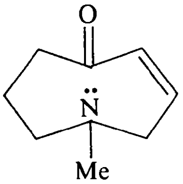
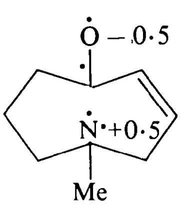
There are three main results: (i) There is a weak intermolecular hydrogen bond, O(22)–H···O′(18) [O(22)···O′(18) = 2·84 (1) Å and ∠OHO = 111 (1)°]. (ii) The macrocycle displays pseudo twofold symmetry, where the pseudo-axis goes from C(1)–C(8) to C(13)–C(14). This pseudosymmetry decreases when approaching the pyrrolizidine ring. Bond distances and angles generally agree with those found in retusamine (Wunderlich, 1967) and jacobine (Fridrichsons & Mathieson, 1963). (iii) Especially interesting is the short intra-annular distance of 2·18 (1) Å between N(4) and C(8). Some work has been done on N···C=O interactions by Bürgi, Dunitz & Shefter (1973); they found some relationships between the C···N distance and the geometry around both atoms. We find it useful to interpret our otosenine results with the electron-repulsion distribution theory (Linnett, 1966). This scheme shows models of the pyrrolizidine group for: (*a*) no N–C bond, (*b*) a one-electron N–C bond and (*c*) a two-electron N–C bond (single bond). Otosenine is better understood with model (*b*), which is also supported by some special features of the pyrrolizidine geometry: (1) a three-electron bond distance, C∸O = 1·26 Å, (2) a C(1)C(7)O(18) plane, with a 0·13 Å deviation of C(8) towards N, (3) an increased average value for the CNC angle of 115°, indicating that only one electron of the N pair repels the three N–C bonds, the other electron being shared between N(4) and C(8).



(*a*)



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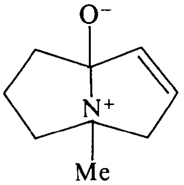

(*c*)

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Adamantylideneadamantane Peroxide. A Stable 1,2-Dioxetane

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Abstract. $C_{20}H_{28}O_2$, monoclinic, $P2_1/c$, $a = 18{\cdot}59$ (1), $b = 9{\cdot}89$ (1), $c = 13{\cdot}24$ (1) Å, $\beta = 105{\cdot}3$ (1)°, $D_m = 1{\cdot}27$, $D_x = 1{\cdot}28$ g cm^{-3}, $Z = 6$. The structure was solved by direct methods and refined to an R_w of 0·11 for 2164 reflections with $\sin\theta/\lambda \le 0{\cdot}6$ Å^{-1}. The molecule contains a four-membered ring in which a peroxide group is connected by two C atoms.

Introduction. Adamantylideneadamantane-1,2-dioxetane (I, Fig. 1) was synthesized by Wieringa, Strating, Wijnberg & Adam (1972). Although (I) is the most stable dioxetane known, it slowly decomposes into adamantanone at room temperature. The presence of the four-membered dioxetane ring makes the molecule interesting and it was decided to determine its geometry by X-ray diffraction.

Crystals were obtained by slow evaporation of the solute from a solution of (I) in acetone. The density was determined by flotation in K_2HgI_4 solutions. The symmetry relations between the reflections and the systematic extinctions observed on Weissenberg photographs taken at room temperature indicated the space group $P2_1/c$. The cell constants were determined on a Nonius CAD-4 automatic diffractometer. The cell contains six molecules.

In space group $P2_1/c$ four molecules (A) may lie in general positions, whereas at least one set of two molecules (B) must lie on a special position. As the molecules do not contain an inversion centre, disorder has to be assumed for B. At low temperature (−160°C) Weissenberg photographs showed diffuse streaks and super-reflections. This suggests that at lower temperatures the molecules B, for which at room temperature random disorder was assumed, tend to be ordered. The diffuse spots were not investigated further. It was decided to measure the intensities at room temperature to study the geometry of A.

The intensities were measured on an Enraf–Nonius computer-controlled automatic four-circle diffractometer with Zr-filtered Mo radiation and a crystal 0·55 × 0·40 × 0·35 mm. With a θ–2θ scan 4157 reflections with $\theta < 25°$ were recorded. The orientation of the crystal and its reflecting power were checked with a set of orientation control and intensity reference reflections. The orientation appeared to change with time and a strong reduction in the reflected intensities (down to 65% of the original value) was noticed, indicating deterioration of the crystal. Thus the intensities are not very accurate. The unwanted effects were corrected for by regular calculation of a new orientation matrix and by putting the intensities on the same relative scale by means of the reference reflections. In addition corrections for Lorentz and polarization effects were made.

Attempts to solve the structure with *MULTAN* were not successful. Visual inspection of the Patterson synthesis gave rough information about the packing of the molecules, but failed to give a starting model. With the semi-automated symbolic addition program *SIMPEL* and the aid of its authors H. Schenk, N. van der Putte, A. W. Overbeek & G. Olthof (University of Amsterdam), two adamantane skeletons were found for A which, however, in view of the valence angles, were not positioned in the correct way relative to each other. For the starting set of reflections selected by *MULTAN* several sign combinations were used, obtained by changing each time one, or a few, of the signs calculated for the starting set on the basis of the above model. From one of the E maps, containing 286 terms with $E > 1{\cdot}9$, a rough model for A could be deduced. After least-squares refinement two centrosymmetrically related structures for B were found from a difference map. In the refinement in $P2_1/c$ both structures of B were taken into account with population parameters of 0·5. Isotropic temperature factors were used for the non-hydrogen atoms of B and anisotropic temperature factors for those of A. The scattering factors for O and C were taken from Cromer & Mann (1968) and that of H from Stewart, Davidson & Simpson (1965). H atoms were placed at geometrically reasonable positions. The C–H distances were constrained to 1·08 Å and the H isotropic temperature factors, U, were kept 0·4 Å^2 larger than the (average) U values of their respective C atoms. The function minimized was $\Sigma w[k|F_o| - |F_c|]^2$ with $w = [\sigma_c^2(F_o) + 0{\cdot}0012F_o^2]^{-1}$, $\sigma_c^2(F_o)$ being the variance due to counting statistics; 2164 reflections with $|F_o| > 3\sigma_c(F_o)$ were used. $R_w = (\Sigma w[F_o - F_c]^2/\Sigma wF_o^2)^{1/2}$ decreased to 0·11. In the final difference map no significant maxima or minima were observed.

In space group Pc, which lacks the inversion centre, no disorder for B needs to be assumed. Refinement in

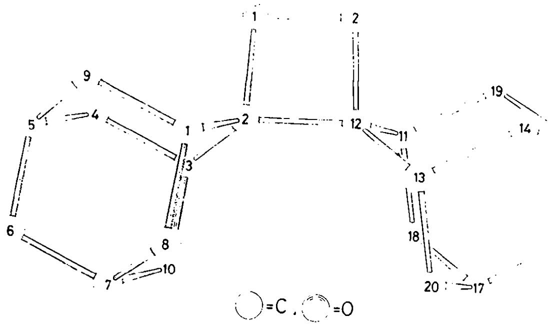

Fig. 1. Schematic drawing of the non-hydrogen atoms of the molecule and numbering scheme.

Table 1. *Final coordinates* (×10^4) *of the non-hydrogen atoms of A in* $P2_1/c$

For numbering of atoms see Fig. 1. Standard deviations as calculated by the least-squares program are given in parentheses in units of the last digit.

	x	y	z
C(1)	4168 (3)	−1321 (6)	4007 (4)
C(2)	3341 (3)	−955 (6)	3663 (4)
C(3)	3011 (3)	−1439 (6)	2541 (4)
C(4)	3087 (3)	−2982 (7)	2515 (5)
C(5)	3915 (4)	−3363 (7)	2851 (6)
C(6)	4323 (4)	−2738 (8)	2118 (5)
C(7)	4248 (3)	−1215 (7)	2153 (5)
C(8)	4588 (3)	−707 (6)	3264 (5)
C(9)	4244 (4)	−2847 (7)	3971 (5)
C(10)	3438 (3)	−814 (4)	1811 (4)
C(11)	2312 (3)	922 (6)	3573 (4)
C(12)	3100 (3)	380 (6)	4089 (4)
C(13)	3621 (3)	1574 (7)	4439 (5)
C(14)	3352 (4)	2380 (7)	5249 (5)
C(15)	2555 (4)	2926 (8)	4762 (5)
C(16)	2566 (4)	3836 (8)	3847 (5)
C(17)	2831 (4)	3033 (7)	3016 (5)
C(18)	2321 (3)	1850 (7)	2653 (4)
C(19)	2041 (4)	1723 (7)	4378 (5)
C(20)	3620 (3)	2489 (7)	3509 (5)
O(1)	2978 (2)	−1664 (4)	4377 (3)
O(2)	3942 (2)	−403 (5)	5011 (3)

Table 2. *Bond lengths and angles in the central part of A*

C(2)–O(1)	1·476 (8) Å	C(1)–C(2)–C(3)	109·3 (5)°	C(11)–C(12)–C(13)	108·7 (5)°
C(12)–O(2)	1·474 (7)	C(12)–C(2)–C(1)	117·3 (4)	C(2)–C(12)–C(11)	117·9 (4)
O(1)–O(2)	1·491 (7)	C(12)–C(2)–C(3)	122·8 (4)	C(2)–C(12)–C(13)	123·4 (5)
C(2)–C(12)	1·549 (9)	C(12)–C(2)–O(1)	86·9 (4)	C(2)–C(12)–O(2)	86·8 (4)
C(2)–C(1)	1·527 (8)	O(1)–C(2)–C(1)	106·9 (4)	O(2)–C(12)–C(11)	106·4 (5)
C(2)–C(3)	1·527 (8)	O(1)–C(2)–C(3)	109·9 (5)	O(2)–C(12)–C(13)	109·6 (4)
C(12)–C(11)	1·540 (8)	O(2)–O(1)–C(2)	88·9 (4)	O(1)–O(2)–C(12)	89·2 (4)
C(12)–C(13)	1·520 (9)				

Dihedral angles

[C(1),C(2),C(3)] ∧ [C(11),C(12)C(13)]	62·4°
[O(2),O(1),C(2)] ∧ [O(2),C(12),C(2)]	30·3
[O(1),O(2),C(12)] ∧ [O(1),C(2),C(12)]	30·4

Pc with, for *B*, one of the centrosymmetrically related models with a population 1, increased the standard deviations by a factor of two and *R* by 0·01. Therefore the disordered model in $P2_1/c$ was assumed to be correct.

The final parameters of *A* in $P2_1/c$ are listed in Table 1.*

For the computer calculations the XRAY system (1975) was used.

Discussion. The packing of the molecules is shown in Fig. 2. Between the molecules there are no distances shorter than the expected van der Waals distances. As the bond lengths and angles of *B* are inaccurate owing to the disorder, we consider only *A* in this discussion. The structure of *A* with the short non-bonded distances is given in Fig. 3. In Fig. 4 and Table 2 geometrical data for the central part of the molecule are given; bond lengths and angles for the adamantane groups are listed in Table 3.

At the 3% significance level (χ^2 test) all C–C bonds in the adamantane groups are equal to the mean, 1·531 Å; the C–C–C angles lie close to the tetrahedral value. Figs. 3 and 4 show that the four-membered ring is not planar. The molecule is twisted around the central

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* Lists of structure factors, anisotropic temperature factors, and the final parameters of *B* have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32877 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

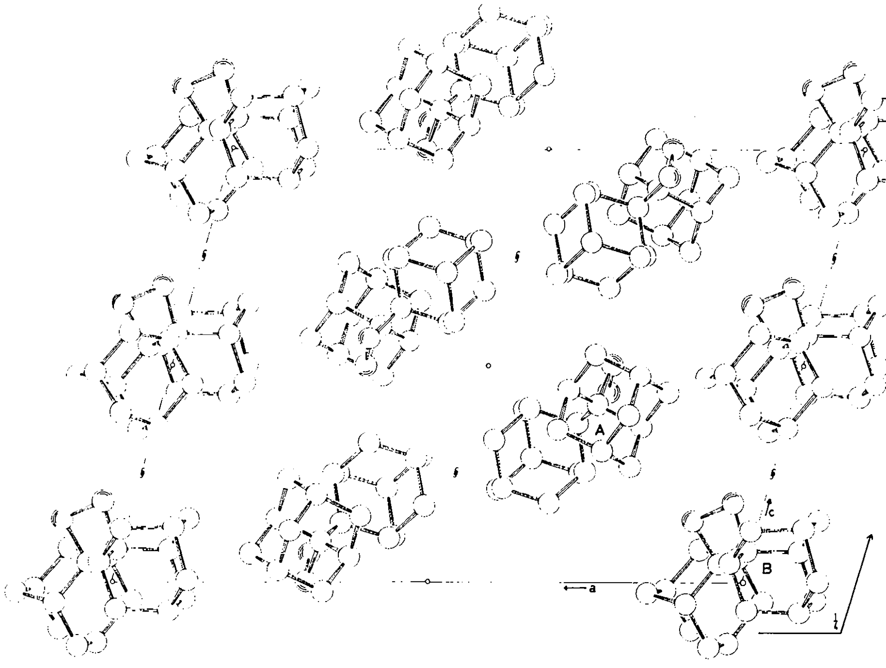

Fig. 2. Projection of the structure along **b**. The centre of inertia of *A* lies at (0·3302, 0·0019, 0·3548). Molecules of type *B* with centre of inertia at (0·0095, −0·0018, 0·0164) are disordered; only one of the two molecules superimposed in the average structure is given.

Table 3. *Bond lengths* (Å) *and angles* (°) *in the adamantane groups of A*

C(1)–C(2)	1·527 (8)	C(11)–C(12)	1·540 (8)
C(1)–C(8)	1·533 (9)	C(11)–C(18)	1·529 (9)
C(1)–C(9)	1·518 (9)	C(11)–C(19)	1·517 (10)
C(2)–C(3)	1·527 (8)	C(12)–C(13)	1·520 (9)
C(3)–C(4)	1·534 (9)	C(13)–C(14)	1·524 (10)
C(3)–C(10)	1·532 (9)	C(13)–C(20)	1·528 (9)
C(4)–C(5)	1·532 (9)	C(14)–C(15)	1·547 (9)
C(5)–C(6)	1·513 (11)	C(15)–C(16)	1·514 (10)
C(5)–C(9)	1·535 (9)	C(15)–C(19)	1·526 (10)
C(6)–C(7)	1·515 (10)	C(16)–C(17)	1·539 (11)
C(7)–C(8)	1·525 (8)	C(17)–C(18)	1·503 (9)
C(7)–C(10)	1·508 (9)	C(17)–C(20)	1·536 (9)

C(2)–C(1)–C(8)	110·9 (5)	C(12)–C(11)–C(18)	110·7 (5)
C(2)–C(1)–C(9)	108·7 (5)	C(12)–C(11)–C(19)	108·8 (4)
C(8)–C(1)–C(9)	107·8 (5)	C(18)–C(11)–C(19)	108·8 (5)
C(1)–C(2)–C(3)	109·3 (5)	C(11)–C(12)–C(13)	108·7 (5)
C(2)–C(3)–C(4)	108·5 (5)	C(12)–C(13)–C(14)	108·6 (5)
C(2)–C(3)–C(10)	110·3 (5)	C(12)–C(13)–C(20)	110·5 (4)
C(4)–C(3)–C(10)	108·7 (5)	C(14)–C(13)–C(20)	109·0 (5)
C(3)–C(4)–C(5)	109·2 (5)	C(13)–C(14)–C(15)	110·2 (5)
C(4)–C(5)–C(6)	110·4 (5)	C(14)–C(15)–C(16)	109·1 (6)
C(4)–C(5)–C(9)	108·2 (6)	C(14)–C(15)–C(19)	108·2 (6)
C(6)–C(5)–C(9)	110·2 (5)	C(16)–C(15)–C(19)	109·6 (5)
C(5)–C(6)–C(7)	108·7 (6)	C(15)–C(16)–C(17)	109·9 (6)
C(6)–C(7)–C(8)	109·8 (5)	C(16)–C(17)–C(18)	109·6 (6)
C(6)–C(7)–C(10)	110·2 (5)	C(16)–C(17)–C(20)	109·0 (5)
C(8)–C(7)–C(10)	109·3 (5)	C(18)–C(17)–C(20)	108·3 (6)
C(7)–C(8)–C(1)	109·7 (5)	C(17)–C(18)–C(11)	110·6 (5)
C(1)–C(9)–C(5)	110·1 (5)	C(11)–C(19)–C(14)	110·3 (6)
C(3)–C(10)–C(7)	110·2 (5)	C(13)–C(20)–C(17)	110·4 (6)

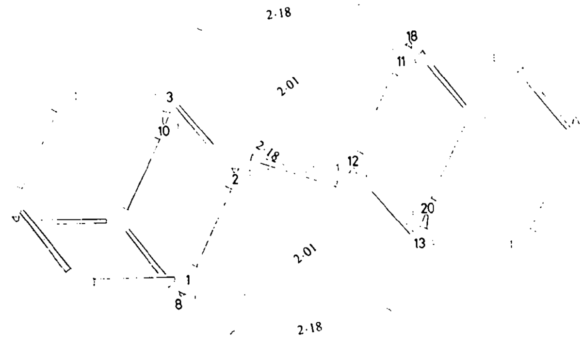

Fig. 3. *A* seen along the line connecting the centres of O(1)–O(2) and C(2)–C(12), with short non-bonded distances. Apart from the distances shown, the distances of type C(1)···C(13) = 3·14 Å also are shorter than the sum of the van der Waals radii.

C(2)–C(12) bond so that the shortest H··· H distances are enlarged, though they are still shorter than the 2·40 Å given by Pauling (1960) for the H··· H van der Waals distance. Because of the presence of the four-membered ring the angles around C(2) and C(12) show large deviations from the tetrahedral value; the angles at the O atoms are 90°. C(2)–C(12), 1·549 Å, is slightly, though not significantly, longer than the adamantane C–C bonds. As far as is known to the authors, geometrical data for dioxetane rings are not available. The O–O length is not significantly different from that in H_2O_2 (1·47 ± 0·02 Å; Sutton, 1958), but the C–O length of 1·475 (7) Å in the dioxetane ring is significantly larger than the 1·423 Å in 1,4-dioxan (Davis & Hassel, 1963).

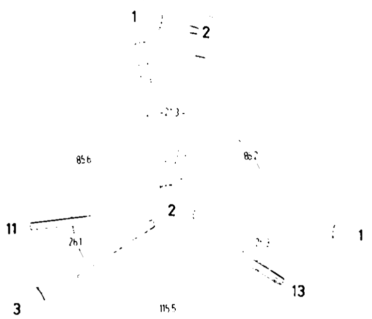

Fig. 4. *A* seen along C(2)–C(12), with torsion angles.

The implications of the observed geometry for the chemical properties of the molecule will be discussed elsewhere.

We thank Professor H. Wijnberg and Drs H. Numan for suggesting the structure determination and providing the compound. The computations were done at the Computing Centre of the University of Groningen.

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