *z* axis with H atoms omitted.

C(13), C(15), C(16); the substituents lie further out of this plane, C(17) by 0.37, C(10) by 0.22, C(25) by 0.21 Å. Similar but smaller effects are observed for the ring C(3–8). The ring C(19–24) is planar with an r.m.s. deviation of 0.004 Å.

Compound (2) crystallizes with three independent molecules in the asymmetric unit, one of which is shown in Fig. 2. The expected *endo* geometry is confirmed. The three molecules differ in the conformation of the seven-membered ring, with torsion angles about C(6)—C(9), C(9)—C(10) and C(10)—C(11) of 58, –13 and –39° for molecule 1, 44, 8 and –54° for molecule 2 and 33, 20 and –60° for molecule 3. A least-squares fit of molecule 2 to molecule 1 [except for C(9), C(10), C(20), C(21), C(23), C(24)] gave an r.m.s. deviation of 0.04 Å, and a fit of molecule 3 to molecule 1 [inverted, O(1) also omitted] gave 0.06 Å r.m.s. deviation. The bridgehead-atom deviations in the methano-bridged rings are smaller than in (1), only one of 12 values being > 0.04 Å, and are thus scarcely significant. Other features are similar to those of (1). A hydrogen bond of 2.97 Å is formed between O(1) of molecules 1 and 2. No further short contacts are observed. The molecular packing involves layers of molecules parallel to the *yz* plane and is shown in Fig. 3.

Compound (3), in contrast to (1) and (2), has only one independent molecule per asymmetric unit (Fig. 4). The expected *endo* geometry is again confirmed. The conformation is similar to that of molecule 2 of

compound (2), with smaller deviations from mirror symmetry. The torsion angles about C(6)—C(9), C(9)—C(10) and C(10)—C(11) are –49, 0 and 50°, respectively. An inverted fit of all atoms gave an r.m.s. deviation of 0.09 Å, the major deviations arising from a small rotation of the ring C(11–16). Bridgehead-atom deviations are 0.03 Å or less. The molecules are linked by weak hydrogen bonds (O...O 3.09 Å) across the threefold axes (symmetry operator: $-x + y, -x, z$). The molecular packing is shown in Fig. 5.

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Structure of Ethylenediammonium 3,5-Dinitrobenzoate

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Abstract. $0.5\text{C}_2\text{H}_{10}\text{N}_2^+\cdot\text{C}_7\text{H}_3\text{N}_2\text{O}_6^-$, $M_r = 242.17$, triclinic, $P\bar{1}$, $a = 6.737$ (1), $b = 7.803$ (7), $c = 10.444$ (1) Å, $\alpha = 94.767$ (8), $\beta = 108.30$ (1), $\gamma = 97.43$ (1)°, $V = 512.4$ (2) Å³, $Z = 2$, $D_x =$

1.570 g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 1.282$ cm⁻¹, $F(000) = 250$, room temperature, $R = 0.046$, $wR = 0.054$ for 2396 observed reflections with $F_o \geq 5.0\sigma(F_o)$. The molecular complex in the lattice is extensively bonded through intermolecular and intramolecular hydrogen bonds with at least one O atom of each dinitrobenzoate substituent and each H

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