1334 *J. Org. Chem.* **2001,** *66,* 1334−1338

The C−N Rotation Barrier of the Lithium Enolate of Acetamide: An ab Initio and Density Functional Theory Investigation

James K. Pugh and Andrew Streitwieser*

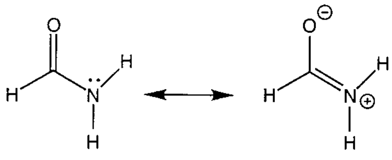
Department of Chemistry, University of California, Berkeley, California 94720-1460

astreit@socrates.berkeley.edu

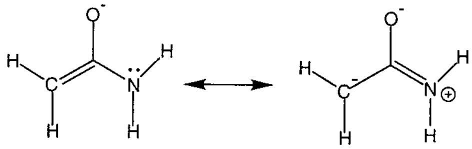
Received August 24, 2000

Semiempirical (PM3), ab initio (HF/6-31+G(d) and MP2/6-31+G(d)), and density functional (pBP/DN*) calculations are used to investigate the rotation barrier of the carbon−nitrogen bond in a simple enolate anion: lithium acetamide, **1**. For comparison, the amidate anion **2**, vinylamine **3**, and a simulated dimer **4** were also calculated. In all systems, the barrier to rotation was found to be less than 10 kcal mol^{-1} in agreement with experiment. The correlated calculations show the barrier to be lowest for the anion **2**. The results show conjugation effects in **1** and **2** comparable to that in vinylamine **3** and imply that polarization effects are more important than charge transfer in amine conjugation.

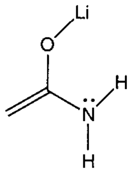
The amide bond has received much attention because of its importance in understanding peptides and proteins. The C−N bond in amides is known to have relatively high rotation barriers of 17−20 kcal mol^{-1}.[1−3] The source of the restricted C−N bond rotation in amides has been the topic of much recent controversy centering around the role of the charge-transfer conjugation resonance structure II.[4−14] We have recently studied the lithium ion-pair acidities and aggregation of the lithium enolates of some *N*,*N*-dialkylamides in THF.[15] In the course of this work, we found that the lithium enolate of *N*,*N*-dimethyldiphenylacetamide undergoes C−N bond rotation rapidly on the NMR time scale even at −90 °C, indicating a barrier of less than 10 kcal mol^{-1}.[16] In the enolate ion of an amide the carbon is no longer electron deficient, and a structure such as **II** should no longer apply. The barrier to rotation should accordingly be much smaller. There remains the question of the comparison of conjugation in resonance structure **III** with vinylamine and the role of amine charge transfer as in the resonance structure **IV**. In this paper we present a computational study of the rotational barrier of the lithium salt of acetamide **1** for comparison with the experimental results and with corresponding enolate anion **2** and with vinylamine **3**.



I **II**



III **IV**



1

Computational Methodology

Several basis sets and theory levels were used in this study: HF/6-31+G(d),[17−21] pBP,[22] DN*,[23] and MP2[24,25]/

---

(1) Kessler, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 219.

(2) Steward, W. E.; Siddall, I. T. H. *Chem. Rev.* **1970**, *70*, 517.

(3) Noe, E. A.; Raban, M. *J. Am. Chem. Soc.* **1975**, *97*, 5811.

(4) Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1987**, *109*, 5935−43.

(5) Wiberg, K. B.; Breneman, C. M. *J. Am. Chem. Soc.* **1992**, *114*, 831−40.

(6) Wiberg, K. B.; Hadad, C. M.; Rablen, P. R.; Cioslowski, J. *J. Am. Chem. Soc.* **1992**, *114*, 8644−54.

(7) Wong, M. W.; Wiberg, K. B. *J. Phys. Chem.* **1992**, *96*, 668−71.

(8) Wiberg, K. B.; Rablen, P. R.; Rush, D. J. *J. Am. Chem. Soc.* **1995**, *117*, 4261−70.

(9) Wiberg, K. B.; Rablen, P. R. *J. Am. Chem. Soc.* **1995**, *117*, 2201−9.

(10) Laidig, K. E.; Cameron, L. M. *J. Am. Chem. Soc.* **1996**, *118*, 1737−42.

(11) Yamada, S. *J. Org. Chem.* **1996**, *61*, 941−6.

(12) Hiberty, P. C.; Lauvergnat, D. *J. Am. Chem. Soc.* **1997**, *119*, 9478−82.

(13) Forgarasi, G.; Szalay, P. G. *J. Phys. Chem.* **1997**, *101*, 1400−8.

(14) Wiberg, K. B. *Acc. Chem. Res.* **1999**, *32*, 922−9.

(15) Facchetti, A.; Streitwieser, A. *J. Org. Chem.* **1999**, *64*, 2281−6.

(16) Kim, Y.-J.; Streitwieser, A.; Chow, A.; Fraenkel, G. *Org. Lett.* **1999**, *1*, 2069−71.

(17) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724−8.

(18) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163−8.

(19) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213−22.

(20) Hariharan, P. C.; Pople, J. A. *J. Mol. Phys.* **1974**, *27*, 209−14.

(21) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257−61.

(22) The perturbative Becke−Perdew model included in Spartan 5.1: Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3089−3100. Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822−4.

(23) A split valence basis set included in the Spartan 5.1 suite of programs: Hehre, W. J.; Lou, L. *A Guide to Density Functional Calculations in Spartan*; Wavefunction, Inc.: Irvine, CA, 1997.

(24) Head-Gordon, M.; Pople, J. A.; Frisch, M. *J. Chem. Phys. Lett.* **1988**, *153*, 503−6.

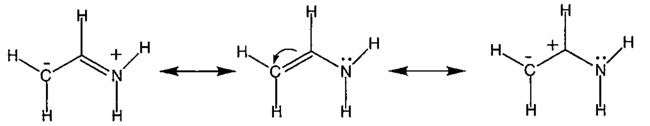
(25) Frisch, M. J.; Head-Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* **1990**, *166*, 275−80.

10.1021/jo001286t CCC: $20.00

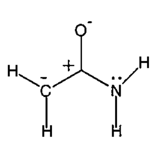
Table 1. Energies of Lithium Acetamide (1), Acetamide Anion (2), Vinylamine (3), and the LiOH Mixed Aggregate (4)

compound	HF/6-31+g(d)[a]	pBP/DN*[b]	MP2/6-31+g(d)[c]	MP2/6-31+g(d)//HF/6-31+g(d)[d]	PM3[e]
1	−214.781471	−216.151469	−215.398746	−215.460267	−32.651
1a	−214.771871	−216.144761	−215.391173	−215.452675	−30.541
1s[f]	−214.769029	−216.142084	−215.388349	−215.449724	−30.141
2	−207.294269	−208.626440	−207.915917	−207.974001	−48.120
2a	−207.285432	−208.623835	−207.909782	−207.967272	−46.400
2s	−207.278700	−208.618474	−207.903137	−207.959768	−44.111
3	−132.994807	−133.922552	−133.434429	−133.489928	14.050
3a	−132.987575	−133.911965	−133.413068	−133.481054	18.259
3s	−132.985001	−133.909582	−133.410549	−133.478622	17.745
4	−297.783372	−299.640907		−298.687811	−124.295
4a	−297.769315	−299.627147		−298.674475	−121.367
4s	−297.768227	−299.625151		−298.678568	−119.692

[a] Energies in au from HF/6-31+g(d) + (unscaled) ZPE HF/6-31+g(d). [b] Energies in au from pBP/DN* + (unscaled) ZPE pBP/DN*. [c] Energies in au from MP2/6-31+g(d) + (unscaled) ZPE MP2/6-31+g(d). [d] Energies in au; does not include ZPE. [e] Heat of formation in kcal mol^{-1}. [f] COLi constrained to 180°.



V 3 VI



VII

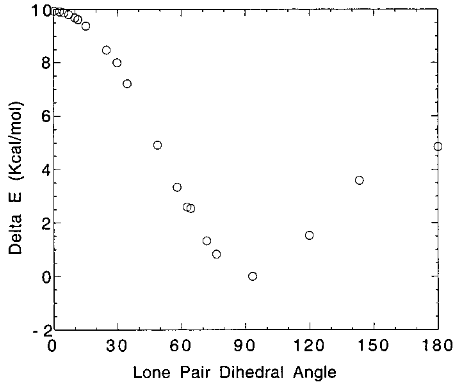


Figure 1. Rotation function for acetamide enolate ion **2** at HF/6-31G(d,s). The barriers are 9.93 and 4.85 kcal mol^{-1}.

6-31+G(d) levels were conducted using Spartan 5.1[26] and Gaussian 94.[27] The version of 6-31G* in MacSpartan Plus[28] uses six d-functions; since this is equivalent to five d-functions plus an s-function with the same effective exponent, it is symbolized here as 6-31G(d,s).

The full rotational potential curve was determined for the free anion **2** using HF/6-31G(d,s). The curve was generated by constraining one OCNH dihedral angle and allowing all other parameters to optimize. This procedure gives the function in Figure 1 and shows two barriers at 9.9 and 4.9 kcal mol^{-1}. The dihedral angle was determined from the mean of the two OCNH angles with 0° defined as the lone pair eclipsed with the C−O bond ("syn"). A similar curve was generated for the lithium amidate **1** with the C−O−Li bond further constrained to 180° (Figure 2). Comparable barriers were found at 7.3 and 5.2 kcal mol^{-1}. For some of the points it was necessary to constrain both OCNH dihedral angles and find the minimum in one of the angles. For both **1** and **2** the lower barrier is that in which the lone pair is anti to the C−O bond, and in the most stable structure the lone pair is almost orthogonal to the amidate plane. Similar rotation functions generated by PM3 give two barriers that are closer together. These functions are given in the Supporting Information (Figures S1 and S2).

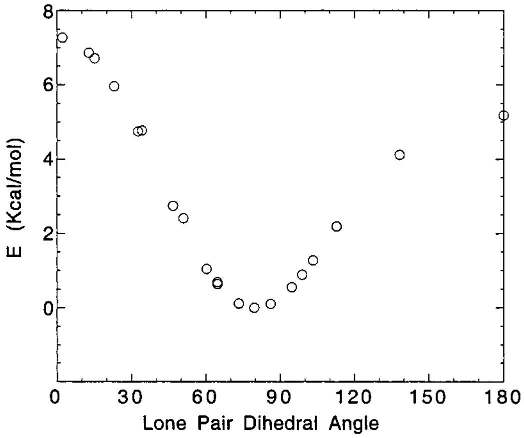


Figure 2. Rotation function for **1** with Li−O−C constrained to 180° at HF/6-31G(d,s). The two barriers are 5.18 and 7.28 kcal mol^{-1}.

These stationary points were also computed at several theory levels and characterized by frequency calculations; the two maxima, syn (**1s** and **2s**) and anti (**1a** and **2a**), are transition structures with one imaginary frequency whereas the minimum energy structures, **1** and **2**, have all frequencies real. The results are summarized for energies and energy differences in Tables 1 and 2 and some structural parameters in Figure 3. Complete coordinates are given in the Supporting Information.

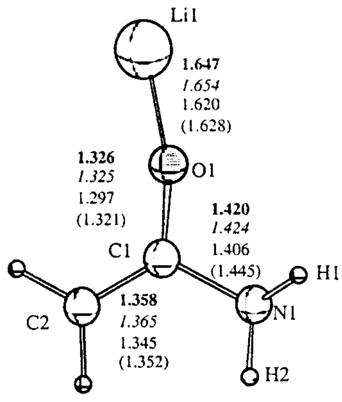
The C−O−Li bond angles in **1** and **1a** are (HF) 158.2° and 165.8°, respectively. Without constraints the lithium cation in **1** tends to coordinate with the nitrogen lone pair whenever the lone pair is sufficiently close and particularly in the syn structure **1s**. Such coordination is less likely in a donor solvent such as THF; thus, in all of the

---

(26) Spartan IBM version 5.1. Wavefunction, Inc.: Irvine, CA, 1991−1999.

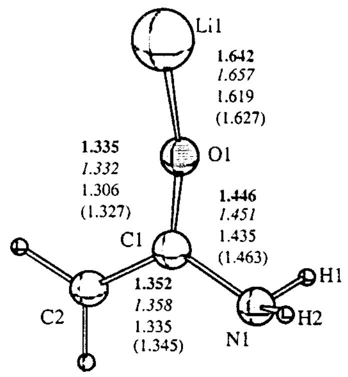
(27) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(28) MacSpartan Plus. Wavefunction, Inc.: Irvine, CA, 1996.



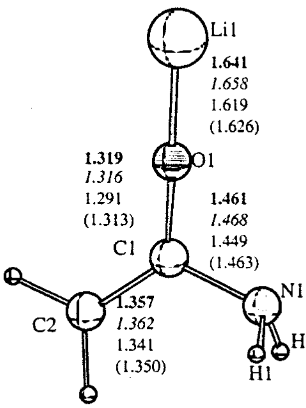
1

C2-C1-N1: **122.04°** *121.92°* 121.58° (123.05°)
C2-C1-O1: **125.12°** *124.79°* 125.10° (124.38°)
N1-C1-O1: **112.77°** *113.26°* 113.29° (112.51°)
H1-N1-C1-O1: **35.90°** *36.66°* 35.47° (31.98°)
H2-N1-C1-O1: **160.22°** *162.20°* 162.52° (155.71°)
H1-N1-H2: **110.41°** *110.76°* 111.50° (110.16°)



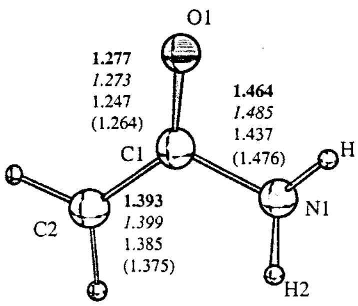
1a

C2-C1-N1: **118.48°** *118.53°* 118.64° (121.48°)
C2-C1-O1: **124.72°** *124.78°* 125.06° (124.42°)
N1-C1-O1: **116.80°** *116.69°* 116.31° (114.10°)
H1-N1-C1-O1: -59.81°
H2-N1-C1-O1: 59.81°
H1-N1-H2: **108.75°** *108.72°* 108.62° (109.17°)



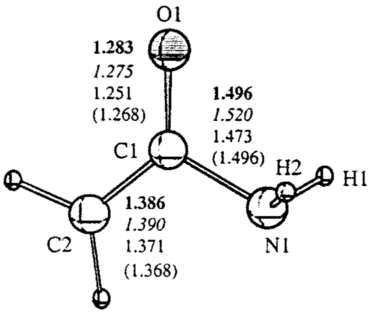
1s

C2-C1-N1: **121.69°** *121.33°* 121.03° (124.76°)
C2-C1-O1: **124.78°** *124.87°* 125.04° (125.14°)
N1-C1-O1: **113.53°** *113.81°* 113.93° (110.10°)
H1-N1-C1-O1: 121.74°
H2-N1-C1-O1: -121.74°
H1-N1-H2: **106.54°** *106.61°* 106.33° (107.58°)



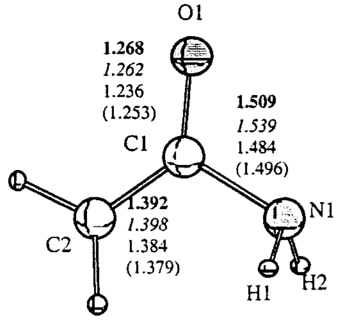
2

C2-C1-N1: **116.19°** *115.96°* 116.69° (117.76°)
C2-C1-O1: **129.10°** *129.32°* 128.57° (129.20°)
N1-C1-O1: **114.71°** *114.73°* 114.75° (113.04°)
H1-N1-C1-O1: **25.50°** *28.98°* 26.08° (18.88°)
H2-N1-C1-O1: **144.72°** *146.22°* 149.15° (139.34°)
H1-N1-H2: **109.49°** *108.64°* 110.52° (108.45°)



2a

C2-C1-N1: **113.93°** *113.49°* 114.79° (116.90°)
C2-C1-O1: **129.27°** *129.68°* 128.92° (129.37°)
N1-C1-O1: **116.80°** *116.83°* 116.29° (113.74°)
H1-N1-C1-O1: -57.96°
H2-N1-C1-O1: 57.96°
H1-N1-H1: **108.52°** *108.80°* 108.03° (107.13°)



2s

C2-C1-N1: **115.82°** *115.05°* 115.85° (117.65°)
C2-C1-O1: **128.66°** *129.31°* 128.31° (129.14°)
N1-C1-O1: **115.52°** *115.64°* 115.84° (113.21°)
H1-N1-C1-O1: 121.73°
H2-N1-C1-O1: -121.73°
H1-N1-H2: **107.69°** *108.11°* 107.18° (107.76°)

Figure 3. Molecular geometries for lithium acetamide (**1**, **1a**, and **1s**), the amidate anion (**2**, **2a**, and **2s**), vinylamine (**3**, **3a**, and **3s**), and the simulated dimer of lithium acetamide (**4**, **4a**, and **4s**). Values are from MP2/6-31+G(d) (bold type), pBP/DN* (italics), HF/6-31+G(d) (regular type), and PM3 (parenthesis) optimizations.

calculations of **1s** the C−O−Li bond was constrained to 180°. Constraining to 180° increases the minimum energy structure by 0.2−0.5 kcal mol^{-1} and changes other structural parameters by small amounts; for example, the HNH bond angle increases by about 0.5° and the methylene bond angle increases by about 0.05°.

Although vinylamine has previously been studied computationally[29−33] it was calculated again to facilitate comparisons at the same theory levels. The rotation function at HF/6-31G(d,s) is summarized in Figure 4 and some structural features are summarized in Figure 3.

Results and Discussion

The structures are all quite similar at the various theory levels with bond distances within about 0.01−0.02 Å and bond angles within about 1−2°. The PM3 results vary more widely but would be acceptable for some purposes.

In general, all of the systems studied have barriers of rotation about the carbon−nitrogen bond less than 10 kcal mol^{-1} in agreement with the experimental results. For both **1** and **2** the rotation barrier is lower for the anti transition structure in which the nitrogen lone pair is 180° from the carbonyl group when coordination of the nitrogen lone pair with lithium cation is precluded. In the anti-transition structure the pyramidal NH_2 group is staggered with respect to the adjacent bond, the C−O bond in **1** and **2**, and the lone-pair is orthogonal to the π-bond. For vinylamine also, the lower barrier is anti and

---

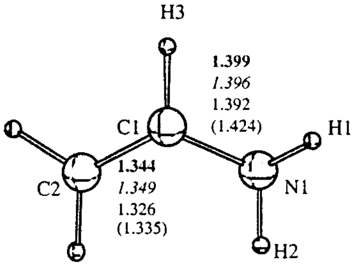
(29) Wiberg, K. B.; Schreiber, S. L. *J. Org. Chem.* **1988**, *53*, 783−5.

(30) Wiberg, K. B.; Rosenberg, R. E. *Tetrahedron Lett.* **1989**, *30*, 5981−5984.

(31) Wiberg, K. B.; Rosenberg, R. E.; Rablen, P. R. *J. Am. Chem. Soc.* **1991**, *113*, 2890−8.

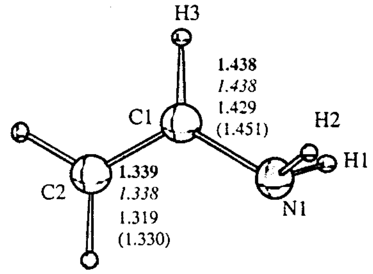
(32) Head-Gordon, M.; Pople, J. A. *J. Phys. Chem.* **1993**, *97*, 1147−51.

(33) Wiberg, K. B.; Laidig, K. E. *J. Org. Chem.* **1992**, *57*, 5092−101.



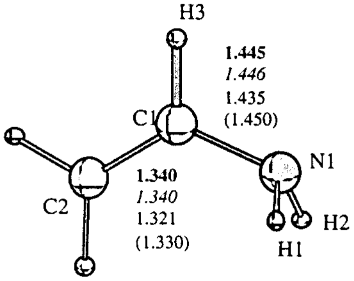
3

C2-C1-N1: **125.93°** *126.77°* 126.56° (123.34°)
C2-C1-H3: **120.37°** *119.80°* 119.97° (121.89°)
N1-C1-H3: **113.54°** *113.29°* 113.39° (114.55°)
H1-N1-C1-H3: **35.93°** *34.20°* 35.44° (41.32°)
H2-N1-C1-H3: **166.22°** *168.44°* 166.16° (165.81°)
H1-N1-H2: **111.15°** *112.41°* 111.19° (110.73°)



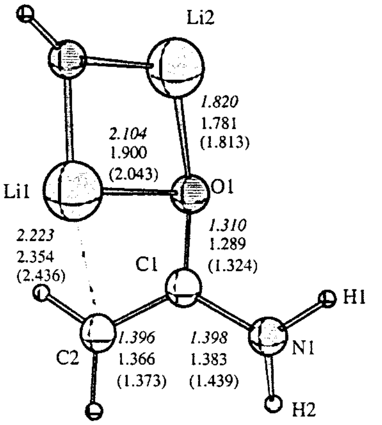
3a

C2-C1-N1: **120.87°** *121.52°* 121.97° (119.91°)
C2-C1-H3: **120.12°** *119.45°* 119.92° (121.59°)
N1-C1-H3: **119.01°** *119.02°* 118.12° (118.50°)
H1-N1-C1-H3: -59.29°
H2-N1-C1-H3: 59.29°
H1-N1-H2: **106.99°** *106.89°* 106.83° (109.36°)



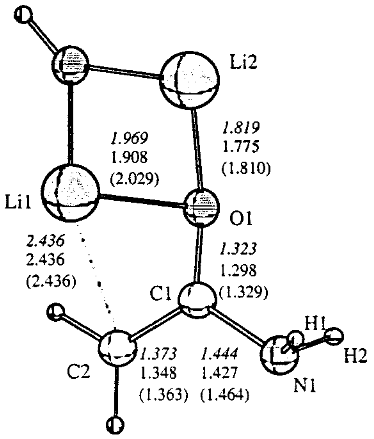
3s

C2-C1-N1: **125.81°** *126.31°* 126.09° (119.91°)
C2-C1-H3: **120.12°** *119.60°* 119.85° (121.59°)
N1-C1-H3: **114.08°** *114.09°* 114.06° (118.50°)
H1-N1-C1-H3: 121.73°
H2-N1-C1-H3: -121.73°
H1-N1-H1: **105.93°** *105.85°* 105.66° (107.46°)



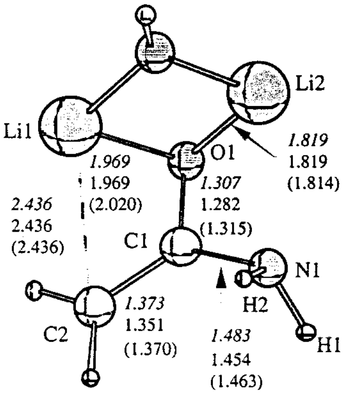
4

C2-C1-N1: *121.36°* 122.05° (123.12°)
C2-C1-O1: *122.53°* 122.29° (122.81°)
N1-C1-O1: *115.67°* 115.27° (114.04°)
H1-N1-C1-O1: *-15.93°* -20.82° (-22.39°)
H2-N1-C1-O1: *-152.40°* -155.71° (-147.84°)
H1-N1-H1: *112.35°* 111.57° (110.29°)



4a

C2-C1-N1: *117.74°* 118.70° (121.78°)
C2-C1-O1: *123.74°* 123.51° (122.96°)
N1-C1-O1: *118.48°* 117.69° (115.23°)
H1-N1-C1-O1: 60.07°
H2-N1-C1-O1: -60.07°
H1-N1-H2: *106.80°* 108.39° (109.23°)



4s

C2-C1-N1: *121.56°* 121.91° (124.90°)
C2-C1-O1: *124.88°* 124.34° (122.58°)
N1-C1-O1: *112.37°* 112.75° (112.51°)
H1-N1-C1-O1: -120.62°
H2-N1-C1-O1: 120.62°
H1-N1-H2: *107.29°* 107.35° (108.92°)

Figure 3. (continued)

involves a similar staggering of the NH_2 group with the adjacent vinyl C−H bond.

The role of conjugation in vinylamine has been discussed previously. Wiberg[14] has pointed out the usefulness of group separation energies (GSE) in understanding the electronic structure of functional groups. We apply his approach to the amidate anion system (Table 3). Although he used G2 energies, we find essentially the same results for vinylamine with MP2/6-31+G* energies. The $\Delta H\pi$ term comes from the rotation barrier and is subtracted from the total GSE to get the σ bond contribution, $\Delta H\sigma$. This term is high for the amidate anion because of the high electronegativity difference between nitrogen and an anionic moiety. The term is smaller but still substantial for the neutral lithium ion pair. The $\Delta H\pi$ numbers are a little larger for **1** and **3** than for **2**. Wiberg associates this term approximately with the conjugation effect, and by this criterion the amino groups in **1** and **3** are slightly more conjugating than in **2**. For vinylamine, the HNH bond angle is consistent with this interpretation. The amino group in vinylamine is highly pyramidal with a H−N−H bond angle of 110.9° (6-31G*; 111.2°

Table 2. Relative Barriers to Rotation of the C−N Bond for Vinylamine (2), Acetamide Anion (3), Lithium Acetamide (1), and Simulated Dimer for Lithium Acetamide (4)

compd	HF/6-31+g(d)[a]	pBP/DN*[b]	MP2/6-31+g(d)[c]	MP2/6-31+g(d)//HF/6-31+g(d)[d]	PM3
1	0	0	0	0	0
1a	6.02	4.21	4.75	4.76	2.11
1s[e]	7.81	5.89	6.52	6.62	2.51
2	0	0	0	0	0
2a	5.55	1.63	3.85	4.22	1.72
2s	9.77	5.00	8.02	8.93	4.01
3	0	0	0	0	0
3a	4.54	6.64	5.13	5.57	4.21
3s	6.15	8.14	6.71	7.09	3.70
4	0	0		0	0
4a	8.82	8.63		8.37	2.93
4s	9.50	9.89		5.80	4.60

[a] Energies in kcal mol^{-1} from HF/6-31+g(d) + (unscaled) ZPE HF/6-31+g(d) calculations. [b] Energies in kcal mol^{-1} from pBP/DN* + (unscaled) ZPE pBP/DN* calculations. [c] Energies in kcal mol^{-1} from MP2/6-31+g(d) + (unscaled) ZPE MP2/6-31+g(d) calculations. [d] Energies in kcal mol^{-1}; does not include ZPE. [e] COLi constrained to 180°.

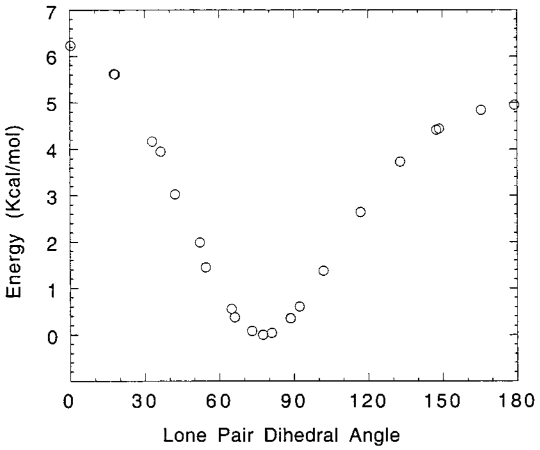
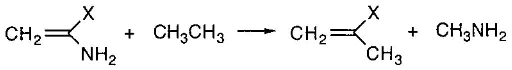


Figure 4. Energy of vinylamine as a function of the lone pair dihedral angle at 6-31G(d,s). The two maxima are at 6.23 and 4.95 kcal mol^{-1}.

Table 3. Group Separation Energy Changes for Vinylamine Derivatives at MP2/6-31+G* + (unscaled) ZPE MP2/6-31+G* (kcal mol^{-1})



X	GSE	Δ*H*π	Δ*H*σ
H, **3**[a]	6.5	5.1	1.4
O$^-$; **2**	12.1	3.9	8.2
O$^-$ Li$^+$; **1**	9.1	4.8	4.3

[a] Wiberg (ref 14) reports 6.1, 5.1, and 1.3 kcal mol^{-1}, respectively, at the G2 level.

MP2), but less pyramidal than an alkylamine (methylamine 6-31G* = 106.9°). At the rotation transition structure, in which the lone pair can no longer conjugate, the HNH bond angle is essentially that of an alkylamine, 105.93° (MP2; 6-31+G* is 106.83°). Conjugation had been thought to mean resonance of the type indicated by structure V, but Wiberg has shown that it is better represented by polarization of the type indicated in structure VI. This polarization is caused by the nitrogen lone pair,[31] and this nitrogen lone pair is attracted to the resulting positive carbon. A similar polarization was noted previously for vinyloxide anion[34] and a comparable attraction of the lone pair would apply; that is, resonance structure VII applies rather than IV. Consistent with this interpretation is the HNH bond angle in **1**, 110.4° (MP2), and in **2** 109.5° (MP2). On rotation to the anti-transition structure, these bond angles decrease somewhat (108.7° for **1a**, 108.5° for **2a** (MP2) but not as much as in vinylamine.

Lithium amidates are known to aggregate in solution,[15] and dimerization was noted in the determination of the experimental rotation barrier.[16] Thus, computations were extended to a model aggregate with LiOH, **4**. This model retains the coordination of the amidate oxygen to two lithiums. Computations were done at the same basis set levels as the small structures except that the MP2 calculations were done at the 6-31+G(d) geometries. Such single point calculations are in good agreement with the full MP2 optimizations for the other systems tested.

Rotation in the syn-sense still produces coordination of the nitrogen lone pair with one of the lithiums and is of doubtful significance in a coordinating solvent. Even in the absence of such coordination, the other lithium bends toward the negative β-carbon (Figure 3). This effect is also of dubious significance for a solvated lithium cation. Accordingly, the computed rotation barriers, which in any event differ by only a few kcal mol^{-1} from the monomer (Table 2), are of only minor interest.

Conclusions

All of the rotation barriers calculated are less than 10 kcal mol^{-1}, in agreement with the experimental result for *N*,*N*-dimethyl-diphenylacetamide.[16] All of the theory levels used give the barrier for the lithium salt **1** somewhat higher than that of the free anion **2**. The barriers at the correlated levels are somewhat greater than the HF levels; the PM3 barriers are much lower than the ab initio results and clearly cannot be trusted for this purpose. Computed structures and changes on rotation are consistent with a model in which conjugation of the amino nitrogen with the double bond is comparable to that in vinylamine even though charge transfer to an anionic system would be expected to be inhibited. Polarization of the double bond rather than charge transfer is the important feature of the electronic structure.

Acknowledgment. This research was supported in part by NSF grants 9528273 and 9980367.

Supporting Information Available: Figures of PM3 results and tables of coordinates of optimized structures. This information is available free of charge via the Internet at http://pubs.acs.org. This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO001286T

---

(34) Siggel, M. R. F.; Streitwieser, A.; Thomas, T. D. *J. Am. Chem. Soc.* **1988**, *110*, 8022−8.