

O(1) of the reference molecule and the methyl group of the molecule at $x, \frac{1}{2}-y, -\frac{1}{2}+z$. The O...C distance is 3.37 Å, the O...HC distance 2.76 Å. A corresponding contact occurs between the methyl group at x, y, z and O(1) at $x, \frac{1}{2}-y, \frac{1}{2}+z$. We assume that the interaction between these atoms is repulsive; the forces on O(1) and CM of the reference molecule are almost parallel and have a large component normal to the plane of the five-membered ring, as can be seen from the stereoscopic packing diagram (Fig. 3). The ring can take up this force by folding about the line C(1)...C(12) towards the C(3)-C(4) bond with the result that C(6) and O(2) are displaced from the plane of C(1), C(11), N, C(12). The displacements of O(1) and O(2) from the vertical mirror plane of the idealized molecule are almost equal (0.06 Å) but in opposite directions so that the twofold axis is nearly preserved. This can be seen in Fig. 2.

We have no explanation for the apparent difference between the lengths of the two C=C double bonds. Previous studies on [4,4,4]propellatriene (Ermer, Gerdil & Dunitz, 1971) and [4,4,2]propella-3,8-diene-11,12-dione (Fink, van der Helm & Nealy, 1975) suggest a tendency for the C=C double bonds in this type of molecule to be slightly shorter than normal.

Crystals of 11,13-dioxo-12-methyl-12-aza[4,4,3]propella-2,4,8-triene are isomorphous with the title compound ($a=11.490$, $b=12.378$, $c=7.925$ Å, $\beta=94.97^\circ$,

space group $P2_1/c$, $Z=4$). X-ray analysis (Seiler, 1975) shows that the crystal structure is very similar to the one described here, but is disordered with respect to the positions occupied by the individual six-membered rings. The packing arrangement is very similar to that shown in Fig. 3 and, in particular, it also shows a short O(1)...CM contact (3.35 Å).

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syn-8,9-Epoxy-11,13-dioxo-12-methyl-12-aza[4,4,3]propell-3-ene

BY M. KAFTORY* AND J. D. DUNITZ

Laboratory for Organic Chemistry, Swiss Federal Institute of Technology, Universitätstrasse 16, 8006 Zürich, Switzerland

AND O. S. MILLS

Department of Chemistry, University of Manchester, Manchester M1 39 PL, England

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Abstract. Monoclinic, $P2_1/c$, $a=7.297$, $b=13.658$, $c=12.226$ Å, $\beta=112.0^\circ$, $C_{13}H_{15}NO_3$, $M=233.27$, $Z=4$, $D_x=1.371$ g cm⁻³. The two six-membered rings are in boat form, both folded towards the five-membered ring. The epoxy ring is *syn* with respect to the latter. The molecule deviates significantly from the mirror symmetry expected from its formula.

Introduction. The configuration of the title compound is of interest in connexion with stereochemical studies of [4,4,3]propella-3,8-dienes (Ginsburg, 1974).

Intensities from a crystal, 0.25 × 0.2 × 0.2 mm, were collected in Zürich on an automated Hilger-Watts

Y290 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0.71069$ Å, $\mu=1.02$ cm⁻¹); 1999 reflexions were measured, of which 1445 were above background [$I>1.5\sigma(I)$]. The structure was solved by direct methods and refined by full-matrix least squares with experimental weights. H atoms were included during the later stages. Scattering factors for C, N and O were taken from *International Tables for X-ray Crystallography* (1962) and for H from Stewart, Davidson & Simpson (1965). The final R was 0.049.†

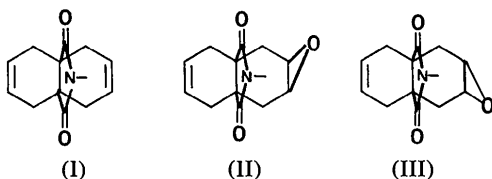
† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31417 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

* Present address: Department of Chemistry, Technion - Israel Institute of Technology, Haifa, Israel.

Meanwhile a second set of intensities (about 800 reflexions) was obtained in Manchester by microdensitometry of Weissenberg photographs. Refinement with this data set led to essentially the same structure but with somewhat lower precision ($R=0.053$). We report here only the results of the Zürich refinement.

Positional and vibrational parameters are listed in Tables 1 and 2. Corresponding interatomic distances and angles involving C, N and O atoms are shown in Fig. 1; the C-H distances (not listed) lie in the range 0.91–1.05 Å.

Discussion. The structure of the diene (I) has already been described (Kaftory & Dunitz, 1976). Epoxidation of this diene yields a major and a minor product in the ratio approximately 6:1 (Oren, Mayer & Ginsburg, 1975), and the present analysis establishes the configuration of the major product as (II), with the epoxy ring *syn* to the five-membered ring, rather than as (III).



The observed bond lengths need little comment. The dimensions of the epoxy ring agree well with those found in other epoxides (Birnbbaum, 1973). As in other propellane derivatives (Kaftory & Dunitz, 1976), the C=C double bond length seems to be somewhat shorter than normal.

The molecule is appreciably distorted from mirror symmetry, as can be seen from Table 3, where 'symmetry equivalent' torsion angles differ by up to 8°. Perhaps the most striking expression of the distortion is the difference of 0.135 Å between the distances $O \cdots C(11) = 2.864(3)$ Å and $O \cdots C(12) = 2.999(3)$ Å.

Table 2. *syn*-8,9-Epoxy-11,13-dioxo-12-methyl-12-aza[4,4,3]propell-3-ene

Atomic coordinates ($\times 10^3$) and isotropic B values ($B=8\pi^2U$) for hydrogen atoms (e.s.d.'s in parentheses).

	x	y	z	B (Å ²)
H(2, 1)	374 (4)	274 (2)	284 (2)	3.7 (7)
H(2, 2)	325 (4)	267 (2)	147 (3)	5.5 (7)
H(3)	116 (6)	152 (3)	194 (3)	6.5 (12)
H(4)	258 (6)	26 (3)	331 (4)	7.9 (13)
H(5, 1)	550 (5)	121 (2)	458 (3)	5.9 (9)
H(5, 2)	620 (5)	20 (2)	426 (3)	7.2 (9)
H(7, 1)	833 (5)	209 (2)	489 (3)	4.1 (8)
H(7, 2)	947 (5)	114 (2)	485 (3)	5.7 (9)
H(8)	1143 (5)	217 (3)	424 (3)	8.0 (10)
H(9)	1014 (5)	332 (2)	276 (3)	8.9 (10)
H(10, 1)	672 (5)	342 (2)	326 (3)	5.2 (8)
H(10, 2)	656 (6)	347 (3)	196 (3)	7.9 (11)
HM(1)	706 (6)	50 (3)	1 (3)	7.6 (10)
HM(2)	717 (6)	-43 (3)	70 (3)	8.5 (10)
HM(3)	903 (6)	18 (3)	96 (4)	8.8 (12)

In this case, the molecular distortion does not seem to be attributable to crystal packing forces. There is indeed a rather short intermolecular $O \cdots C$ contact of 3.14 Å, between the epoxy O and the methyl C

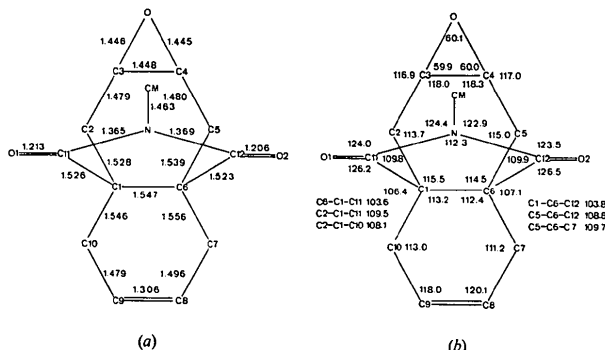


Fig. 1. *syn*-8,9-Epoxy-11,13-dioxo-12-methyl-12-aza[4,4,3]propell-3-ene. (a) bond distances, (b) bond angles.

Table 1. *syn*-8,9-Epoxy-11,13-dioxo-12-methyl-12-aza[4,4,3]propell-3-ene

Atomic coordinates ($\times 10^4$) and vibrational tensor components ($\times 10^3$) for non-hydrogen atoms (e.s.d.'s in parentheses). The U_{ij} values (Å²) correspond to the temperature factor expression $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* \dots)]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O	3247 (3)	513 (2)	1843 (2)	76 (1)	75 (1)	73 (1)	-28 (2)	41 (2)	-35 (2)
O(1)	5408 (3)	2010 (1)	356 (1)	78 (1)	57 (1)	33 (1)	9 (2)	21 (2)	12 (2)
O(2)	8544 (4)	-214 (2)	3150 (2)	124 (2)	62 (1)	50 (1)	50 (3)	28 (2)	12 (2)
N	7229 (3)	827 (1)	1604 (2)	43 (1)	40 (1)	31 (1)	2 (2)	15 (2)	-5 (2)
C(1)	5967 (3)	2085 (2)	2457 (2)	43 (1)	29 (1)	34 (1)	0 (2)	14 (2)	-2 (2)
C(2)	3803 (4)	2302 (2)	2236 (2)	57 (2)	56 (2)	45 (1)	12 (3)	22 (3)	-3 (3)
C(3)	2617 (4)	1417 (2)	2210 (3)	51 (2)	77 (2)	71 (2)	-11 (3)	32 (3)	-29 (4)
C(4)	3515 (5)	654 (2)	3065 (3)	92 (3)	59 (2)	75 (2)	-27 (4)	58 (4)	-25 (3)
C(5)	5563 (5)	800 (2)	3915 (2)	99 (2)	47 (2)	46 (2)	0 (3)	43 (3)	5 (3)
C(6)	6960 (4)	1297 (2)	3403 (2)	54 (2)	39 (1)	28 (1)	6 (2)	14 (2)	0 (2)
C(7)	8817 (5)	1694 (2)	4425 (2)	72 (2)	76 (2)	32 (1)	18 (3)	5 (3)	-11 (3)
C(8)	10081 (4)	2294 (3)	3961 (3)	46 (2)	110 (3)	62 (2)	-15 (4)	16 (3)	-42 (4)
C(9)	9272 (5)	2936 (3)	3127 (3)	76 (2)	80 (2)	70 (2)	-38 (4)	35 (4)	-32 (4)
C(10)	7104 (5)	3066 (2)	2695 (2)	80 (2)	38 (2)	58 (2)	-11 (3)	30 (3)	-9 (3)
C(11)	6120 (3)	1661 (2)	1339 (2)	41 (1)	36 (1)	35 (1)	-5 (2)	15 (2)	0 (2)
C(12)	7676 (4)	534 (2)	2746 (2)	61 (2)	45 (2)	34 (1)	12 (3)	14 (2)	3 (2)
CM	7680 (4)	233 (2)	740 (2)	62 (2)	61 (2)	43 (1)	5 (3)	22 (3)	-16 (3)

atoms, but since its direction coincides roughly with the approximate mirror planes of both molecules involved (see packing diagram, Fig. 3), it can hardly be responsible for the symmetry lowering. The origin of the distortion has therefore to be sought in intramolecular interactions.

The mirror-symmetric molecule with a planar 5-ring has one obviously unfavourable interaction; the inward pointing lone pair orbital on the epoxy O is directed towards the *p*-orbital of the imide N. In the observed molecule this interaction is ameliorated by a slight pyramidalization of the N atom, which is found to lie 0.054 Å from the plane of C(11), C(12), CM,

away from the epoxy ring. The corresponding displacement of CM from the plane of C(11), N, C(12) is 0.159 Å and it is towards the epoxy O, as expected (because the developing *sp*³ orbital should be concentrated on the side opposite to the epoxy O).

For a pyramidal N, preservation of optimal overlap with the π -orbitals of the carbonyl groups requires out-of-plane deformation of the 5-membered ring, as can easily be seen by inspection of a model. Two deformation modes have to be considered: (1) displacement of N from the plane of the remaining four atoms to give an envelope form with preservation of mirror symmetry, (2) twist about the central C(1)–C(6), which

Table 3. *syn*-8,9-Epoxy-11,13-dioxo-12-methyl-12-aza[4,4,3]propell-3-ene

Selected torsion angles. Those related by the approximate mirror plane appear on the same line.

C(1)—C(2)—C(3)—C(4)	+41°	C(6)—C(5)—C(4)—C(3)	−39°
C(2)—C(3)—C(4)—C(5)	−1		
C(6)—C(1)—C(2)—C(3)	−42	C(1)—C(6)—C(5)—C(4)	+35
C(5)—C(6)—C(1)—C(2)	+4		
C(9)—C(10)—C(1)—C(6)	+41	C(8)—C(7)—C(6)—C(1)	−44
C(10)—C(9)—C(8)—C(7)	+2		
C(8)—C(9)—C(10)—C(1)	−46	C(9)—C(8)—C(7)—C(6)	+44
C(10)—C(1)—C(6)—C(7)	+4		
C(2)—C(1)—C(6)—C(7)	−122	C(5)—C(6)—C(1)—C(10)	+130
C(1)—C(6)—C(12)—N	+1	C(6)—C(1)—C(11)—N	−6
C(6)—C(12)—N—C(11)	−6	C(1)—C(11)—N—C(12)	+8
C(11)—C(1)—C(6)—C(12)	+3		
O(1)—C(11)—C(1)—C(6)	+175	O(2)—C(12)—C(6)—C(1)	180
O—C(3)—C(2)—C(1)	−28	O—C(4)—C(5)—C(6)	+30
C(2)—C(3)—O—C(4)	+108	C(5)—C(4)—O—C(3)	−109

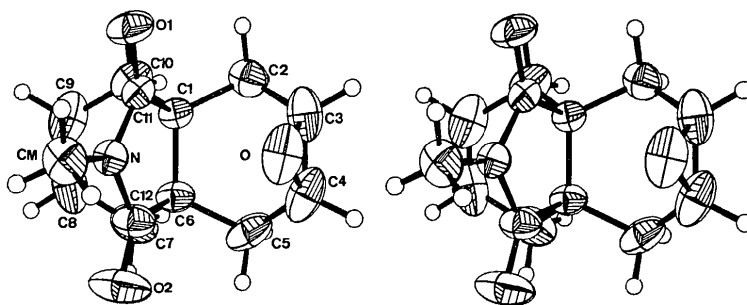


Fig. 2. *syn*-8,9-Epoxy-11,13-dioxo-12-methyl-12-aza[4,4,3]propell-3-ene: stereoscopic view of molecule, showing vibration ellipsoids at the 50% probability level (Johnson, 1965).

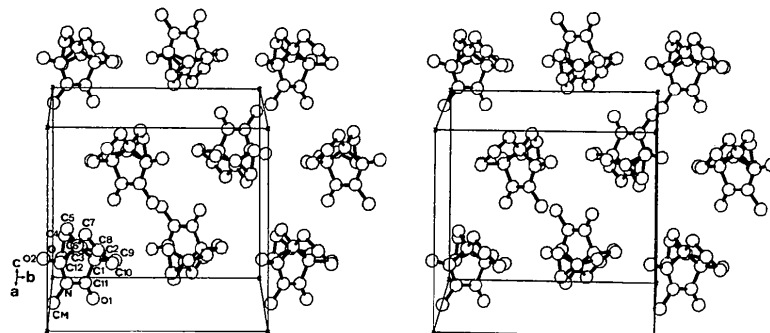


Fig. 3. Stereoscopic view of crystal structure of *syn*-8,9-epoxy-11,13-dioxo-12-methyl-12-aza[4,4,3]propell-3-ene.

reduces eclipsing, with destruction of mirror symmetry. The actual deformation is a combination of (1) and (2), and the overall effect is to displace the N atom to one side of the mean plane of the 5-membered ring and the carbonyl C(11) to the other, towards the epoxy ring.

The short O...C(11) distance of 2.86 Å can also be regarded as the expression of an attractive intramolecular O...C=O interaction (Bürgi, Dunitz & Shefter, 1974). Although the lone-pair orbital of the epoxy O cannot point exactly towards C(11), the O...C=O approach angle of 110.6° is nearly optimal. As described above, the approach of C(11) towards O could be driven by factors other than direct attraction, but there is also a significant shear of the entire epoxy ring from its 'normal' position, centred on the mean mirror plane, towards the C(11) side of the molecule. The displacements are 0.055 Å for the midpoint of C(3) and C(4) and 0.065 Å for the O atom. The midpoint of C(11) and C(12) is displaced from the mean mirror plane by 0.014 Å but in the opposite direction.

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2,4-Dimethyl-1,5-benzodiazepinium Chloride Dihydrate, and its Isomorphous Bromide

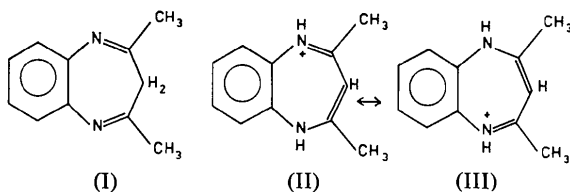
BY J. CLARE SPEAKMAN AND FRANCIS B. WILSON

Chemistry Department, The University, Glasgow G12 8QQ, Scotland

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Abstract. C₁₁H₁₃N₂Cl·2H₂O, orthorhombic, *Pbca*, *a* = 19.325 (11), *b* = 6.900 (4), *c* = 18.734 (10) Å, *D_m* = 1.29 g cm⁻³, *Z* = 8, *D_x* = 1.301. The cation, C₁₁H₁₃N₂⁺, has all its atoms, except the six methyl H, nearly coplanar, and appears to be stabilized by electron delocalization, which partially accounts for the intense colour. There are various hydrogen bonds involving the NH groups, the Cl⁻ ion and the H₂O molecules. The bromide, C₁₁H₁₃N₂Br·2H₂O, is isomorphous: *a* = 19.60 (5), *b* = 6.97 (2), *c* = 19.08 (5) Å, *D_m* = 1.45, *D_x* = 1.473.

Introduction. A base, C₁₁H₁₂N₂, to which formula (I) was assigned, was prepared by Thiele & Steimmig (1907) who also described a hydrochloride, C₁₁H₁₃N₂⁺Cl⁻·2H₂O. This salt is the title compound and (II) and (III) would now be used to represent its cation.



Though the free base is colourless, the hydrohalides are intensely coloured, deep violet in aqueous solution and almost black in the crystals. Mr D. Lloyd (Lloyd & Marshall, 1956) gave us samples of both chloride and bromide. These crystals being isomorphous, the problem was attractive, in 1963, for X-ray study. Structural analysis would be of interest because of the ring system, and perhaps in connexion with the colour.

Crystals, from aqueous solution containing a trace of excess HCl (or HBr), were fine needles, elongated parallel to *b*, and with (100) as the best developed faces though {102} were also present. Preliminary work was on the bromide (Cu radiation, visual estimates of intensities), approximate positions for most of the atoms (but not H) being found by the heavy-atom method (Wilson, 1971). From this basis a more accurate study of the chloride, for which $\mu(\text{Mo}) = 3.3 \text{ cm}^{-1}$, followed. The crystal habit was unfavourable for precise intensity measurements, but a crystal was found with dimensions 0.37 × 0.14 × 0.10 mm; the longest dimension was parallel to *b*, about which the crystal was mounted. Measurements were made on a Hilger-Watts four-circle diffractometer which the ω - θ scan. Of some 1500 reflexions observed out to $\theta = 20^\circ$, 1400 were independent;