

between the two sets of parallel planes is 9.4° . The occurrence of two sets of parallel planes is not uncommon and is found in both phenanthrene and anthracene (Mason, 1961). The interplanar angles observed in these two structures are 56 and 52° , respectively. The angular magnitudes of the compounds are much larger than the interplanar angle observed in our crystallographic investigation of the title compound. This difference can be attributed to the altered molecular packing caused by the exocyclic substituents.

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Structure of a Derivative of Mitindomide, the Maleimide–Benzene Photoadduct,* $C_{20}H_{20}N_2O_8$

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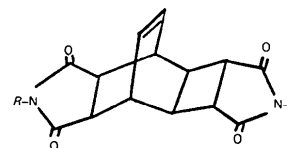
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Abstract. $M_r = 416.39$, orthorhombic, $Pca2_1$, $a = 16.646$ (7), $b = 15.890$ (4), $c = 7.222$ (2) Å, $U = 1910$ (1) Å³, $Z = 4$, $D_m = 1.444$, $D_x = 1.448$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.71$ cm⁻¹, $T = 298$ K, $F(000) = 872$. Final $R = 0.0646$ for 2322 observed reflections measured on a diffractometer. The structure of the adduct (I) was determined *via* the diacetate of the bis(hydroxymethyl) derivative (III). The monomeric units clearly show that the imide rings have the *exo-endo* configuration, confirming the 1,2 photoaddition as *exo* and the 1,4 Diels–Alder addition as *endo*. The two imide rings are nearly coplanar (dihedral angle = 4.1°) and the distance between the two nitrogens is 7.79 Å.

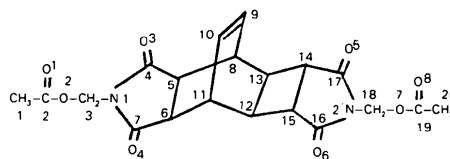
Introduction. The photosensitized reaction of maleimide with a large excess of benzene yields an insoluble adduct (I) (Bradshaw, 1966; Arkhipova, Zhubanov & Saidenova, 1972) whose structure has been presumed

based on analogy with the known photoadduct of maleic anhydride and benzene (Bryce-Smith, Vickery & Frey, 1967; Grovenstein, Rao & Taylor, 1961). Since this compound (I) shows strong and reproducible antitumor activity in a number of test systems (Lomax & Narayanan, 1981), it was important to confirm this structural assignment.



(I) $R = H$

(II) $R = \text{CH}_2\text{OH}$



(III)

* 4,6,11,13-Tetraoxo-5,12-diazapentacyclo[7.5.2.0^{2,8}.0^{3,7}.0^{10,14}]-hexadec-15-ene-5,12-diyldimethylene diacetate.

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Experimental. Reaction of (I) with formaldehyde in dimethylformamide gave the bis(hydroxymethyl) derivative (II) in excellent yield. When (II) was treated with acetic anhydride in pyridine, the diacetate (III) was easily isolated by standard techniques. Slow recrystallization of this compound (III) from hot acetic acid gave beautiful crystals, many of which were suitable for X-ray analysis.

Density measured by flotation in hexane-carbon tetrachloride, crystal $ca\ 0.15 \times 0.25 \times 0.6$ mm, Syntex $P2_1$ diffractometer, take-off angle 6.74° , Mo $K\alpha$ radiation filtered by graphite monochromator, unit-cell parameters by least-squares refinement of 15 machine-centered reflections (2θ from 13.8 to 25.8°), 3003 independent reflections out to $2\theta = 60^\circ$ using $\theta-2\theta$ scans, background counts at beginning and end of each scan, $h, k, l \geq 0$; intensities of three standard reflections, measured every 97 scans, did not vary; 2322 observed reflections [$F \geq 3\sigma(F)$], L_p correction but none for

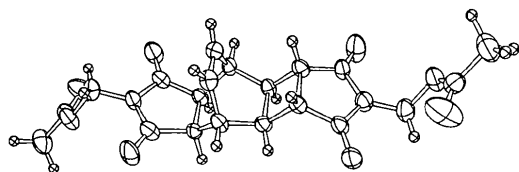


Fig. 1. ORTEP diagram (Johnson, 1976) of the derivative of the maleimide-benzene photoadduct.

Table 1. Fractional coordinates and U_{eq} values ($\text{\AA}^2 \times 10^3$)

	x	y	z	U_{eq}
C(1)	0.2977 (3)	0.5923 (3)	0.30416	70
C(2)	0.2609 (3)	0.5064 (2)	0.320 (1)	44
C(3)	0.1401 (2)	0.4294 (2)	0.374 (1)	41
C(4)	0.1505 (2)	0.3175 (2)	0.126 (1)	37
C(5)	0.1062 (2)	0.2956 (2)	-0.048 (1)	31
C(6)	0.0406 (2)	0.3635 (2)	-0.067 (1)	32
C(7)	0.0533 (2)	0.4209 (2)	0.097 (1)	40
C(8)	0.0650 (2)	0.2076 (2)	-0.031 (1)	36
C(9)	0.0078 (2)	0.2101 (2)	0.126 (1)	38
C(10)	-0.0491 (2)	0.2703 (2)	0.112 (1)	37
C(11)	-0.0432 (2)	0.3218 (2)	-0.060 (1)	36
C(12)	-0.0475 (2)	0.2656 (2)	-0.232 (1)	34
C(13)	0.0184 (2)	0.1934 (2)	-0.211 (1)	33
C(14)	-0.0499 (2)	0.1275 (2)	-0.205 (1)	35
C(15)	-0.1140 (2)	0.1966 (2)	-0.231 (1)	30
C(16)	-0.1518 (2)	0.1780 (2)	-0.416 (1)	37
C(17)	-0.0565 (2)	0.0714 (2)	-0.369 (1)	38
C(18)	-0.1397 (2)	0.0619 (3)	-0.653 (1)	47
C(19)	-0.2599 (3)	-0.0151 (2)	-0.592 (1)	42
C(20)	-0.2962 (3)	-0.0995 (3)	-0.566 (1)	67
O(1)	0.2971 (2)	0.4431 (2)	0.308 (1)	76
O(2)	0.1807 (2)	0.5085 (2)	0.346 (1)	49
O(3)	0.2047 (2)	0.2782 (2)	0.199 (1)	58
O(4)	0.0144 (2)	0.4827 (2)	0.140 (1)	61
O(5)	-0.0181 (2)	0.0096 (2)	-0.406 (1)	67
O(6)	-0.2005 (2)	0.2187 (2)	-0.498 (1)	56
O(7)	-0.1801 (2)	-0.0171 (2)	-0.620 (1)	52
O(8)	-0.2945 (2)	0.0500 (2)	-0.582 (1)	90
N(1)	0.1176 (2)	0.3916 (2)	0.200 (1)	38
N(2)	-0.1180 (2)	0.1028 (2)	-0.483 (1)	38

$$U_{eq} = \frac{1}{3} \sum U_{ii}$$

Table 2. Bond lengths (\AA) and angles ($^\circ$)

C(1)-C(2)	1.500 (5)	C(2)-O(1)	1.176 (5)
C(2)-O(2)	1.348 (5)	C(3)-O(2)	1.442 (5)
C(3)-N(1)	1.444 (6)	C(4)-C(5)	1.494 (7)
C(4)-O(3)	1.220 (5)	C(4)-N(1)	1.404 (5)
C(5)-C(6)	1.541 (4)	C(5)-C(8)	1.563 (5)
C(6)-C(7)	1.508 (6)	C(6)-C(11)	1.545 (5)
C(7)-O(4)	1.217 (4)	C(7)-N(1)	1.385 (5)
C(8)-C(9)	1.481 (6)	C(8)-C(13)	1.533 (6)
C(9)-C(10)	1.350 (6)	C(10)-C(11)	1.492 (6)
C(11)-C(12)	1.534 (6)	C(12)-C(13)	1.593 (5)
C(12)-C(15)	1.557 (5)	C(13)-C(14)	1.547 (5)
C(14)-C(15)	1.542 (4)	C(14)-C(17)	1.487 (6)
C(15)-C(16)	1.508 (6)	C(16)-O(6)	1.197 (5)
C(16)-N(2)	1.405 (5)	C(17)-O(5)	1.201 (4)
C(17)-N(2)	1.403 (5)	C(18)-O(7)	1.444 (5)
C(18)-N(2)	1.436 (6)	C(19)-C(20)	1.485 (5)
C(19)-O(7)	1.342 (5)	C(19)-O(8)	1.186 (5)
O(1)-C(2)-C(1)	124.3 (4)	O(2)-C(2)-C(1)	113.1 (4)
O(2)-C(2)-O(1)	122.6 (4)	N(1)-C(3)-O(2)	111.1 (4)
O(3)-C(4)-C(5)	127.6 (4)	N(1)-C(4)-C(5)	108.8 (3)
N(1)-C(4)-O(3)	123.5 (4)	C(6)-C(5)-C(4)	105.2 (3)
C(8)-C(5)-C(4)	111.0 (3)	C(8)-C(5)-C(6)	108.9 (2)
C(7)-C(6)-C(5)	104.7 (3)	C(11)-C(6)-C(5)	109.6 (2)
C(11)-C(6)-C(7)	111.1 (3)	O(4)-C(7)-C(6)	128.0 (4)
N(1)-C(7)-C(6)	109.1 (3)	N(1)-C(7)-O(4)	122.9 (4)
C(9)-C(8)-C(5)	108.5 (3)	C(13)-C(8)-C(5)	106.6 (3)
C(13)-C(8)-C(9)	109.2 (3)	C(10)-C(9)-C(8)	114.4 (4)
C(11)-C(10)-C(9)	113.8 (4)	C(10)-C(11)-C(6)	108.9 (3)
C(12)-C(11)-C(6)	105.3 (3)	C(12)-C(11)-C(10)	110.7 (3)
C(13)-C(12)-C(11)	108.1 (3)	C(15)-C(12)-C(11)	116.0 (3)
C(15)-C(12)-C(13)	89.0 (2)	C(12)-C(13)-C(8)	108.9 (3)
C(14)-C(13)-C(8)	116.7 (4)	C(14)-C(13)-C(12)	89.1 (2)
C(15)-C(14)-C(13)	91.3 (2)	C(17)-C(14)-C(13)	116.0 (3)
C(17)-C(14)-C(15)	106.3 (3)	C(14)-C(15)-C(12)	90.6 (2)
C(16)-C(15)-C(12)	115.5 (4)	C(16)-C(15)-C(14)	104.8 (3)
O(6)-C(16)-C(15)	128.2 (4)	N(2)-C(16)-C(15)	107.7 (3)
N(2)-C(16)-O(6)	124.1 (4)	O(5)-C(17)-C(14)	129.0 (4)
N(2)-C(17)-C(14)	107.8 (3)	N(2)-C(17)-O(5)	123.2 (4)
N(2)-C(18)-O(7)	111.8 (4)	O(7)-C(19)-C(20)	113.6 (4)
O(8)-C(19)-C(20)	125.6 (4)	O(8)-C(19)-O(7)	120.7 (4)
C(3)-O(2)-C(2)	117.5 (3)	C(19)-O(7)-C(18)	117.6 (3)
C(4)-N(1)-C(3)	125.4 (4)	C(7)-N(1)-C(3)	122.0 (3)
C(7)-N(1)-C(4)	112.2 (4)	C(17)-N(2)-C(16)	113.3 (3)
C(18)-N(2)-C(16)	125.3 (4)	C(18)-N(2)-C(17)	121.4 (3)

absorption or extinction; direct methods using *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) which generated a series of E maps, one of which correctly located all non-H atomic positions; full-matrix least-squares refinement on F with isotropic temperature factors gave $R = 0.126$; all non-methyl H atoms located from difference synthesis, methyl H atom added as group parameter; further refinement with all non-H atoms anisotropic (non-methyl H atoms not refined) reduced R to 0.0646 ($R_w = 0.0703$). Maximum least-squares shift to error ratio = 0.175, final difference Fourier maximum 0.37, minimum -0.29 e \AA^{-3} , atomic scattering factors as in *SHELX* (Sheldrick, 1976). A weighting scheme with $w = 1.5/[(\sigma_F)^2 + 0.002F^2]$ was used.*

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39596 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The space group *Pbcm* exhibits the same systematic absences as *Pca*2₁. However, with *Z* = 4 the site symmetry imposed by the space group is inconsistent with the symmetry of the molecule.

Fig. 1 is an *ORTEP* diagram (Johnson, 1976) of the molecule illustrating 50% probability ellipsoids for all non-H atoms and arbitrary spheres of radius about 0.4 Å for H atoms. Atomic positions are listed in Table 1 and distances and angles between all non-H atoms are shown in Table 2. The structure determined for compound (III) indicates that the structure of (I) has been correctly assumed in the literature and indirectly confirms the structure of the analogous maleic anhydride–benzene photoadduct.

Very recently, the complete structure of a derivative of (I), in which the imide ring fused to the four-membered ring was opened by prolonged hydrolysis, has been determined by X-ray crystallography (Pettit, Paull, Herald, Herald & Riden, 1983). Assuming no rearrangement occurred during the basic hydrolysis the same structure and stereochemistry was indicated by this study.

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Structure of the 1/1 Complexes of [2.2.2]Paracyclophane and [2.2.2.2]Paracyclophane with Tetracyanoethylene, C₂₄H₂₄·C₆N₄ (I) and C₃₂H₃₂·C₆N₄ (II)

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Abstract. (I): $M_r = 440.36$, triclinic, $P\bar{1}$, $a = 9.057$ (6), $b = 22.646$ (9), $c = 6.830$ (5) Å, $\alpha = 104.85$ (5), $\beta = 103.25$ (5), $\gamma = 106.35$ (5)°, $V = 1229$ Å³, $Z = 2$, $D_x = 1.15$ Mg m⁻³, $\lambda(\text{Cu K}\alpha) = 1.5418$ Å, $\mu = 0.545$ mm⁻¹, $F(000) = 464$, $T = 293$ K; (II): $M_r = 544.45$, monoclinic, $C2/c$, $a = 27.298$ (8), $b = 6.727$ (3), $c = 17.156$ (6) Å, $\beta = 105.25$ (5)°, $V = 3039$ Å³, $Z = 4$, $D_x = 1.18$ Mg m⁻³, $\lambda(\text{Cu K}\alpha) = 1.5418$ Å, $\mu = 0.548$ mm⁻¹, $F(000) = 1152$, $T = 293$ K. The structures were refined to *R* values of 0.085 (I) and 0.066 (II) for 2604 and 1438 observed intensities respectively. In (I), the three benzene rings of the paracyclophane molecules are related by a threefold pseudo-axis of symmetry. In (II), the paracyclophane

molecule lies on a centre of symmetry and is not planar. In both compounds, 1/1 complexes are formed with tetracyanoethylene molecules (TCNE) lying on centres of symmetry. Each TCNE is situated between symmetrically related paracyclophane molecules. In (I) only two of the three aromatic rings of each paracyclophane are involved in the charge transfer with TCNE. This leads to a one-dimensional charge transfer approximately along a lattice body diagonal and not to a two-dimensional one, as might be expected from the threefold pseudo-symmetry observed in the [2.2.2]-paracyclophane crystal structure. In (II) the charge-transfer direction is along a face diagonal in a sandwich arrangement.