the molecules included in the earlier correlation, in agreement with the general chemical experience that anilines are more weakly basic than aliphatic amines. Structural expression of the tendency towards delocalization of the N lone pair is also seen in the N–C(T1) distance of 1·390 Å, comparable to that found in other aniline derivatives, in the relatively small deviation from coplanarity of the tertiary amino group (angle sum, 355·9°) and in the orientation of the benzene ring with respect to this group (Fig. 2). The internal bond angles at the *p*-substituted positions of the benzene ring are both less than 120° [for an extensive discussion of similar effects see Domenicano, Vaciago & Coulson (1975)].

Fig. 2 shows a stereo view of the overall molecular conformation, Fig. 3 the packing of molecules in the cell.

This work was supported by the Swiss National Fund for the the Advancement of Scientific Research.

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Incipient Nucleophilic Additions. II. 11-Methyl-11-azabicyclo[5, 3, 1]undecan-4-one

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(*Received* 28 *July* 1975; *accepted* 9 *August* 1975)

Abstract. Monoclinic, $P2_1/n$, $a=7\cdot033$, $b=13\cdot980$, $c=10\cdot656$ Å, $\beta=93\cdot26°$, $C_{11}H_{16}NO$, $M=178\cdot26$, $Z=4$, $D_x=1\cdot150$ g cm^{-3}. The bicyclic molecule has an approximate mirror plane, in which the N atom and carbonyl group lie. The ten-membered ring adopts the usual BCB conformation but the eight-membered ring occurs in the unusual 'saddle' (BB) conformation with a transannular N···C=O distance of 2·457 Å, corresponding to a strong donor–acceptor interaction.

Introduction. A small sample of the title compound (Leonard, Morrow & Rogers, 1957) shared the same fate as the sample of 1-*p*-tolyl-1-azacyclooctan-5-one described in the preceding paper (Kaftory & Dunitz, 1975). The crystals are hygroscopic and had to be

Table 1. 11-*Methyl*-11-*azabicyclo*[5,3,1]*undecan*-4-*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 $T=\exp[-2\pi^2(U_{11}h^2a^{*2}+\ldots 2U_{12}hka^*b^*\ldots)]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O	−706 (2)	3777 (1)	4305 (2)	51 (1)	83 (1)	94 (1)	−2 (1)	15 (1)	1 (2)
N	1955 (2)	3096 (1)	2250 (1)	43 (1)	43 (1)	51 (1)	0 (1)	−3 (1)	−2 (1)
C(1)	3899 (2)	3057 (1)	2833 (2)	43 (1)	56 (1)	52 (1)	6 (1)	0 (1)	3 (2)
C(2)	4261 (2)	3924 (2)	3685 (2)	42 (1)	73 (1)	56 (1)	−3 (2)	−6 (1)	−7 (2)
C(3)	2576 (3)	4119 (2)	4483 (2)	52 (1)	77 (1)	52 (1)	−1 (2)	−2 (1)	−14 (2)
C(4)	624 (2)	4156 (1)	3817 (2)	47 (1)	53 (1)	66 (1)	2 (1)	3 (1)	−10 (2)
C(5)	231 (3)	4833 (2)	2726 (2)	60 (1)	51 (1)	85 (1)	13 (2)	−7 (2)	−5 (2)
C(6)	1526 (3)	4770 (1)	1632 (2)	80 (1)	48 (1)	67 (1)	6 (2)	−12 (2)	9 (2)
C(7)	1696 (3)	3738 (1)	1167 (2)	63 (1)	55 (1)	50 (1)	2 (2)	−12 (2)	1 (2)
C(8)	3217 (4)	3603 (2)	203 (2)	108 (2)	74 (1)	48 (1)	0 (2)	8 (2)	5 (2)
C(9)	5215 (4)	3634 (2)	821 (2)	81 (1)	91 (2)	73 (1)	−13 (2)	32 (2)	−7 (3)
C(10)	5424 (3)	2923 (2)	1885 (2)	52 (1)	81 (2)	74 (1)	7 (2)	10 (2)	−11 (2)
C(M)	1119 (3)	2159 (2)	2038 (3)	65 (1)	53 (1)	84 (1)	−9 (2)	−2 (2)	−6 (2)

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sealed in capillaries to protect them from moisture.

Intensities from a crystal, 0·3 × 0·25 × 0·25 mm, were collected on an automated Hilger–Watts Y290 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}79$ cm^{-1}). Of the 1849 symmetry-independent reflexions measured, the intensities of 1430 were significantly above background. The structure was solved by direct methods and refined by full-matrix least-squares analysis with the weighting scheme of Dunitz & Seiler (1973) with $r = 5{\cdot}0$ Å^2. 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), for H from Stewart, Davidson & Simpson (1965). The final R was 0·045.*

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 listed) lie in the range 0·90–1·01 Å.

Table 2. 11-*Methyl*-11-*azabicyclo*[5,3,1]*undecan*-4-*one*: *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)
HC(1)	393 (2)	251 (1)	341 (2)	4·0 (3)
HC(21)	531 (3)	378 (2)	422 (2)	5·1 (4)
HC(22)	457 (3)	450 (2)	320 (2)	4·2 (4)
HC(31)	250 (4)	359 (2)	512 (3)	6·3 (6)
HC(32)	275 (4)	472 (2)	492 (3)	6·3 (6)
HC(51)	26 (4)	548 (2)	307 (3)	7·1 (6)
HC(52)	−109 (4)	473 (2)	245 (3)	6·7 (6)
HC(61)	277 (3)	505 (1)	190 (2)	4·7 (4)
HC(62)	107 (4)	513 (2)	98 (3)	6·8 (7)
HC(7)	45 (4)	357 (2)	80 (3)	5·7 (6)
HC(81)	303 (5)	407 (3)	−41 (4)	7·6 (8)
HC(82)	299 (4)	298 (2)	−20 (3)	6·6 (7)
HC(91)	540 (3)	427 (2)	108 (2)	5·7 (5)
HC(92)	608 (4)	348 (2)	20 (3)	6·7 (6)
HC(101)	528 (4)	228 (2)	158 (3)	6·1 (6)
HC(102)	661 (4)	294 (2)	234 (2)	6·1 (6)
HM(1)	−18 (6)	223 (3)	176 (3)	8·1 (9)
HM(2)	179 (4)	178 (2)	143 (3)	7·1 (6)
HM(3)	117 (5)	179 (3)	283 (4)	8·3 (8)

Discussion. Bond lengths and angles (Fig. 1) need no special discussion apart from the comment that bonds at the two ends of the molecule appear to be slightly shortened by thermal motion effects. The torsion-angle pattern shows that the molecule displays a non-crystallographic mirror plane in very good approximation. The ten-membered ring has essentially the same conformation as that observed in many cyclodecane derivatives (Dunitz, 1968), the six-membered ring has the usual chair conformation, and the eight-membered ring adopts the 'saddle' or BB type of conformation, but considerably deformed from its ideal D_{2d} symmetry to make one of the 1,5 distances much shorter than the others. A stereo view of the molecule is shown in Fig. 2.

On the basis of its abnormally large dipole moment (4·87 D in benzene) and its strongly displaced carbonyl absorption (Leonard, Morrow & Rogers, 1957) the molecule was expected to show a strong transannular N···C=O interaction.* This expectation is now confirmed by structural evidence. The observed N···C=O distance is 2·46 Å and the deviation Δ of the carbonyl C(4) from the plane of its three bonded neighbours is 0·098 Å, in reasonable agreement with the Δ of 0·116 Å calculated from the relationship $d(\mathrm{N}\cdots\mathrm{C}) = -1{\cdot}701 \log \Delta + 0{\cdot}867$ Å derived by Bürgi, Dunitz & Shefter (1973) from empirical correlations of data obtained from analogous molecules.

Birnbaum (1974) has obtained an approximately linear correlation between N···C=O distances and carbonyl absorption maxima for distances between 2 and 3 Å; in this range, a shortening of 0·1 Å corresponds to a frequency lowering of about 11 cm^{-1}. The distance of 2·46 Å observed in the title compound would correspond to a carbonyl absorption maximum at about 1650 cm^{-1}. According to Leonard (1960) the carbonyl absorption of the title compound is actually strongly solvent dependent: 1666 cm^{-1} (C_6H_{12}), 1656 cm^{-1} (CCl_4), 1641 cm^{-1} (CH_3CN), 1631 cm^{-1} (CH_2Cl_2), 1613 cm^{-1} ($CHCl_3$). The corresponding distances, estimated from Birnbaum's correlation, would cover the range 2·60 to 2·11 Å. The energy variation along the reaction path is presumably rather flat and

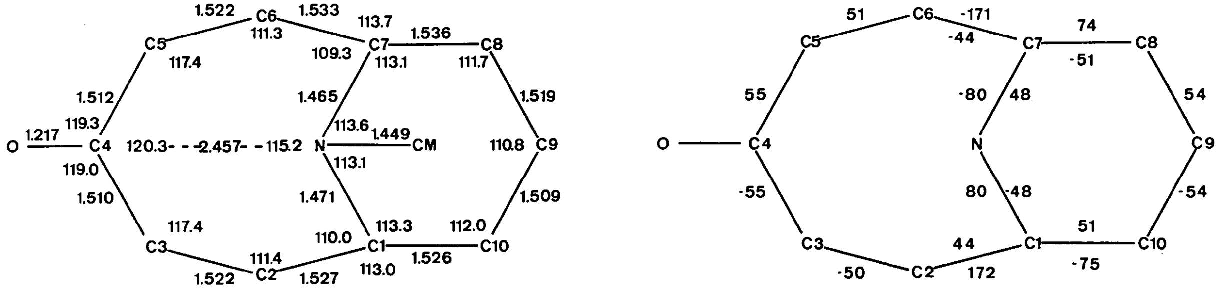

Fig. 1. 11-Methyl-11-azabicyclo[5,3,1]undecan-4-one: left, bond distances and angles; right, torsion angles in the bicyclic skeleton.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31322 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

* *Note added in proof:*– For C-13 n.m.r. evidence on this point see Nakashima & Maciel (1972).

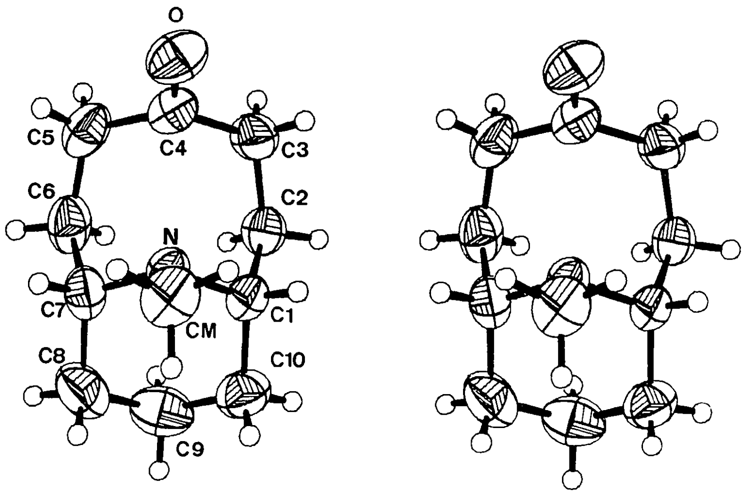

Fig. 2. 11-Methyl-11-azabicyclo[5,3,1]undecan-4-one: stereoscopic view of molecule, showing vibration ellipsoids at the 50% probability level (Johnson, 1965).

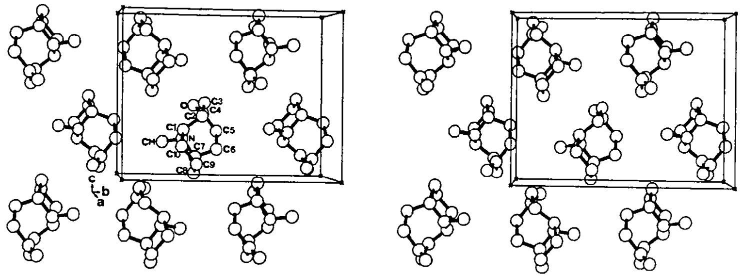

Fig. 3. Stereoscopic view of crystal structure of 11-methyl-11-azabicyclo[5,3,1]undecan-4-one.

hence susceptible to small perturbations. If the Birnbaum correlation is used to estimate N···C=O distances in crystals from spectral measurements in solution, these will have to be carried out under carefully defined standard conditions.

Fig. 3 shows a stereoscopic view of the molecular packing.

This work was supported by the Swiss National Fund for the Advancement of Scientific Research.

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