Oxidation of ethane resulted in the formation of C_2H_5, C_2H_3, and C_3H_7 radicals.

It is suggested that the photoionization mass spectrometer will be extremely useful for studying gas-phase free-radical reactions. Any free radical with an ionization potential less than the argon resonance line energy (11.83 eV) and a steady-state concentration on the order of 10^{-10} mol/l. should be readily detectable in reacting gases at pressures of a few Torr. Improvements in detector design and pumping speed may improve this sensitivity by several orders of magnitude.

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I. T. N. Jones, Kyle D. Bayes*
Department of Chemistry, University of California
Los Angeles, California 90024
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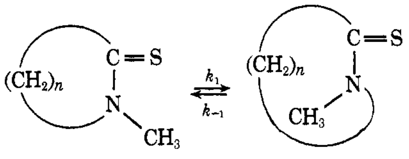
Molecular Structures of Medium- and Large-Membered *N*-Methylthiolactams and the Dynamics of Their Syn–Anti Interconversion

Sir:

A detailed conformational description of medium- (8–12) and large-membered ring compounds is potentially available from an approach which combines dynamic studies (nmr) and static molecular structure determination (X-ray).[1] We now report the molecular structures of the 9- and 13-membered *N*-methylthiolactams (I, n = 7 and 11), as well as activation parameters and thermodynamic equilibration data for the syn–anti interconversion (I $\rightleftarrows$ II) for the 12- and 13-membered ring systems.[2,3]



I, syn II, anti

The 9-, 12-, and 13-membered *N*-methylthiolactams exist as crystalline solids; however, upon dissolution at room temperature in organic solvents the 12- and 13-membered systems display *N*-methyl doublet absorption in the nmr indicative of the equilibration process I $\rightleftarrows$ II. The nine-membered ring does not show this behavior due to the presence of only the syn form. Using the $W_{1/2}$ method for this $P_{\mathrm{I}} \neq P_{\mathrm{II}}$ system,[4a,b] the activation parameters listed in Table I were determined.

With pure crystalline diastereomers in hand, E_a, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ could also be obtained by direct equilibration.[5] To obtain these data (Table I) a crystalline sample of the 12- or 13-membered compounds was dissolved at −50°. Only one *N*-methyl peak occurred in the nmr at this temperature, and the relationship[6] $\ln([\mathrm{I}]_0 - [\mathrm{I}]_e)/([\mathrm{I}] - [\mathrm{I}]_e) = (k_1 + k_{-1})t$, where [I] = concentration of I at time t, $[\mathrm{I}]_0$ = concentration of I at t = 0, and $[\mathrm{I}]_e$ = concentration of I at equilibrium, was employed in the temperature range where equilibration took place (5–10°). Comparison of the results from the two methods reveals excellent internal agreement (Table I).

Table I. Activation Parameters for I $\rightleftarrows$ II Obtained by the $W_{1/2}$ Method and Direct Equilibration

Ring size	Solvent	E_a, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Method
12	$C_6H_5NO_2$	23.3	22.6	3.0	$W_{1/2}$
		22.8	22.1	6.2	$W_{1/2}$ + equil
13	$C_6H_5NO_2$	22.6	22.0	5.0	$W_{1/2}$
	$C_6H_5NO_2$ + $CDCl_3$	21.9	21.2	3.2	$W_{1/2}$ + equil
16	$C_6H_5NO_2$	22.4	21.7	5.0	$W_{1/2}$

Furthermore, determination of the equilibrium constant $K = k_1/k_{-1}$ = II/I at various temperatures yielded the thermodynamic data listed in Table II. The syn form is enthalpically favored in both the 12- and 13-membered systems. As might be expected, the enthalpy difference is smaller in the larger ring.

Table II. Thermodynamic Parameters for I $\rightleftarrows$ II[a]

Ring size	$\Delta F_{273°}$, kcal/mol	ΔH, kcal/mol	ΔS, eu
12	2.60	2.38	−0.8
13	1.43	1.26	−0.6

[a] Obtained from a plot of log K *vs.* $1/T$.

The stereochemistry of both molecules was established by single-crystal X-ray analysis. The *syn*-*N*-methylthiocapryllactam crystallizes in the orthorhombic space group $Pna2_1$ with a = 16.621 (3), b = 8.729 (2), and c = 6.908 (2) Å. The lauryllactam crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 12.266 (3), b = 17.193 (4), and c = 6.435 (2) Å. The structures were solved using the symbolic addition procedure for noncentrosymmetric crystals[7] and refined to final R factors of 0.043 for the capryllactam and 0.053 for the lauryllactam.

Figures 1 and 2 show the bond lengths and angles for the 9- and 13-membered *syn*-*N*-methylthiolactams, respectively. Table III presents the torsion angles.

The thioamido group in each case is nonplanar with a torsion angle of 12.8°. There are four antiperiplanar conformational units ($\omega \sim \pm 180°$) in *syn*-*N*-methylthiolauryllactam which would be expected in a ring of this size. Two antiperiplanar conformational units were found in 1,6-*trans*-diaminocyclodecane dihydrochloride (ten-membered ring),[8] four such units were

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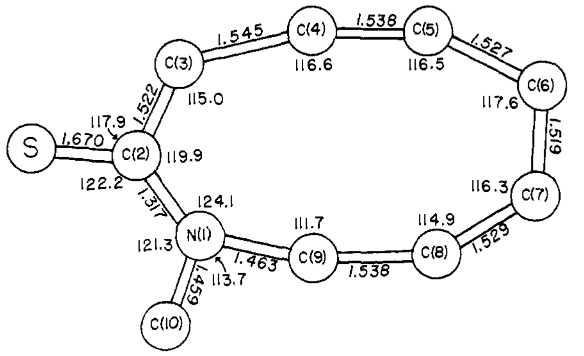

Figure 1. Bond lengths and bond angles for *N*-methylthiocapryllactam. Not intended to show actual molecular shape.

Table III. Torsional Angles for *N*-Methylcaprylthiolactam and *N*-Methyllaurylthiolactam

N-Methyllaurylthiolactam Angle	Deg	*N*-Methylcaprylthiolactam Angle	Deg
C(13)-N(1)-C(2)-C(3)	12.8	C(9)-N(1)-C(2)-C(3)	12.8
N(1)-C(2)-C(3)-C(4)	−95.7	N(1)-C(2)-C(3)-C(4)	−93.8
C(2)-C(3)-C(4)-C(5)	−173.5	C(2)-C(3)-C(4)-C(5)	90.4
C(3)-C(4)-C(5)-C(6)	−57.8	C(3)-C(4)-C(5)-C(6)	−100.5
C(4)-C(5)-C(6)-C(7)	−67.0	C(4)-C(5)-C(6)-C(7)	57.2
C(5)-C(6)-C(7)-C(8)	159.5	C(5)-C(6)-C(7)-C(8)	62.6
C(6)-C(7)-C(8)-C(9)	−74.7	C(6)-C(7)-C(8)-C(9)	−82.2
C(7)-C(8)-C(9)-C(10)	−78.2	C(7)-C(8)-C(9)-N(1)	−48.2
C(8)-C(9)-C(10)-C(11)	169.3	C(8)-C(9)-N(1)-C(2)	99.1
C(9)-C(10)-C(11)-C(12)	−62.7		
C(10)-C(11)-C(12)-C(13)	−55.5		
C(11)-C(12)-C(13)-N(1)	−178.5		
C(12)-C(13)-N(1)-C(2)	−102.4		

found in azacyclododecane hydrochloride (12-membered ring),[9] and six were found in 1,8-diazacyclotetradecane dihydrobromide (14-membered ring).[10]

There is an approximate dyad axis (with respect to torsion angles) in the ring skeleton of the lauryllactam passing through the center of the N(1)–C(2) bond and through C(8). There are no antiperiplanar partial conformations in the nine-membered ring. The torsion angles group around the synclinal conformation ($\omega \sim \pm 60°$) and ±100°, which is near the unfavorable anticlinal conformation ($\omega \sim \pm 120°$). The conformation of *syn*-*N*-methylthiocapryllactam is similar to that of one of the two independent molecules of cyclononylamine[11] which has one synperiplanar torsion angle of 26°.

The observed conformation of *N*-methylthiolauryllactam is very similar to the structure of one of the forms of dimethyl-1-hydroxycyclotridecyl phosphonate.[12] Both molecules have a string of nine successive torsional angles in common. Only the two atoms of the amido group occupy different relative positions.

Finally the conformation observed for *N*-methylthiocapryllactam is quite different from that observed for capryllactam itself (anti in crystal), but it is virtually identical with that of the protonated capryllactam (syn in crystal).[13,14]

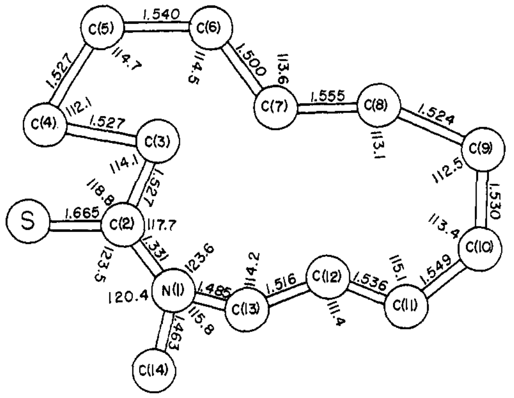

Figure 2. Bond lengths and bond angles for *N*-methylthiolauryllactam. Not intended to show actual molecular shape.

Large-membered *N*-methylthiolactams selectively crystallize into the enthalpically favored syn diastereomeric form, but undergo facile equilibration in solution at room temperature. This contrasts with the behavior of the analogous *N*-methyllactams in which the anti form predominates at equilibrium.[2] We explain this reversal on the basis of the greater steric size of sulfur relative to oxygen.[15]

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R. M. Moriarty,* Ei-Lan Yeh
V. A. Curtis, C.-L. Yeh
University of Illinois at Chicago Circle
Chicago, Illinois 60680

J. L. Flippen, J. Karle
U. S. Naval Research Laboratory
Washington, D. C. 20390

K. C. Ramey
Research and Development Department
Arco Chemical Company, A Division of Atlantic Richfield Company
Glenolden, Pennsylvania 19036

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Electron Spin Resonance Spectra of Phenol Anion Radicals Generated in Argon Matrices. Establishment of Their Ketonic Structure

Sir:

The possibility of generating and investigating the esr spectra of charged species within an argon matrix by means of the photoelectron transfer technique has been well established.[1] We report in this communication the esr spectra and their analyses of the phenol anion radicals generated by this technique.

Shown in Figure 1 is the esr spectrum obtained from an argon matrix containing Na atoms (0.1 atom %) and phenol (1 atom %) after it had been irradiated with yellow light ($\lambda > 5500$ Å) for 5 min. Prior to the photoirradiation, the matrix exhibited only the esr spectrum of the Na atoms.[2] The photoinduced signal in Figure

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