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# Incipient Nucleophilic Additions. I. 1-*p*-Tolyl-1-azacyclooctan-5-one

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**Abstract.** Monoclinic, $P2_1/c$, $a=5{\cdot}730$, $b=18{\cdot}284$, $c=12{\cdot}809$ Å, $\beta=112{\cdot}71°$, $C_{14}H_{19}NO$, $M=217{\cdot}31$, $Z=4$, $D_x=1{\cdot}166$ g cm$^{-3}$. The eight-membered ring adopts the usual boat-chair conformation with a 1,5-transannular N···C=O distance of 2·76 Å, corresponding to a weak donor–acceptor interaction.

**Introduction.** In this series of papers we take the view that attractive intramolecular interactions can be regarded as representing incipient stages of chemical reactions, here nucleophilic addition to the carbonyl group.

A small sample of the title compound (Leonard & Oki, 1955), sealed under nitrogen, was obtained from Professor N. J. Leonard in 1960, mislaid soon afterwards, eventually forgotten and finally rediscovered in 1973 when our interests had turned towards N···C=O interactions as examples of incipient stages of nucleophilic addition reactions (Bürgi, Dunitz & Shefter, 1973).

Intensities from a crystal, 0·3 × 0·2 × 0·2 mm, were collected on an automated Hilger–Watts Y290 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0{\cdot}71069$ Å, $\mu=0{\cdot}78$ cm$^{-1}$). Of the 1502 symmetry-independent reflexions measured, the intensities of 1105 were significantly above background. The structure was solved by direct methods and refined by full-matrix least-squares analysis with experimental weights. The H atoms were included during the later stages. Scattering factors for C, N and O were taken from *International Tables for X-ray Crystallography*

Table 1. 1-*p-Tolyl*-1-*azacyclooctane*-5-*one*: *atomic coordinates* (× 10$^4$) *and vibrational tensor components* (× 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 | 9004 (6) | 2336 (2) | 4482 (3) | 59 (2) | 159 (3) | 129 (3) | −16 (4) | 43 (4) | −24 (5) |
| N | 3993 (6) | 1313 (2) | 3017 (3) | 65 (2) | 60 (2) | 78 (2) | 0 (4) | 19 (4) | −2 (4) |
| C(1) | 3338 (8) | 1106 (2) | 3966 (4) | 74 (6) | 71 (3) | 114 (4) | −13 (5) | 45 (6) | −14 (6) |
| C(2) | 5237 (11) | 1360 (3) | 5070 (4) | 131 (5) | 112 (4) | 80 (3) | −14 (7) | 47 (7) | 10 (6) |
| C(3) | 5846 (9) | 2153 (3) | 5180 (4) | 101 (4) | 123 (4) | 102 (4) | −33 (7) | 54 (6) | −47 (7) |
| C(4) | 6832 (9) | 2439 (2) | 4345 (4) | 63 (3) | 89 (3) | 104 (3) | −24 (6) | 42 (6) | −29 (6) |
| C(5) | 5105 (10) | 2881 (3) | 3351 (6) | 88 (4) | 72 (3) | 184 (6) | −1 (6) | 35 (8) | 21 (8) |
| C(6) | 2761 (13) | 2590 (3) | 2637 (4) | 180 (6) | 74 (4) | 98 (4) | −9 (8) | −6 (8) | 16 (6) |
| C(7) | 2342 (9) | 1861 (3) | 2253 (4) | 78 (3) | 78 (4) | 128 (4) | 20 (6) | 15 (6) | 6 (6) |
| CT(1) | 5413 (7) | 842 (2) | 2644 (4) | 57 (2) | 46 (2) | 72 (3) | −10 (4) | 18 (4) | −2 (4) |
| CT(2) | 5667 (9) | 934 (2) | 1620 (4) | 109 (4) | 70 (3) | 80 (3) | −1 (5) | 32 (6) | 12 (5) |
| CT(3) | 7105 (11) | 464 (3) | 1270 (4) | 127 (4) | 91 (4) | 94 (4) | −20 (7) | 60 (7) | −12 (6) |
| CT(4) | 8383 (8) | −116 (3) | 1903 (5) | 73 (3) | 63 (3) | 117 (4) | −16 (5) | 42 (6) | −21 (6) |
| CT(5) | 8140 (8) | −212 (2) | 2923 (4) | 78 (3) | 60 (3) | 100 (4) | 0 (5) | 26 (6) | 4 (5) |
| CT(6) | 6710 (8) | 250 (2) | 3291 (3) | 75 (3) | 64 (3) | 77 (3) | −1 (5) | 28 (5) | 3 (5) |
| CM | 10020 (9) | −609 (3) | 1518 (5) | 107 (4) | 108 (4) | 182 (5) | −22 (6) | 82 (8) | −52 (8) |

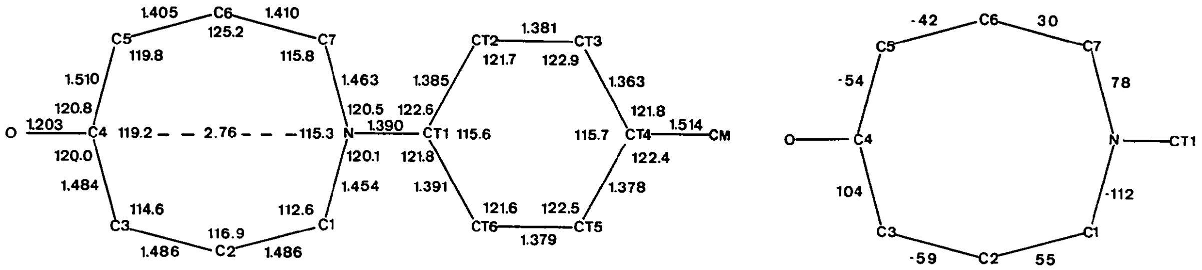

Fig. 1. 1-*p*-Tolyl-1-azacyclooctan-5-one: left, bond distances and angles (some subject to systematic error arising from disorder in crystal structure); right, torsion angles in eight-membered ring.

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Table 2. 1-*p-Tolyl*-1-*azacyclooctane-5-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$^2$) |
|---|---|---|---|---|
| HC(11) | 166 (8) | 136 (3) | 385 (4) | 10 (1) |
| HC(12) | 313 (8) | 57 (3) | 400 (4) | 8 (1) |
| HC(21) | 457 (8) | 128 (2) | 568 (4) | 10 (1) |
| HC(22) | 695 (8) | 111 (3) | 522 (4) | 11 (1) |
| HC(31) | 426 (9) | 237 (2) | 510 (4) | 10 (1) |
| HC(32) | 729 (9) | 224 (3) | 600 (4) | 9 (1) |
| HC(51) | 498 (8) | 335 (3) | 358 (4) | 12 (1) |
| HC(52) | 609 (8) | 287 (2) | 282 (4) | 14 (1) |
| HC(61) | 195 (8) | 263 (2) | 323 (4) | 14 (1) |
| HC(62) | 183 (8) | 293 (3) | 200 (4) | 11 (1) |
| HC(71) | 57 (9) | 170 (3) | 202 (4) | 12 (1) |
| HC(72) | 279 (9) | 186 (2) | 159 (4) | 13 (1) |
| HT(2) | 479 (8) | 128 (2) | 113 (4) | 9 (1) |
| HT(3) | 719 (8) | 58 (2) | 53 (4) | 9 (1) |
| HT(5) | 899 (8) | −64 (3) | 342 (4) | 7 (1) |
| HT(6) | 666 (8) | 16 (2) | 405 (4) | 9 (1) |
| HM(1) | 1062 (36) | −101 (9) | 214 (12) | 9 (3) |
| HM(2) | 1147 (31) | −30 (7) | 136 (18) | 5 (3) |
| HM(3) | 891 (22) | −80 (10) | 68 (12) | 13 (3) |

(1962), for H from Stewart, Davidson & Simpson (1965). The final $R$ was 0·074.*

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 0·90–1·09 Å.

**Discussion.** The large, anisotropic vibration parameters of some of the atoms (Table 1) indicate that the crystal structure is disordered to a certain extent. The conformation of the eight-membered ring is similar to that found in cyclooctane derivatives (boat-chair) with the N and carbonyl C atoms on opposite sides of the approximate mirror plane through C(2) and C(6). As a result of the disorder, apparent bond lengths in the eight-membered ring are systematically too short, bond angles too wide (Fig. 1). The atom affected most seriously is C(6), which has one of the largest, most anisotropic temperature factors. Various attempts were made to identify alternative ring conformations that might be present in minor amounts, but the results were not conclusive.

Although the observed transannular N···C=O distance of 2·76 Å is about 0·5 Å less than the sum of the C and N packing radii, the N···C=O interaction must be quite weak, judging from the normal carbonyl absorption maximum at 1698 cm$^{-1}$ (Leonard & Oki, 1955; Birnbaum, 1974) and from the very small out-of-plane deviation ($\Delta = 0·016$ Å) of the carbonyl C from the plane of its three bonded neighbours. On the basis of our previous correlations (Bürgi, Dunitz & Shefter, 1973) an N···C=O distance of 2·76 Å should correspond to a $\Delta$ of 0·077 Å, about five times larger than that observed. Although the disorder in the ring conformation may affect the observed value somewhat, the amino group of the title compound, with its aryl substituent, is evidently less nucleophilic than those of

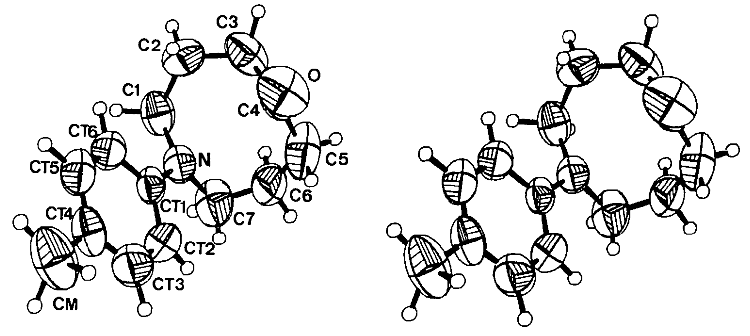

Fig. 2. 1-*p*-Tolyl-1-azacyclooctan-5-one: stereoscopic view of molecule, showing vibration ellipsoids at the 50% probability leve (Johnson, 1965).

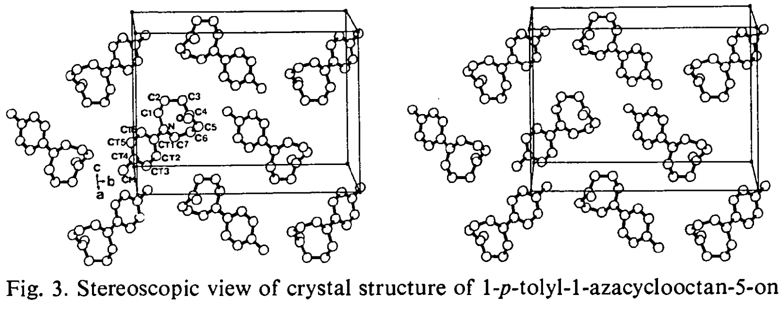

Fig. 3. Stereoscopic view of crystal structure of 1-*p*-tolyl-1-azacyclooctan-5-one.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31321 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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.

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

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**Abstract.** Monoclinic, $P2_1/n$, $a=7{\cdot}033$, $b=13{\cdot}980$, $c=10{\cdot}656$ Å, $\beta=93{\cdot}26°$, $C_{11}H_{16}NO$, $M=178{\cdot}26$, $Z=4$, $D_x=1{\cdot}150$ 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* (×10⁴) *and vibrational tensor components* (×10³) *for non-hydrogen atoms* (*e.s.d.'s in parentheses*)

The $U_{ij}$ values (Å²) correspond to the temperature factor expression $T=\exp[-2\pi^2(U_{11}h^2a^{*2}+\ldots2U_{12}hka^*b^*\ldots)]$.

| | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| 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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