

## 11,13-Dioxo-12-methyl-12-aza[4,4,3]propella-3,8-diene

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**Abstract.** Monoclinic,  $P2_1/c$ ,  $a = 11.943$ ,  $b = 11.834$ ,  $c = 7.828$  Å,  $\beta = 92.12^\circ$ ,  $C_{13}H_{15}NO_2$ ,  $M = 217.27$ ,  $Z = 4$ ,  $D_x = 1.305$  g cm $^{-3}$ . The two six-membered rings are in the boat form, both folded towards the five-membered ring, but the molecule is significantly distorted from the  $mm2$  symmetry implied by its structural formula.

**Introduction.** The molecular conformation is of interest in connexion with stereochemical studies of reactions of [4,4,3]propella-3,8-dienes with electrophilic reagents (Ginsburg, 1974).

Intensities were collected on an automated Hilger-Watts Y290 diffractometer with graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å,  $\mu = 0.95$  cm $^{-1}$ ); 1940 reflexions were measured, of which 1550 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 0.041.† Final 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 shown) lie in the range 0.93–1.04 Å.

Table 2. 11,13-Dioxo-12-methyl-12-aza[4,4,3]propella-3,8-diene

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

	$x$	$y$	$z$	$B$ (Å $^2$ )
H(2, 1)	277 (2)	-68 (2)	-73 (3)	4.3 (6)
H(2, 2)	389 (2)	3 (2)	-37 (3)	4.4 (6)
H(3)	464 (2)	-166 (2)	79 (3)	5.9 (6)
H(4)	350 (2)	-275 (2)	267 (3)	5.4 (6)
H(5, 1)	152 (2)	-189 (2)	132 (3)	5.6 (6)
H(5, 2)	171 (2)	-209 (2)	332 (3)	5.0 (6)
H(7, 1)	33 (2)	-40 (2)	132 (3)	5.2 (6)
H(7, 2)	23 (2)	-46 (2)	340 (3)	6.1 (7)
H(8)	-7 (2)	147 (2)	309 (3)	7.2 (8)
H(9)	115 (2)	261 (2)	137 (3)	6.3 (7)
H(10, 1)	261 (2)	177 (2)	-4 (3)	5.0 (7)
H(10, 2)	165 (2)	87 (2)	-61 (3)	4.4 (7)
HM(1)	448 (3)	143 (3)	547 (4)	9.2 (9)
HM(2)	426 (3)	23 (3)	646 (4)	8.1 (8)
HM(3)	343 (2)	132 (2)	654 (4)	8.2 (8)

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† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31416 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

**Discussion.** Fig. 1 shows that chemically equivalent molecular parameters differ by up to 0.023 Å in bond lengths, 1.5° in bond angle and 7° in torsion angle (the parameters shown in Fig. 1 have not been corrected for thermal motion effects; such corrections would

Table 1. 11,13-Dioxo-12-methyl-12-aza[4,4,3]propella-3,8-diene

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 (Å $^2$ ) 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(1)	4287 (1)	1412 (1)	2295 (2)	48 (1)	61 (1)	53 (1)	-23 (1)	-1 (1)	12 (1)
O(2)	1929 (1)	-441 (1)	5710 (2)	57 (1)	92 (1)	34 (1)	-9 (2)	10 (1)	11 (2)
N	3247 (1)	554 (1)	4307 (2)	37 (1)	41 (1)	28 (1)	-2 (1)	-1 (1)	-2 (1)
C(1)	2655 (1)	287 (1)	1419 (2)	32 (1)	37 (1)	28 (1)	-2 (1)	-2 (1)	2 (1)
C(2)	3308 (2)	-443 (2)	167 (2)	48 (1)	46 (1)	30 (1)	-1 (2)	4 (2)	1 (2)
C(3)	3817 (2)	-1459 (2)	1034 (2)	53 (1)	44 (1)	40 (1)	6 (2)	-1 (2)	-6 (2)
C(4)	3213 (2)	-2050 (2)	2062 (2)	68 (1)	38 (1)	43 (1)	1 (2)	-3 (2)	-2 (2)
C(5)	2033 (2)	-1709 (2)	2333 (2)	65 (1)	46 (1)	48 (1)	-21 (2)	6 (2)	1 (2)
C(6)	1892 (1)	-415 (2)	2585 (3)	32 (1)	47 (1)	33 (1)	-9 (2)	0 (1)	1 (2)
C(7)	653 (2)	-84 (2)	2424 (3)	33 (1)	86 (2)	50 (1)	-3 (2)	-1 (2)	5 (2)
C(8)	505 (2)	1159 (2)	2418 (3)	43 (1)	104 (2)	57 (1)	27 (3)	-2 (2)	0 (3)
C(9)	1160 (2)	1798 (2)	1485 (3)	64 (1)	61 (1)	64 (1)	24 (2)	-16 (2)	0 (2)
C(10)	2026 (2)	1239 (2)	423 (2)	46 (1)	49 (1)	41 (1)	4 (2)	-10 (2)	7 (2)
C(11)	3502 (1)	828 (1)	2660 (2)	34 (1)	33 (1)	37 (1)	-1 (2)	-2 (1)	3 (2)
C(12)	2318 (1)	-127 (2)	4386 (2)	37 (1)	48 (1)	33 (1)	2 (2)	3 (1)	4 (2)
CM	3899 (2)	933 (2)	5820 (2)	62 (1)	60 (1)	37 (1)	-2 (2)	-16 (2)	-10 (2)

increase all bond lengths by 0.005–0.008 Å). The torsion angle pattern indicates that, of the three symmetry elements of the idealized  $mm2$  molecule, the dyad axis is preserved in best approximation. Both six-membered rings adopt the boat form with the planes containing the C=C double bonds and their substituents folded toward the central five-membered ring as seen in the stereoscopic view of the molecule (Fig. 2).

The five-membered ring is not quite planar, C(6) lying 0.08 Å from the mean plane of the other four atoms, which are coplanar to within 0.002 Å – the torsion angle C(1)–C(11)–N–C(12) is zero. Of the

three ring substituents, O(1) and CM, attached to C(11) and N, respectively, lie within 0.007 Å of the C(1), C(11), N, C(12) plane, whereas O(2) deviates by 0.04 Å. The main intramolecular force tending to pucker the ring would be the one tending to reduce eclipsing around C(1)–C(6) and this would lead to a twist form with the diad axis through C(1)–C(6). The observed form is close to this twist form but significantly distorted from it (Fig. 1). To account for the kind of distortion that occurs it seems necessary to invoke the effect of crystal packing forces. The shortest intermolecular contact occurs between the carbonyl

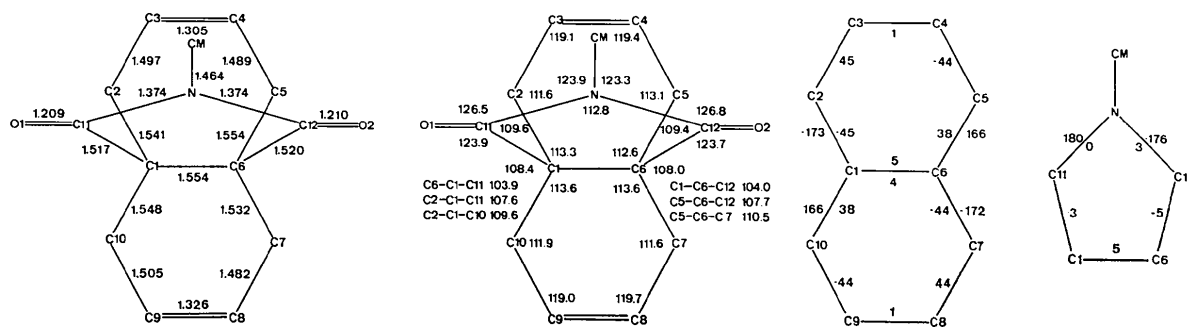


Fig. 1. Bond distances, bond angles and torsion angles in 11,13-dioxo-12-methyl-12-aza[4,4,3]propella-3,8-diene. The e.s.d.'s of bond distances are typically 0.003 Å, of bond angles 0.2–0.3°. Thermal motion corrections increase all bond distances by 0.005–0.008 Å.

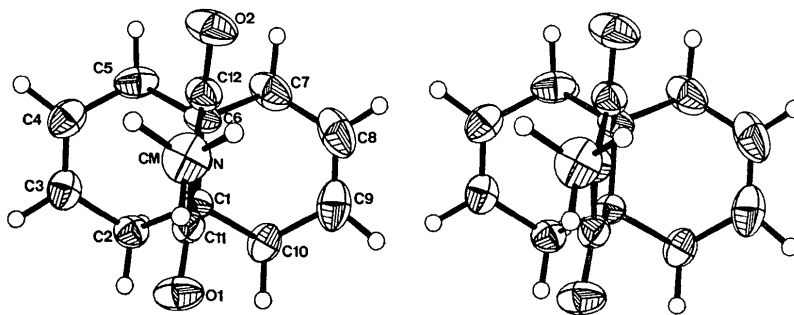


Fig. 2. 11,13-dioxo-12-methyl-12-aza[4,4,3]propella-3,8-diene. Stereoscopic view of molecule, showing vibration ellipsoids at the 50% probability level (Johnson, 1965).

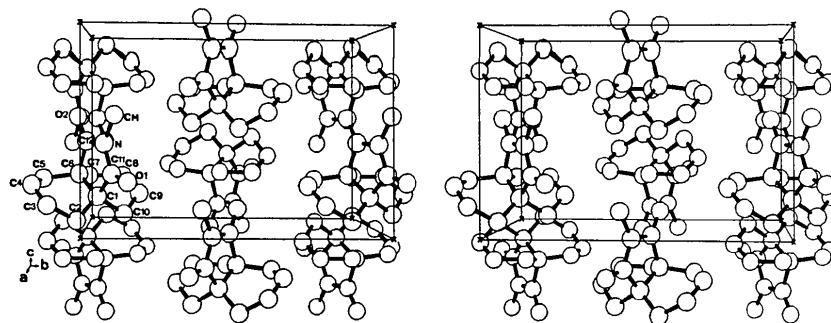


Fig. 3. Stereoscopic view of crystal structure of 11,13-dioxo-12-methyl-12-aza[4,4,3]propella-3,8-diene. The corresponding 2,4,8-triene has the same crystal structure but is disordered (see text).

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

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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<sup>-3</sup>. 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<sup>-1</sup>); 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.†

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