Tetrahedron Letters Vol. 22, pp 921 - 924
©Pergamon Press Ltd. 1981. Printed in Great Britain

0040-4039/81/0301-0921$02.00/0

GEOMETRIES AND ROTATIONAL BARRIERS OF ALKYLAMIDES AND LITHIUM ALKYLAMIDES.

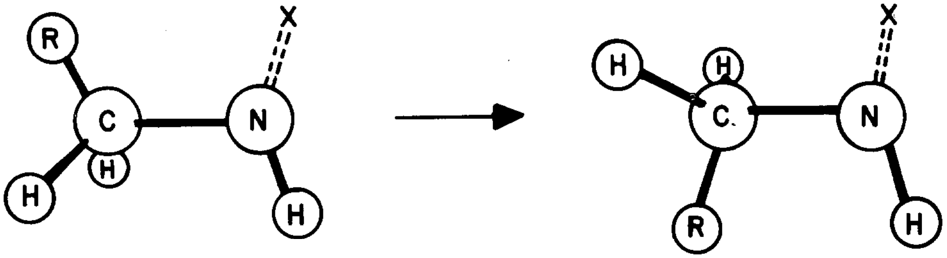
Nelson G. Rondan and K. N. Houk[1]
Department of Chemistry, Louisiana State University
Baton Rouge, Louisiana 70803
and
Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

Abstract: The barriers to rotation of methylamide, ethylamide and the corresponding lithium amides have been computed at the *ab initio* 4-31G level. The barriers to rotation about the C-N bond are higher for amides than for amines, but are lowered by coordination with Li^+.

Sterically hindered dialkylamides are useful bases in organic synthesis, because of the high basicities and low nucleophilicities of these species.[2] These properties have been attributed to the high degree of steric congestion about nitrogen in such species. Nevertheless, little is known about the precise shapes of such species. As part of a program to investigate synthetically useful carbanion reactions, and specifically to understand rotational barriers in lithium salts of imine anions,[3] *ab initio* calculations with a split-valence (4-31G for C, N and H; 5-21G for Li)[4] basis set have been carried out on some of these species. This basis set has been shown to give reasonable geometrical predictions for anions and for lithium compounds in work by Schleyer and Pople and their coworkers.[5]

We have fully optimized the geometries of methylamide and lithium methylamide in the staggered (dihedral angle HNCH = 180°), perpendicular (HNCH = 90°), and eclipsed (HNCH = 0°) conformations. For ethylamide and lithium ethylamide, the methyl group geometry was fixed at standard values (r_{CH} = 1.09 Å, <HCH = 109.5°) and all other geometrical parameters were optimized in the three conformations. The results are summarized in the Figure and the Table. The results are compared to 4-31G calculations carried out on STO-3G geometries,[6] or 4-31G calculations on standard geometries.[7]

Amines. The experimental barrier to rotation of methylamine is 1.98 kcal/mol,[8] with the staggered conformation most stable. In the series ethane, methylamine, methanol, the barrier to rotation is approximately 1 kcal/mol per H-H eclipsing interaction in the eclipsed conformation.[7] The calculated barrier to rotation about the CN bond for ethylamine is 0.6 kcal/mol higher than that in methylamine.[9]



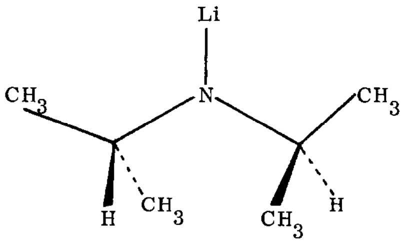
	R	X	ΔE (kcal/mol)
1:	H	$:^-$	+2.78
2:	Me	$:^-$	+3.85
3:	H	Li	+1.95
4:	Me	Li	+2.84
5:	H	H	+1.96[6] (2.13)[7]
6:	Me	H	(+2.75)[7]

Amides. Methylamide[10] has a calculated barrier to rotation of 2.78 kcal/mol, nearly 1 kcal/mol higher that that of methylamine. Similarly, the ethylamide barrier is $\sim$1 kcal/mol higher than that of ethylamine. The higher barrier to rotation in the amide as compared to the amine is notable, since there is only one hydrogen on nitrogen in the former, and the CN bond is longer in the amide than in the amine. Methanol, which is isoelectronic with methylamide, has a barrier of 1.12 kcal/mol at the 4-31G level.[7] This suggests that as charge builds up on the heteroatom, lone pair-CH bond repulsion increases, which is compatible with the increase in lone pair energy with an increase in charge on the heteroatom. Model calculations on the ethyl anion, radical, and cation support this interpretation.

Lithium Amides. Lithium methylamide and lithium ethylamide have barriers of 1.95 and 2.84 kcal/mol, very close to the corresponding amine barriers. The amine moieties are planar in the lithium amides, and the most stable conformations are those with the NH bond staggered and the NLi eclipsed with respect to the CH bonds. The lower barriers to rotation in the lithiated species as compared to the amides can be attributed to the Li$^+$ Coulombic stabilization of N lone-pairs, and perhaps to weak Li-H(C) interactions, which would destabilize the most stable staggered conformation more than the eclipsed.

Solvated Lithium Amides. At this time we can only speculate upon the influence of solvation upon these conformations and rotational barriers: we expect that coordination of "Li^+" to Lewis basic solvents will increase the N-Li bond length, restoring amide anion character to the nitrogen, increasing the C-N rotational barriers. Solvated lithium amides are expected to have rotational barriers higher than those of amines.

For synthetically useful species such as LDA, the preferred (chiral) conformation shown below is expected to be favored in solution.



Acknowledgement. We are grateful to the National Institutes of Health for financial support of this research.

References and Notes

1. Address correspondence to the University of Pittsburgh.
2. H. O. House, "Modern Synthetic Reactions", Benjamin, Menlo Park, California, 1972.
3. R. R. Fraser, N. Chuaqui-Offermanns, K. N. Houk, and N. G. Rondan, *J. Organometallic Chem.*, in press.
4. W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, J. A. Pople, GAUSSIAN 70, QCPE 236, 1973; STO-3G: W. J. Hehre, R. F. Steward, J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969); 4-31G: R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).
5. J. D. Dill, J. A. Pople, *J. Chem. Phys.*, **62**, 2921 (1975); J. D. Dill, P. v. R. Schleyer, J. A. Pople, *J. Am. Chem. Soc.*, **98**, 1663 (1976); A. L. Hinde, A. Pross, L. Radom, *J. Computational Chem.*, **1**, 118 (1980) and references therein; see also R. W. Strozier, N. G. Rondan, K. N. Houk, R. R. Fraser, and N. Chuaqui-Offermanns, *J. Am. Chem. Soc.*, **102**, 1426 (1980).
6. W. A. Lathan, L. A. Curtiss, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, **11**, 175 (1974).
7. L. Radom, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **94**, 2371 (1972).
8. T. Nishikawa, T. Itoh, and S. Shimoda, *J. Chem. Phys.*, **23**, 1735 (1955); D. R. Lide, *ibid.*, **27**, 343 (1957).

9. Studies of Propylamine and Methyl ethylamine were recently reported: N. L. Allinger, U. Burkert, and S. Profeta, Jr., J. Computational Chem., 1, 281 (1980).

10. An STO-3G optimization of staggered methylamide was reported previously: D. J. DeFrees, J. E. Bartmess, J. K. Kim, R. T. McIver, Jr., W. J. Hehre, J. Am. Chem. Soc., 99, 6451 (1977).

TABLE. 4-31G Optimized Geometries of Alkylamides and Lithium Alkylamides.[a,b]

	1		2		3		4	
	stag.[c]	ecl.[c]	stag.	ecl.	stag.	ecl.	stag.	ecl.
N-Li	—	—	—	—	1.746	1.750	1.749	1.749
N-H	1.035	1.030	1.029	1.206	1.007	1.006	1.007	1.006
N-C	1.453	1.463	1.446	1.448	1.463	1.467	1.455	1.463
$C-H_1$	1.099	1.111	—	—	1.091	1.090	—	—
$C-H_2$	1.124	1.114	1.118	1.111	1.095	1.093	1.093	1.091
C-C	—	—	1.536	1.557	—	—	1.532	1.538
<LiNC	—	—	—	—	129.4	130.2	128.6	131.3
<HNC	106.1	106.6	107.3	107.2	109.0	109.9	109.9	109.6
$<H_1CN$	109.0	116.9	—	—	110.0	112.8	—	—
<CCN	—	—	108.6	116.4	—	—	110.8	113.4
<DCN[d]	137.6	131.3	135.7	129.7	132.0	129.6	129.1	126.7
$<H_2CH_3$	102.5	103.1	102.5	103.0	106.6	106.5	105.6	105.8

(a) Distances in Å, angles in degrees.

(b) Total energies of the staggered conformations of 1, 2, 3, and 4 are -94.36991, -133.35545, -101.93022, and -140.91184 au, respectively.

(c) "Stag." and "Ecl." refer to staggered and eclipsed conformations, respectively.

(d) D is a dummy atom which lies on the $<H_2CH_2$, bisector.

(Received in USA 27 October 1981)