HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.
HECTOR, D. S. (1889). *Chem. Ber.* **22**, 1176–1180.
KURZER, F. (1965). *Adv. Heterocycl. Chem.* **5**, 126–133.
KURZER, F. & SANDERSON, P. M. (1963). *J. Chem. Soc.* pp. 3333–3336.
L'ABBÉ, G., VERHELST, G., TOPPET, S., KING, G. S. D. & BRIERS, J. (1976). *J. Org. Chem.* **41**, 3403–3406.
SATO, S., KINOSHITA, T., HATA, T. & TAMURA, C. (1972). *Acta Cryst.* A**28**, S25.
SHELDRICK, G. M. (1976). Personal communication.

Acta Cryst. (1978). B**34**, 3245–3248

Low-Temperature Refinement of the Structure of 11-Methyl-11-azabicyclo[5.3.1]undecan-4-one

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The structure of $C_{11}H_{19}NO$ has been refined with new X-ray diffraction data collected at 98 K. Crystals are monoclinic, $P2_1/n$; $a = 6{\cdot}940\,(1)$, $b = 13{\cdot}819\,(3)$, $c = 10{\cdot}561\,(2)$ Å, $\beta = 93{\cdot}04\,(2)^\circ$. Comparison of the results with those of the room-temperature analysis reveals systematic differences in bond lengths. When rigid-body libration corrections are applied these differences disappear and virtually identical molecular geometries are obtained for the two temperatures, except that the pyramidality at the N atom appears to be slightly less pronounced at the higher temperature. The N lone-pair density is clearly visible in a difference map based on the low-temperature data.

Introduction

A room-temperature (RT) analysis of the title compound (Kaftory & Dunitz, 1975) has shown that the molecular conformation is characterized by a short, transannular, non-bonded N···C=O distance of 2·46 Å, corresponding to a strong intramoecular donor-acceptor interaction. From the marked solvent dependence of the carbonyl absorption (from 1666 cm^{-1} in C_6H_{12} to 1613 cm^{-1} in $CHCl_3$) the strength of this interaction would appear to be sensitive to small, external perturbations, with the implication that the potential-energy variation along the N···C distance coordinate might exhibit only a rather shallow minimum with pronounced anharmonicity. Since interatomic separations derived from diffraction methods do not correspond to equilibrium distances (r_e) but rather to the centroids of distributions obtained by averaging over the intra- and intermolecular vibrations (r_g), any pronounced anharmonicity in the potential would lead to slightly different r_g values being observed at different temperatures.

In this paper we describe results of a low-temperature (LT, 98 K) analysis of the title compound and compare them with those of the earlier RT study.

Details of analysis

A single crystal with dimensions 0·50 × 0·40 × 0·35 mm was taken from the original sample and sealed in Araldite as protection against moisture. Cell dimensions (Table 1) and intensities were measured on an Enraf–Nonius CAD-4 diffractometer (graphite-monochromatized Mo $K\alpha$ radiation) equipped with a low-temperature device. During the measurements the crystal was maintained at 98 ± 1 K and no detectable loss of intensity occurred. Of the 2424 independent reflexions recorded ($\theta \leq 24^\circ$), 1670 were regarded as significantly above background ($I > 3\sigma I$).

Table 1. *Crystal data*

11-Methyl-11-azabicyclo[5.3.1]undecan-4-one. Molecular formula:[*] $C_{11}H_{19}NO$, FW = 181·28.

	RT	98 K
a (Å)	7·033	6·940 (1)
b (Å)	13·980	13·819 (3)
c (Å)	10·656	10·561 (2)
β (°)	93·26	93·04 (2)
Z	4	
V ($Å^3$)	1046·0	1011·4
Space group	$P2_1/n$	
D_x (g cm^{-3})	1·15	1·19

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[*] Erroneously given as $C_{11}H_{16}NO$ (FW = 178·26) in Kaftory & Dunitz (1975).

Table 2. *Positional and anisotropic thermal parameters* ($\times 10^4$) *for non-hydrogen atoms* (*e.s.d.'s in parentheses*)

The U_{ij} values (Å^2) correspond to the 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	−744 (1)	3777 (1)	4349 (1)	149 (4)	251 (5)	303 (5)	−5 (4)	44 (4)	7 (4)
N	1945 (1)	3077 (1)	2242 (1)	134 (4)	133 (5)	154 (5)	−2 (3)	−27 (4)	3 (4)
C(1)	3933 (2)	3048 (1)	2814 (1)	123 (5)	181 (5)	151 (6)	18 (4)	3 (4)	9 (5)
C(2)	4310 (2)	3932 (1)	3670 (1)	121 (5)	222 (6)	162 (6)	−11 (4)	−14 (4)	−30 (5)
C(3)	2607 (2)	4125 (1)	4492 (1)	149 (5)	237 (5)	158 (6)	4 (5)	−11 (4)	−36 (5)
C(4)	602 (2)	4160 (1)	3837 (1)	148 (5)	158 (5)	202 (6)	24 (4)	−6 (5)	−39 (5)
C(5)	175 (2)	4841 (1)	2725 (1)	200 (6)	151 (6)	247 (7)	36 (4)	−42 (5)	−11 (5)
C(6)	1486 (2)	4776 (1)	1608 (1)	264 (6)	140 (5)	198 (6)	12 (5)	−30 (5)	20 (5)
C(7)	1649 (2)	3726 (1)	1143 (1)	207 (5)	163 (6)	150 (6)	9 (4)	−37 (5)	6 (5)
C(8)	3170 (2)	3594 (1)	150 (1)	337 (1)	234 (6)	145 (6)	−10 (5)	11 (5)	18 (5)
C(9)	5220 (2)	3650 (1)	755 (1)	267 (6)	283 (7)	209 (6)	−38 (5)	84 (5)	−14 (6)
C(10)	5474 (2)	2921 (1)	1839 (1)	171 (5)	249 (6)	222 (7)	21 (5)	40 (5)	−32 (6)
C(M)	1152 (2)	2109 (2)	2005 (1)	204 (6)	153 (5)	239 (7)	−31 (5)	−13 (5)	−6 (5)

Table 3. *Positional parameters* ($\times$ 10^3) *and isotropic B values for hydrogen atoms* (*e.s.d.'s in parentheses*)

	x	y	z	B (Å^2)
HC(1)	397 (2)	244 (1)	340 (2)	1·0 (4)
HC(21)	550 (3)	380 (1)	424 (2)	1·6 (4)
HC(22)	459 (2)	453 (1)	314 (2)	1·9 (5)
HC(31)	251 (3)	360 (1)	516 (2)	2·2 (5)
HC(32)	281 (3)	479 (1)	495 (2)	2·7 (5)
HC(51)	26 (3)	551 (1)	308 (2)	2·5 (5)
HC(52)	−126 (3)	471 (1)	242 (2)	1·7 (4)
HC(61)	280 (3)	506 (1)	182 (2)	1·8 (5)
HC(62)	92 (2)	520 (1)	88 (2)	1·9 (4)
HC(7)	29 (3)	352 (1)	72 (2)	2·0 (4)
HC(81)	295 (3)	410 (1)	−53 (2)	2·4 (5)
HC(82)	296 (3)	292 (1)	−26 (2)	2·4 (5)
HC(91)	550 (3)	433 (1)	108 (2)	2·2 (4)
HC(92)	618 (3)	350 (1)	10 (2)	2·7 (5)
HC(101)	535 (3)	224 (1)	148 (2)	2·3 (5)
HC(102)	677 (3)	297 (1)	227 (2)	2·0 (5)
HCM(1)	−27 (3)	216 (1)	167 (2)	2·8 (5)
HCM(2)	187 (3)	173 (1)	134 (2)	2·4 (5)
HCM(3)	113 (3)	174 (1)	284 (2)	2·5 (5)

The structure was refined by full-matrix least-squares analysis [XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972), atomic scattering factors of Cromer & Mann (1968), modified weighting system (Dunitz & Seiler, 1973) with r = 4·0 Å^2 in the final refinement cycles], starting from the RT parameters and terminating with the parameters listed in Tables 2 and 3. The final R was 0·033 (R_w = 0·038).* E.s.d.'s in interatomic distances involving C, N and O atoms (Fig. 1) are of the order of 0·002 Å, those in C–H distances (all between 0·99 and 1·06 Å) about ten times larger.

Discussion

The interatomic distances obtained in the LT study (Fig. 1) are slightly (up to 0·02 Å) but consistently longer than those from the RT analysis. On the other hand, comparison of the bond angles (and torsion angles) between the two analyses shows no particular trends, except for the bond angles at N:

	RT	LT
C(1)–N–C(M)	113·1°	112·4°
C(7)–N–C(M)	113·6	112·7
C(1)–N–C(7)	115·2	115·3.

The bond-angle sum is thus decreased by 1·5° in the LT study, *i.e.* the N atom has apparently become slightly more pyramidal. The remaining bond angles agree within better than 0·5°, and a separate listing of the LT values seems superfluous.

The analysis of the vibrational tensors obtained in the two analyses leads to the following results:

(1) Atomic mean-square vibrational amplitudes at 98 K are uniformly about 30% of those at RT; the ratio of individual diagonal terms U_{ii}(LT)/U_{ii}(RT) lies within the range 0·28–0·33.

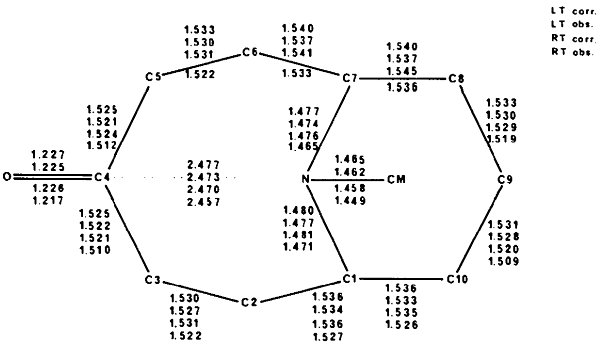

Fig. 1. Bond lengths (Å) in the 11-methyl-11-azabicyclo[5.3.1]-undecan-4-one molecule.

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* Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33729 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(2) According to the test proposed by Rosenfield, Trueblood & Dunitz (1978) the molecule behaves as a reasonably rigid body, *i.e.* the condition $\Delta_{A,B} = z^2_{A,B} - z^2_{B,A} \sim 0$ (Hirshfeld, 1976) is obeyed just as well for non-bonded pairs of C, N, O atoms as for bonded pairs. From the LT parameters the same r.m.s. value of Δ (15×10^{-4} Å^2) is obtained for the 64 non-bonded pairs as for the 14 bonded pairs. The larger $|\Delta|$ values (those $>22 \times 10^{-4}$ Å^2) all involve three atoms, the N and O (for which the U_{ij} values may be suspected to be contaminated by lone-pair electron density) and the methyl C(M). Omission of Δ's involving these atoms reduces $\langle\Delta^2\rangle^{1/2}$ to 10×10^{-4} Å^2 for the remaining non-bonded pairs and to 12×10^{-4} Å^2 for the remaining bonded pairs; these values are comparable with the average standard deviation in Δ ($\sim 10 \times 10^{-4}$ Å^2).

(3) As might be expected from the previous result, analysis of the vibrational ellipsoids in terms of rigid-body motion (Schomaker & Trueblood, 1968) leads to excellent agreement between observed and calculated U_{ij} values, both for the RT and LT data. With the revised program *THMB* (Trueblood, 1977) we obtain:

	RT	98 K
$R(U_{ij})$*	0·048	0·055
$\langle\Delta^2(U_{ij})\rangle^{1/2}$	23	8×10^{-4} Å^2
$\langle\sigma(U_{ij})\rangle$	15	6×10^{-4} Å^2.

The eigenvalues of the **L** tensor are: at RT, 9·64, 5·51, 4·79 × 10^{-3} rad^2; at 98 K, 2·81, 1·53, 1·50 × 10^{-3} rad^2. Those of the **T** tensor are: at RT, 5·33, 4·29, 3·60 × 10^{-2} Å^2; at 98K, 1·67, 1·31, 1·10 × 10^{-2} Å^2. Corresponding eigenvectors have much the same orientation at both temperatures, the long axis of both the **L** and **T** ellipsoids pointing roughly along the long axis of the molecule.

(4) When corrections for the different amounts of molecular libration at the two temperatures are applied (Cruickshank, 1956), the systematic difference between the RT and LT bond lengths disappears. In fact, the two sets of corrected interatomic distances (including the transannular non-bonded N···C=O distance) are virtually identical (Fig. 1). Libration corrections to bond angles and torsion angles are negligible at both temperatures.

We conclude that the bicyclic skeleton behaves as a rigid body that shows no detectable difference in its structural parameters between RT and 98 K. In particular, and contrary to our initial presumption, the r_g separations relevant to the N···C=O interaction are virtually identical at the two temperatures. The deviation of the carbonyl C(4) from the plane of its bonded neighbours is 0·097 Å at both temperatures; for the N···C distance, we obtain 2·477 (2) Å at 98 K and 2·470 (3) Å at RT, not significantly different from the mean.

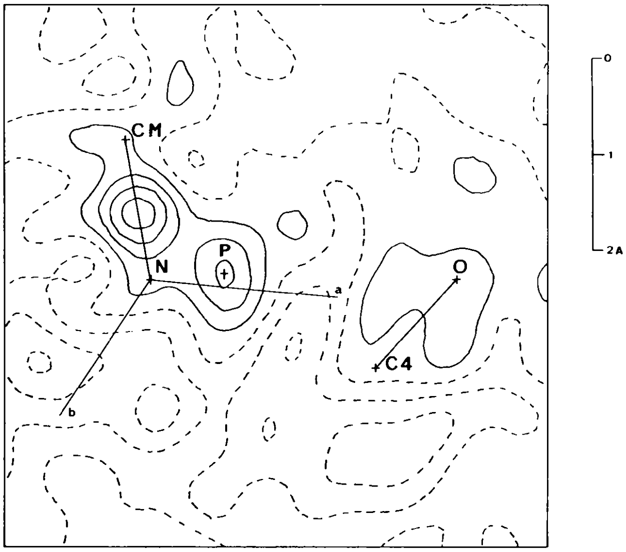

Fig. 2. Difference electron density in a plane through C(M), N, C(4), O. Contour lines are drawn at intervals of 0·05 e Å^{-3}, with the zero and negative contours dotted. The line *a* shows the direction of the local threefold axis, *b* the projected direction of the N–C ring bonds.

On the other hand, the difference of 1·5° in the bond-angle sum at N at the two temperatures is probably real and provides a hint of detectable anharmonicity in the potential describing the relative motion of the methyl C(M) with respect to the rigid bicyclic skeleton. The egregious behaviour of this atom in the rigid-body test (point 2, above) also suggests that the potential in question is relatively shallow, in keeping with the low inversion barriers (5–10 kcal mol^{-1}) characteristic of alicyclic amines (Lehn, 1970).

An electron-density difference map, calculated at the conclusion of the LT least-squares analysis, shows distinct maxima at or close to the mid-points of all C–C and C–N bonds. An additional peak (*P* in Fig. 2) can be attributed to the N lone-pair density. This peak lies close to the local approximate threefold axis of the N atom, which, in turn, lies close to the N···C=O direction. Minor peaks that might correspond to O lone-pair density are also present but they are much more diffuse than the N lone-pair peak.

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References

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Cruickshank, D. W. J. (1956). *Acta Cryst.* **9**, 757–758.

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* Here $R(U_{ij})$ is an agreement factor defined as $\sum |\Delta(U_{ij})|/\sum |U_{ij}|$ wnere $\Delta(U_{ij}) = U_{ij}(\text{obs}) - U_{ij}(\text{calc})$, analogous to the usual crystallographic R factor.

DUNITZ, J. D. & SEILER, P. (1973). *Acta Cryst.* B**29**, 589–595.
HIRSHFELD, F. L. (1976). *Acta Cryst.* A**32**, 239–244.
KAFTORY, M. & DUNITZ, J. D. (1975). *Acta Cryst.* B**31**, 2914–2916.
LEHN, J. M. (1970). *Top. Curr. Chem.* **15**, 311–377.
ROSENFIELD, R. E. JR, TRUEBLOOD, K. N. & DUNITZ, J. D. (1978). *Acta Cryst.* A**34**, 828–829.
SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B**24**, 63–76.
STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.
TRUEBLOOD, K. N. (1977). Abstr. 4th Eur. Crystallogr. Meet., Oxford. Paper PI 36.

Acta Cryst. (1978). B**34**, 3248–3255

Einkristallröntgenstrukturanalyse eines Zwitterionischen, Photoisomeren Umlagerungsproduktes eines Sydnons mit Spiranstruktur

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3-Phenylthio-8-oxa-1-aza-2,5-diazoniaspiro[4.5]deca-1,3-diene-2,4-diolate ($C_{12}H_{13}N_3O_3S$) is a photoisomer of a sydnone, and its preparation indicated a new pathway for the photoisomerization of sydnones. The compound crystallizes in the monoclinic space group $P2_1/b$ with a = 12·743 (7), b = 23·106 (4), c = 9·555 (6) Å, γ = 112·40 (3)° and two molecules per asymmetric unit. 4754 independent reflexions were measured on an automatic diffractometer. The structure was solved by direct methods and refined by least-squares methods yielding a final R index of 0·058. The identification of some atomic positions as C or N atoms was sophisticated and was verified by several crystallographic methods. The molecule incorporates a spirane system with a quaternary N at its centre. The bonding relationships are described incorporating a bond–non-bond resonance. The two molecules of the asymmetric unit show slight differences concerning conformation induced by crystal packing.

Einleitung

Die Photoisomerisierung von Sydnonen (1) führt normalerweise über eine Nitriliminzwischenstufe (2) zu den Oxadiazolinonderivaten (3) (Krauch, Kuhls & Piek, 1966). Setzt man in diese Reaktion die Sydnone (1*a*,*b*,*c*) ein, bei denen R^1 eine Aminokomponente und R^2 stets ein Thiophenylrest ist, dann erhält man zwar gleichfalls jeweils ein Isomerisierungsprodukt, dessen spektroskopische Daten (MS, ¹H-NMR, ¹³C-NMR, UV, IR) jedoch nicht vollständig konsistent mit der Formulierung eines Oxadiazolinonderivates sind. Dieser Sachverhalt liess die Vermutung zu, dass hier ein neuer Reaktionsweg vorliegt (Gotthardt, Reiter, Gieren & Lamm, 1978). Da aber aus den spektroskopischen und auch aus chemischen Befunden kein Strukturvorschlag abgeleitet werden konnte, der mit allen diesen Befunden in Übereinstimmung gewesen wäre, haben wir zur Aufklärung der Struktur der neuartigen Isomerisierungsprodukte eine Röntgenstrukturanalyse von (4*a*) durchgeführt. Gleichfalls wurden röntgenographische Untersuchungen an dem zu (4*a*) analogen Isomerisierungsprodukt (4*b*) vorgenommen. Die Ergebnisse der Röntgenstrukturuntersuchungen erlauben es, die Photoisomerisierungsprodukte von (1*a*,*b*,*c*) überraschend als (4*a*,*b*,*c*) zu formulieren.