

Acta Cryst. (1975). B31, 2917**Incipient Nucleophilic Additions. III. 3-Oxa-9-methyl-9-azabicyclo[3,3,1]nonan-7-one**

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Abstract. Monoclinic, $P2_1/c$, $a=8.779$, $b=9.679$, $c=9.514$ Å, $\beta=94.28^\circ$, $C_8H_{13}NO_2$, $M=155.20$, $Z=4$, $D_x=1.308$ g cm $^{-3}$. The bicyclo[3,3,1]nonane skeleton adopts the usual chair-chair conformation with an $O\cdots C=O$ distance of 2.75 Å.

Introduction. Bürgi, Dunitz & Shefter (1974) discussed $O\cdots C=O$ interactions in crystals as representing incipient stages of the nucleophilic addition of O to carbonyl groups. Only a few $O\cdots C=O$ distances less than 2.75 Å were found, so we decided to look for further examples. The title molecule was synthesized for this purpose by Dr C. Ganter (ETH, Zürich).

Details of data collection, structure analysis and refinement were much as in the preceding paper (Kaftory & Dunitz, 1975): the crystal had dimensions $0.2 \times 0.2 \times 0.25$ mm, and 1422 independent reflexions were measured, of which 1067 were significantly above background. The final R was 0.043.† Final positional and vibrational parameters are listed in Tables 1 and 2. Interatomic distances, bond angles and torsion angles involving C, N, O atoms are shown in Fig. 1; the C–H distances (not shown) lie in the range 0.95–1.05 Å.

Discussion. Although the molecule does not lie on a crystallographic mirror plane, it does show the virtual mirror symmetry of the structural formula; the largest differences between pairs of symmetry-equivalent par-

Table 2. 3-Oxa-9-methyl-9-azabicyclo[3,3,1]nonan-7-one: 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(1)	–428 (3)	174 (2)	112 (2)	3.4 (5)
H(2,1)	–544 (3)	87 (2)	309 (2)	3.9 (5)
H(2,2)	–472 (3)	240 (3)	352 (2)	4.2 (5)
H(3,1)	–245 (3)	–93 (3)	490 (3)	5.2 (6)
H(3,2)	–410 (3)	–113 (3)	395 (2)	4.2 (5)
H(4)	–209 (3)	–164 (3)	250 (2)	3.8 (5)
H(5,1)	–12 (3)	–32 (2)	372 (2)	4.4 (5)
H(5,2)	–22 (3)	–3 (2)	210 (2)	3.8 (5)
H(7,1)	–237 (3)	318 (3)	238 (2)	4.2 (6)
H(7,2)	–167 (3)	237 (2)	122 (3)	3.5 (5)
HM(1)	–251 (3)	–125 (4)	3 (3)	6.4 (8)
HM(2)	–171 (3)	26 (3)	1 (3)	5.2 (6)
HM(3)	–348 (3)	5 (3)	–56 (3)	5.2 (6)

ameters are 0.006 Å for bond lengths, 1.0° for bond angles and 3° for torsion angles (Fig. 1). The six-membered ring containing the hetero atom is markedly more puckered than that containing the carbonyl group, as can be seen by comparing the mean bond angles (109.2 vs. 112.2°) or r.m.s. torsion angles (60.7 vs. 52.4°), and the same kind of behaviour has been found in a 3-azabicyclo[3,3,1]nonan-7-one derivative (Kaftory & Dunitz, 1976). The molecule thereby attains a conformation in which the $O\cdots C=O$ distance is 2.75 Å (among the shortest observed) and the $O\cdots C=O$ angle 107° , corresponding to the optimal direction of approach of the nucleophile (Bürgi, Dunitz & Shefter, 1974). The displacement of the carbonyl C from the plane of its three bonded neighbours, although small (0.016 Å), is towards the approaching O atom.

The methyl group is equatorial with respect to the ring containing the O, axial with respect to the ring with the carbonyl substituent. This preference is prob-

Table 1. 3-Oxa-9-methyl-9-azabicyclo[3,3,1]nonan-7-one: 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)	–167 (2)	2281 (2)	3968 (2)	54 (1)	59 (1)	53 (1)	–19 (2)	–7 (2)	–2 (2)
O(2)	–3513 (2)	802 (2)	4360 (1)	46 (1)	54 (1)	36 (1)	–4 (2)	8 (1)	–4 (1)
N	–3288 (2)	–71 (2)	1553 (2)	41 (1)	40 (1)	34 (1)	1 (2)	1 (2)	–4 (2)
C(1)	–3594 (3)	1376 (2)	1890 (2)	41 (1)	42 (1)	36 (1)	5 (2)	–5 (2)	1 (2)
C(2)	–4441 (3)	1394 (3)	3215 (3)	39 (1)	57 (2)	51 (1)	4 (3)	3 (2)	–9 (2)
C(3)	–3132 (3)	–594 (3)	4036 (3)	53 (1)	48 (2)	45 (1)	–10 (2)	4 (2)	6 (2)
C(4)	–2295 (3)	–661 (2)	2710 (2)	45 (1)	33 (1)	42 (1)	2 (2)	0 (2)	0 (2)
C(5)	–746 (3)	87 (3)	2923 (3)	37 (1)	53 (2)	40 (1)	6 (2)	0 (2)	0 (2)
C(6)	–947 (2)	1611 (2)	3100 (2)	36 (1)	49 (1)	37 (1)	–9 (2)	8 (2)	2 (2)
C(7)	–2137 (3)	2258 (3)	2091 (3)	54 (1)	37 (1)	41 (1)	–4 (2)	2 (2)	4 (2)
CM	–2722 (3)	–267 (3)	162 (2)	60 (2)	65 (2)	33 (1)	0 (3)	0 (2)	–11 (2)

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† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31323 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

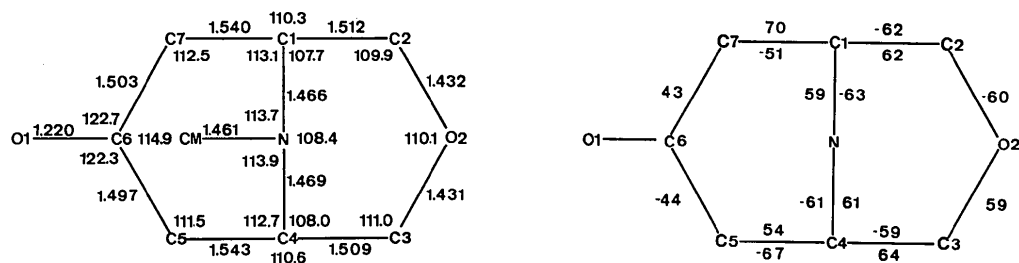


Fig. 1. 3-Oxa-9-methyl-9-azabicyclo[3,3,1]nonan-7-one: left, bond distances and angles; right, torsion angles

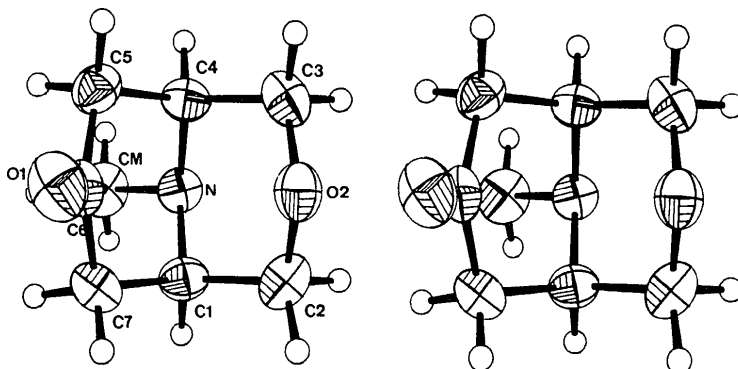


Fig. 2. 3-Oxa-9-methyl-9-azabicyclo[3,3,1]nonan-7-one: stereoscopic view of molecule, showing vibration ellipsoids at the 50% probability level (Johnson, 1965).

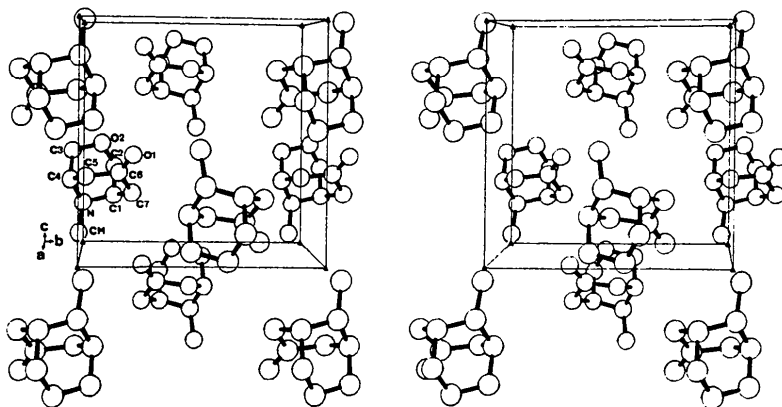


Fig. 3. Stereoscopic view of crystal structure of 3-oxa-9-methyl-9-azabicyclo[3,3,1]nonan-7-one.

ably due to the differing degrees of puckering of the rings, but it is interesting that C(3)–C(4) and C(2)–C(1) are slightly shorter than the corresponding bonds in the other ring.

This difference cannot be attributed to inadequate correction for thermal motion, which would affect both rings to roughly the same extent, leaving the possibility that the shortenings of C(1)–C(2) and C(4)–C(3) are real and due to the influence of the electronegative substituents (Dunitz & Ha, 1972). This would suggest that the analogous C–C shortenings observed in 1,4,7,10,13,16-hexaoxacyclooctadecane and its complexes (Dunitz, Dobler, Seiler & Phizackerley, 1974; Goldberg, 1975) may not be entirely spurious.

Fig. 3 shows the packing of the molecules.

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