Determination of the N1s and O1s Core Energies in Planar and Distorted Lactams and Amides: Relationships with the Concept of Resonance

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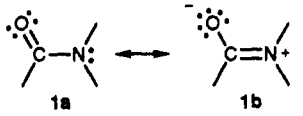
The core ionization energies of three strained lactams have been measured and compared with those of model lactams, amides, amines, and ketones. In general, the high values for N1s and the low values for O1s in planar amide (lactam) linkages compared to those in model amines and ketones are consistent with traditional resonance arguments. The N1s and O1s data for the distorted lactams 1,3-di-*tert*-butylaziridinone and 1-azabicyclo-[3.3.1]nonan-2-one are consistent with a reduced positive charge on nitrogen and a reduced negative charge on oxygen in accord with the classical resonance viewpoint. They are also consistent with other spectroscopic data for distorted lactams. The carbonyl C1s ionization energies are lower in distorted lactams than in planar lactams. The explanation may lie in the relative electronegativities of the nitrogen atoms. ESCA data also suggest the presence of more C^+–O^- character in ketones than in amides. Although 1-pyrrolidinecarboxaldehyde has a distorted amide linkage, its ESCA data are not unambiguously interpretable in terms of reduced resonance. The dependencies of core electron ionization energies upon different amide distortion modes need to be explored using a much expanded set of amides and lactams. The relationships between the resulting experimental ESCA data with various calculations of atomic charge need to be examined.

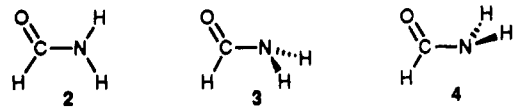
Introduction

The structure of the amide linkage has long been understood through combination of resonance structures **1a** and **1b**.[1] These canonical structures rationalize experimental resonance energies, high N–CO bond rotational barriers, low carbonyl IR frequencies, the tendency for O-protonation instead of N-protonation, hydrolytic stability, and a wide variety of other properties.[2-9]



1a **1b**

In recent years, this traditional view of resonance in explaining the structure and properties of the amide linkage has been challenged in a series of studies based upon the topological properties of the electronic charge density.[10-14] An early conclusion derived from these studies was that the sp^2-hybridized nitrogen in the planar structure[15] of formamide (**2**) is more negative than the sp^3-hybridized nitrogens in the two rotational transition states (**3** and **4**).[10] The order of these predicted "Bader



2 **3** **4**

charges" is opposite to that expected from traditional application of resonance theory. Furthermore, whereas traditional resonance theory would predict a more negative oxygen in **2** than in **3** or **4**, the above-cited calculations predict virtually no difference in charge. The original argument[10] continues that the more electronegative nitrogen in **2** leads to a more positive carbonyl carbon and thus a more polar covalent, stronger, shorter N–CO σ bond than in **3** or **4**. The strong N–CO σ bond in **2**, significantly weakened upon rotation, is considered to be the source of the high amide rotational barrier.[10]

The "Bader-type" analysis outlined above yields a "... molecule as seen by its nuclei".[14] A complementary technique, which calculates nuclear-centered effective point charges reproducing the electrostatic potential field outside the molecular van der Waals radius, produces an external picture of the molecule ("a view from the outside").[10,11,14] It is useful to note that the electrostatic potential model is associated with essentially spherical atoms while the Bader atoms are markedly nonsymmetrical. The associated charges are in accord with the resonance model in that nitrogen is more positive in the planar form. However, both approaches predict little change in the charge on oxygen upon rotation.[10,11,14] This differs from the traditional resonance picture of significant contribution from **1b**. The two analyses predict a more polar, and presumably stronger, N–CO bond but with opposite changes in polarity (C more negative in the planar form viewed "internally"; more positive in the planar for viewed "externally").[14] Although calculations predicted a very slightly longer CO bond in **2** than in **3** or **4**,[10] the structural effect is surprisingly small and has been experimentally

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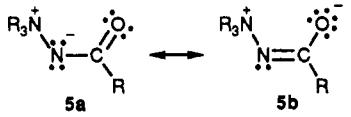
verified using bridgehead bicyclic lactams as model compounds.[16-18] It is germane to note that the methodology for calculation of "Bader charges" has been criticized on the grounds that it neglects the effect of orbital size independent of electronegativity.[19] While explaining the negative "Bader charge" on nitrogen in planar formamide as an artifact of the neglect of orbital size, that study[19] takes no position on the resonance question. At this point, it is worth noting that the widely-employed Mulliken charges are very basis-set dependent.[14]

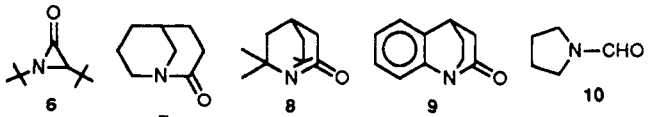
Enhanced reactivities of distorted lactams have been observed systematically and, while reduced resonance was considered, the initial explanation focused upon the structural stabilization of the four-coordinate transition state.[16] A subsequent elegant study by the same research group examined a broad set of structural (X-ray), spectroscopic (IR, ^{15}N, ^{13}C), and conformational data (C–N rotational barriers) and concluded that "...the data seem loosely consistent with the resonance model, but indicate that there are anomalous effects that are at present not understood".[18]

The aforementioned predictions and ambiguities in the nature of atomic charges upon distortion of the amide linkage stimulated the present study. X-ray photoelectron spectroscopy (XPS or ESCA) has been used to derive relative measures of atomic charge.[20,21] The observation that N1s core energies in amides are considerably higher than those in amines has been rationalized in terms of the resonance contribution from **1b**.[22] Particularly relevant is a study relating the N1s core energies and IR carbonyl frequencies of a series of aminimides to the contributions of resonance structures **5a** and **5b**.[23] Increased contribution from **5b** should raise the core ionization energy of N^-, therefore decreasing ($N^+1s - N^-1s$). Furthermore, one would expect enhanced contribution of structure **5b** to decrease the carbonyl frequency. These phenomena were observed in the aminimides despite the complications associated with solid-state ESCA.[23] It is, thus, highly relevant to use ESCA as a new probe for discerning the nature of amide resonance as a function of distortion.



5a **5b**

In the present study, ESCA has been employed to investigate N1s and O1s (and some C1s) core ionization energies of a group of planar and distorted amides and lactams in order to gain a measure of the relative atomic charges. The study focused on distorted lactams **6–9** and amide **10** as well as suitable model compounds.



6 **7** **8** **9** **10**

It is important to remark here that distorted lactam (or amide) linkages are usually "constructed" through their incorporation in a sizeable molecular framework or in a molecule having significant steric repulsions. These factors tend to be associated with higher molecular weights and lower vapor pressures which limit the number of compounds amenable for gas-phase ESCA study. Furthermore, the most distorted (thus, most interesting) lactams are thermally unstable. It is, therefore, unfortunate but not unexpected that the two 2-quinuclidones **8** and **9**, the most distorted lactams investigated in our study, did not yield ESCA data due to their low volatility and probable decomposition upon heating. However, the remaining three molecules (**6**, **7**, and **10**), when referenced to appropriate amides, amines, and ketones furnished useful data and significant conclusions.

Experimental Section

Sources of Compounds for ESCA Study. 1,3-Di-*tert*-butylaziridinone (**6**)[24] and 1-azabicyclo[3.3.1]nonan-2-one (**7**)[25] were synthesized and purified according to published procedures. 5,6-Benzo-1-azabicyclo[2.2.2]octan-2-one (**9**), synthesized according to published procedure,[26] was supplied by Professor R. S. Brown, University of Alberta. 1-Pyrrolidinecarboxaldehyde, 2-methylaziridine, azetidine, 2-pyrrolidone, 1-methyl-2-pyrrolidone, 2-azetidinone, and cyclobutanone were obtained from Aldrich Chemical Co. and used as supplied. 1-*n*-Butyl-2-pyrrolidone was obtained from TCI America and used as supplied. 6,6,7,7-Tetramethyl-1-azabicyclo[2.2.2]octan-2-one (**8**) has been synthesized,[27-29] but the published synthesis yields polymers.[30] The compound was synthesized during the present investigation using dilution techniques and displayed appropriate NMR, IR, and mass spectral data.[30]

Our attempts at synthesis of 1,2-di-*tert*-butylaziridine,[31] 2,3-di-*tert*-butylcyclopropanone,[32] and 1-*tert*-butyl-2-pyrrolidone through reaction of 2-pyrrolidone, sodium, and *tert*-butyl bromide (or iodide) did not provide pure materials suitable for ESCA.

ESCA Measurements. Core-ionization energies were measured in the gas phase using the Oregon State University cylindrical mirror analyzer.[33] The excitation source was aluminum X-rays (1483.553 eV[34]). Neon was mixed with the samples, and the calibration was based on the positions of the neon 1s and 2s lines,[35] and appropriate relativistic corrections are included in the calibration scheme.[36]

Peak positions were determined from nonlinear least-squares fits of Voight functions to the data. The reported core-ionization energies are the average of at least two measurements. On the basis of our experience with measurements of this type, we estimate the uncertainties in the reported numbers to be about 0.05 eV. In general, the agreement between ionization energies determined in this way and those reported by others is consistent with this estimate. However, we find a consistent discrepancy

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Table I. Core Ionization Energies (eV) of Amides, Lactams, Amines, and Ketones Determined in This Study

compound	O 1s	N 1s	C(1) 1s
formamide	537.71	406.33	294.56
dimethylformamide	537.02	405.91	292.17
dimethylacetamide	536.60	405.55	291.67
1-pyrrolidinecarboxaldehyde	536.84	405.52	
N,2′-dimethylacetanilide	536.35	405.33	
1,3-di-*tert*-butylaziridinone	537.36	405.00	290.69
2-azetidinone	537.32	405.76	291.80
2-pyrrolidone	536.98	405.62	291.35
1-methyl-2-pyrrolidone	536.69	405.45	291.48
1-*n*-butyl-2-pyrrolidone	536.58	405.20	
1-azabicyclo[3.3.1]nonan-2-one	536.67	405.07	290.81
2-methylaziridine		404.96	
azetidine		404.70	
propanone[39]	537.98		293.71
cyclobutanone	538.12		293.42
2-butanone	537.82		293.47
2-pentanone	537.77		293.40
3-pentanone	537.73		293.26

Table II. Comparison of N1s Core Energies (eV) for Acyclic and Cyclic Secondary Amines (Data from Table I or Ref 39)

open amine	N1s (eV)	cyclic amine	N1s (eV)	diff (eV)
$(CH_3)_2NH$	404.93			
$CH_3HNC_2H_5$	404.75[a]	azetidine	404.70	−0.05
$(C_2H_5)_2NH$	404.57	pyrrolidine	404.60	+0.03
$C_2H_5NH(n\text{-}C_3H_7)$	404.52[b]	piperidine	404.58	+0.06
$(n\text{-}C_3H_7)_2NH$	404.47			
$CH_3NHC_2H_5$	404.75[a]	2-methylaziridine	404.96	+0.21

[a] Estimate by interpolating dimethylamine and diethylamine. [b] Estimate by interpolating diethylamine and dipropylamine.

between our measurements and those reported by Brown and Tse.[37] Their energies are typically about 0.1 eV higher than those found by us or by others. We believe that the reason for this discrepancy is their calibration scheme, which is based on a neon Auger energy and magnesium X-rays. It has been shown by Carroll, Siggel, and Thomas[38] that this calibration scheme leads to ionization energies that are too high by 0.07 eV. Therefore, in using ionization energies from Brown and Tse,[37] we have decreased their values by 0.07 eV.

Two attempts at the determination of ESCA data for **8** and one attempt at determining ESCA data for **9** failed, apparently due to their low vapor pressures and ready decomposition at the modestly elevated temperatures applied to the sample holder.

Results and Discussion

Table I lists core ionization energies determined in the present study. Table II presents N1s core energies of acyclic and cyclic amines determined in this work or previously reported.[39] Table III presents similar data for amides and lactams and Table IV compares N1s core ionization energies for lactams and amides with those of analogous amines.

It is worthwhile to emphasize, as previously noted by Lindberg and Hedman,[22] that comparison of the N1s core energy in an amide with that in an amine is nicely rationalized by traditional resonance theory. Thus, comparison of N1s in *N*,*N*-dimethylacetamide (405.56 eV) with that estimated for dimethylethylamine (404.66 eV) (see Table IV for both values) indicates that it is much more difficult to remove a core electron from the amide nitrogen. This is consistent with a significant contribution from canonical structure **1b**, although part of the effect may be due to the electronegativity of the carbonyl group to which N is attached in the amide. While one cannot precisely

Table III. Comparison of N1s Core Energies (eV) for Amides and Lactams (Data from Table IV or Ref 39 with 0.07 eV Correction if Applicable)

amide	N1s (eV)	lactam	N1s (eV)	diff (eV)
$HCONH_2$	406.35			
$HCONHCH_3$	406.12			
$HCON(CH_3)_2$	405.87			
$CH_3CON(CH_3)_2$	405.56			
$CH_3CONHCH_3$	405.81[a]	azetidinone	405.76	−0.05
$CH_3CON(C_2H_5)_2$	405.26			
$CH_3CONHC_2H_5$	405.66[b]	2-pyrrolidone	405.62	−0.04
$CH_3CON(CH_3)C_2H_5$	405.41[c]	1-methyl-2-pyrrolidone	405.46	+0.05

[a] Estimated by comparison of *N*-methylformamide, *N*,*N*-dimethylformamide, and N,N-diethylacetamide. [b] Estimated by taking half of the difference between *N*,*N*-diethylacetamide and *N*,*N*-dimethylacetamide and subtracting it from *N*-methylacetamide. [c] Estimated by interpolating *N*,*N*-dimethylacetamide and *N*,*N*-diethylacetamide.

Table IV. Comparison of N1s Ionization Energies between Amines and Amides (or Lactams)[a]

amide or lactam	N1s (eV)	amine	N1s (eV)	diff (eV)
$HCONH_2$	406.35[b-e]	CH_3NH_2	405.15[e]	1.20
$HCONHCH_3$	406.12[c,f]	$(CH_3)_2NH$	404.92[e]	1.20
$HCON(CH_3)_2$	405.87[b-e]	$(CH_3)_3N$	404.81[e]	1.06
$CH_3CON(CH_3)_2$	405.56[b,c]	$(CH_3)_2NC_2H_5$	(404.66)[g]	0.90
$CH_3CON(C_2H_5)_2$	405.26[c]	$(C_2H_5)_3N$	404.35[e]	0.91
2-acetidinone	405.76[b]	azetidine	404.70[b]	1.06
2-pyrrolidone	405.62[b]	pyrrolidine	404.60	1.02
1-methyl-2-pyrrolidone		pyrrolidine		
1-methyl-2-piperidone		piperidine	404.48[j]	0.92

[a] The values listed are those determined in this study or in other studies. Where more than one value is published, the listed number is an average. The values of Brown and Tse[37] have been corrected by subtraction of 0.07 eV (see text and ref 39). [b] This work (see Table I). [c] Brown and Tse, ref 37. A value of 0.07 eV has been subtracted from the ionization energies. [d] Cavell, R. G.; Allison, D. A. *J. Am. Chem. Soc.* 1977, *99*, 4203. [e] Jolly; et al. ref 39. [f] A value of 405.8 eV from footnote *c* appears to be incorrect and was not averaged in. [g] Interpolate $(CH_3)_3N$ and $(C_2H_5)_3N$. [h] Interpolate as in *f* and assume no change on "closure". [i] Use 404.50 for $(C_2H_5)_2NCH_3$ (footnote *g*) and added one-third of the difference between $(n\text{-}C_3H_7)_3N$ and $(C_2H_5)_3N$. [j] Compare piperidine (404.58), pyrrolidine (404.60), and 1-methylpyrrolidine (404.50) (ref 39).

apportion the contributions, some comparisons are illuminating. The N1s core energy in pyrrole (406.15 eV)[39] is appreciably higher than that in pyrrolidine (404.60 eV),[39] and this is readily explained via resonance rather than changes from sp^2 to sp^3 hybridization at the attached carbons. It is also consistent with the large difference between C1s core energies at C2 in pyrrole (290.8 eV) vs C3 (289.9 eV).[39] While a compound such as $CH_3OCH_2NH_2$ could provide an interesting comparison for inductive effects in formamide, data are not available and complications involving carbon hybridization would remain. It is worth noting that the N1s core energies of *n*-butylamine and $CH_3OCH_2CH_2NH_2$ are both 404.88 eV.[39] [A relevant point is that the higher N1s core energy in $HOCH_2CH_2NH_2$ (405.30 eV)[39] reflects intramolecular hydrogen bonding conventionally represented by a resonance structure having a positive nitrogen atom.] Another interesting comparison is furnished by the N1s core energies[39] of 2-methoxypyridine (404.68 eV), 3-methoxypyridine (404.87 eV), 4-methoxypyridine (404.49 eV) and the corresponding 2-, 3-, and 4-methylpyridines (404.63, 404.75, and 404.68 eV). These data are best understood in terms

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of inductive effects being less significant than resonance effects in this series.

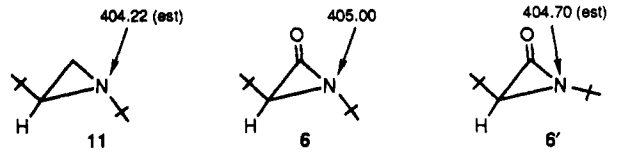
Perhaps more striking and less ambiguous is the comparison between the O1s core ionization energies in amides (or lactams) and those in the corresponding aldehydes and ketones. This comparison had not been made previously due to the relative dearth of data for these standards. Data for selected ketones are found in Table I. One may compare the O1s core energy in *N,N*-dimethylacetamide (536.60 eV) and that estimated for the model ketone 3-methyl-2-butanone (537.66 eV, through comparison of propanone and butanone in Table I) as well as 2-pyrrolidone (536.98 eV) and 3-pentanone (537.73 eV) (see comments below about ring "closure"). The amide O1s core ionization energy is ca. 1.0 eV lower than that of the ketone despite the presence of the electronegative nitrogen in place of carbon. This would be consistent with significant contribution from **1b**. We note further that this effect is seen in esters. Thus, the O1s core ionization energy for the dicoordinate oxygen in ethyl acetate is 539.24 eV,[39] which is ca. 1.1 eV higher than that in diethyl ether (538.11 eV).[39] Despite the presence of a β oxygen, the O1s core ionization energy of the carbonyl oxygen in ethyl acetate (537.82 eV)[39] is only 0.05 eV higher than in 2-pentanone (537.77 eV, see Table I).

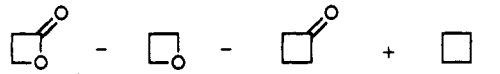
It is important to emphasize that while inductive effects will play a role in all such comparisons, they are virtually impossible to eliminate or quantitate. However, one can reasonably argue that molecular systems which maintain the amide (lactam) linkage intact but "merely" distorted best minimize differences in inductive effects. In this regard, it can also be argued that the great similarity between molecular systems (distorted vs planar amides with corrections for size) should minimize differences in hole-state relaxation which is invaribly related to the size of the molecule or the number of valence electrons but not significantly to hybridization or molecular distortion.

As can be seen from the comparisons shown in Table II, ring "closure" does not appear to affect the core energies for the 4- and 5-membered and, presumably, larger cyclic amines since the discrepancies are very close to the 0.05 eV uncertainty in measurement mentioned in the Experimental Section. The 3-membered aziridine ring has an N1s core energy that is 0.21 eV higher than that in methylethylamine (Table II) and 0.26 eV higher than that in azetidine, another reasonable model. Table III similarly shows that ring "closure" does not appear to affect the core energies for the 4- and 5-membered and, presumably, larger lactams. Table IV presents N1s core energies for amides and lactams and their amine analogues. As noted in this table, the N1s and O1s core ionization energies of Brown and Tse[37] have been lowered by 0.07 eV for reasons described in the Experimental Section. Aside from the formamides where the difference is higher, the amides or lactams have N1s core ionization energies that are 0.96 ± 0.03 eV (n = 6) higher than those of the corresponding amines. This is, as previously mentioned, consistent with a significant resonance contribution from **1b**.[22]

One might initially be surprised that ring "closure" to the β-lactam produces no anomalous shift in N1s core ionization energy since β-lactams are highly strained and are hydrolyzed much more rapidly than their higher homologues. However, the critical issue here is the loss of significant resonance energy which may or may not accompany increased strain energy. 2-Azetidinone is absolutely planar in the gas phase and solid states, and while there are no published thermochemical data for it, ab initio molecular orbital calculations predict only a 2 kcal/mol loss in resonance stabilization in contrast to a 12 kcal/mol loss in the 3-membered ring aziridinone using the same basis set.[40] The difference in O1s ionization energies between β-lactam and cyclobutanone is about equal to the difference between these values for 3-pentanone and 2-pyrrolidone. Similarly, the resonance energy in β-lactone is virtually equal to that in methyl acetate using published thermochemical data (gas-phase enthalpies of formation[41,42] in kilocalories per mole placed below the compounds in isodesmic eqs 1 and 2). These equations compare the energy (or enthalpy) of an amide or lactam with those of the corresponding amines and ketones with subtraction of the appropriate alkane to maintain the atom count and correct for strain energy.[8] The net "stabilization energy" includes both inductive and resonance effects. However, it is used as an operational definition which is particularly useful in the comparison of similar linkages. Therefore, the rapid hydrolyses of β-lactam (2-azetidinone) and β-lactone (2-oxetanone) are due to the loss of ring strain upon opening of the respective 4-membered rings rather than any significant destabilization due to decreased resonance.

Scheme I





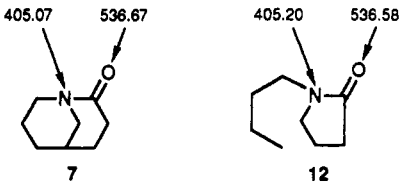
(1) –RE = β-lactone – oxetane – cyclobutanone + cyclobutane
–20.6 = (–67.6) (–19.2) (–21.0) (+6.8)

(2) –RE = $CH_3CO_2CH_3$ – $CH_3OC_2H_5$ – $CH_3COC_2H_5$ + n-C_4H_{10}
–19.6 = (–98.4) (–51.7) (–57.1) (–30.0)

Turning to the distorted lactams, we first examine 1,3-di-*tert*-butylaziridinone (**6**). Ab initio molecular orbital calculations of the unsubstituted lactam using 3-21G and 6-31G* basis sets indicate that this molecule has a pyramidal nitrogen.[40,43] This suggests that the 1,3-di-*tert*-butyl derivative also has a pyramidal nitrogen since it allows a larger dihedral angle between the nonbonded *tert*-butyl substituents, and this is consistent with the conclusions derived from UV photoelectron spectra and MNDO calculations.[44] Furthermore, 1,3-bis(1-adamantyl)aziridinone is also known to have a pyramidal nitrogen.[45] The N1s core energy (405.00 eV) is the lowest of the lactams (amides) investigated in the present study, and the O1s core ionization energy is the highest. In order to best utilize this data one must first obtain or derive suitable model values. An ideal comparison between N1s values would be 1,2-di-*tert*-butylaziridine (**11**), a compound that we were not able to prepare sufficiently pure for ESCA analysis. However, a model N1s core energy of 404.22 eV was derived for this compound through comparison with a variety of other N1s ionization energies.[46]

(40) Greenberg, A.; Chiu, Y.-Y.; Johnson, J. L.; Liebman, J. F. *Struct. Chem.* **1991**, *2*, 117.
(41) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986.
(42) Wiberg, K. B.; Crocker, L. S.; Morgan, K. M. *J. Am. Chem. Soc.* **1991**, *113*, 3447.
(43) Bevilacqua, C. R.; Thomas, T. D., unpublished calculations. See also: Bevilacqua, C. R. *Core-Electron Spectroscopy of Planar and Nonplanar Amides*; Oregon State University, September, 1989.
(44) Treschanke, L.; Rademacher, P. *J. Mol. Struct. (THEOCHEM)* **1985**, *122*, 35.
(45) Wang, A. H.-J.; Paul, I. C.; Talaty, E. R.; Dupuy, A. E., Jr. *J. Chem. Soc., Chem. Commun.* **1972**, 43.

Scheme II

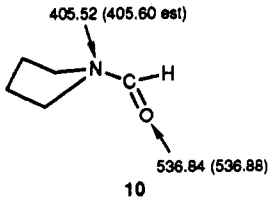


This value is only 0.77 eV lower than that in aziridinone **6** (Scheme I) in contrast to the 0.96 eV difference derived for the six undistorted (nonformamide) amides and lactams in Table IV. The estimation technique undoubtedly introduces some error into the comparison. While there are not enough data to make a detailed statistical study, our experience suggests an additional 0.05 eV error, a number comparable to the experimental error. This difference is consistent with reduced contribution of resonance structure **1b** to aziridinone **6**. It is also consistent with the observation that the carbonyl frequency of this lactam is ca. 13 cm^{-1} higher than that of the cyclopropanone in contrast to the usual situation where the amide (lactam) carbonyl frequency is 50–75 cm^{-1} lower than that of the corresponding ketone.[9] Reduced resonance in aziridinones is a consequence of (a) pyramidal geometry at nitrogen, due in part to the high intrinsic N-inversion barriers in aziridines, which decreases conjugation, and (b) reduced **1b** contribution since the corresponding zwitterionic aziridinone resonance contributor would have cyclopropene character and thus be destabilized due to a large enhancement in strain energy relative to the **1a** structure.[40] Ab initio molecular orbital calculations using the 6-31G* basis set indicate resonance stabilization in aziridinone of only 12.5 kcal/mol, in contrast to 19.9 kcal/mol (19.6 kcal/mol, experimental) in acetamide.[40]

It is important to note that the amide/amine comparison in Table IV is based upon planar N in amides (lactams) and pyramidal N in amines, whereas the N in aziridinone is pyramidal. If one employs the calculational result that planar NH_3 has a N1s core ionization energy 0.3 eV lower than that of pyramidal NH_3,[47] and transfers this to aziridinone, then the hypothetical aziridinone **6'** having planar N would have an N1s core energy of 404.70 eV which is only 0.47 eV higher than that of the corresponding amine. This is the number that would be comparable to the 0.96 eV (amide/amine) difference noted earlier. Of course, planarization would enhance delocalization, and so this comparison is not simple.

Study of the N1s and O1s core energies of 1-azabicyclo[3.3.1]nonan-2-one (**7**) and 1-*n*-butyl-2-pyrrolidone (**12**) furnishes a trenchant comparison (see Scheme II). Since these two molecules have the same number of C, N, and O and are quite similar in substitution, differing mainly in ring "closure", the earlier arguments in this paper indicate that they are directly comparable. The fact that the N1s core energy in the bridgehead lactam is lower by 0.13 eV while the O1s core energy is 0.09 eV higher is consistent with the classical resonance theory of bonding

Scheme III



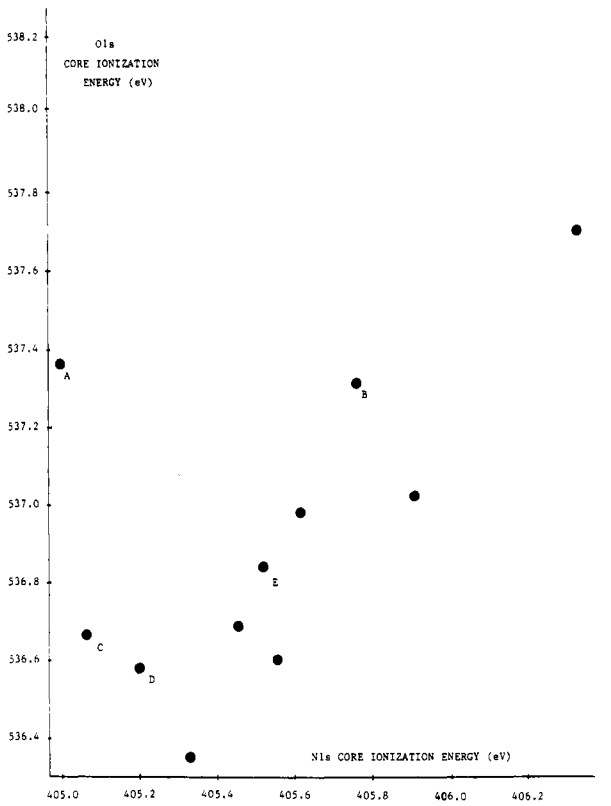


Figure 1. Plot of O1s versus N1s core ionization energies for amides and lactams listed in Table I. The following points are highlighted: (A) 1,3-di-*tert*-butylaziridinone (6); (B) 2-azetidinone; (C) 1-azabicyclo[3.3.1]nonan-2-one (7); (D) 1-*n*-butyl-2-pyrrolidone (12); (E) 1-pyrrolidinecarboxaldehyde.

in these molecules. It is important to note that the comparison between the two molecules is a direct one. Using the estimated 0.05 eV precision still indicates that the N1s result is greater than twice the error limit, although the interpretation is not as clearcut for the O1s data. Nevertheless, it is important to recognize that it is qualitatively in the right direction, whereas a more negative nitrogen in a planar amide would have implied a higher core ionization energy in the distorted lactam. If one uses the average 0.96 eV difference between lactam and amine, the value for **7** would be 0.83 eV assuming that **12** behaves as a normal pyrrolidone and that 1-azabicyclo[3.3.1]nonane is not unusual.

1-Pyrrolidinecarboxaldehyde (**10**) furnishes an interesting test of the assumptions employed in this work. Although a casual glance at the structural formula suggests a normal amide, interplay of various structural factors result in a markedly nonplanar, somewhat twisted amide linkage.[48] One may estimate the N1s and O1s core energies using the following data:[49] $(C_2H_5)_2NCOCH_3$ (N1s, 405.26; O1s, 536.52), $(CH_3)_2NCHO$ (N1s, 405.90; O1s, 537.02) and $(CH_3)_2NCOCH_3$ (N1s, 405.56; O1s, 536.66).

(46) To approximate the N1s energy of **11** we use 2-methylaziridine (404.96 eV). Replacing the *N*-hydrogen with an *n*-butyl group gives a shift of –0.42 eV [1-*n*-butyl-2-pyrrolidone (405.20) minus 2-pyrrolidone (405.62)]. Converting the *n*-butyl group to a *tert*-butyl group gives a shift of –0.19 eV [*tert*-butylamine (404.69) minus *n*-butylamine (404.88)]. Replacement of the 2-methyl group with a 2-*tert*-butyl group yields –0.13 eV. For this we compare tris(*n*-propyl)amine (404.22) with triethylamine (404.35). In this comparison, we use β-methyl substitution on three different chains, whereas the actual change involves three β-methyl substitutions on a single methyl group. (Data are from Table I or ref 39.)

(47) Eyermann, C. J.; Jolly, W. L. *J. Phys. Chem.* **1983**, *87*, 3080.

(48) Lee, S. G.; Hwang, K. W.; Bohn, R. K.; Hillig, K. W., II; Kuczkowski, R. L. *Acta Chem. Scand.* **1988**, *A42*, 603.

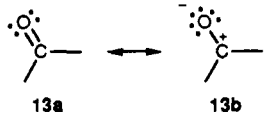
(49) Data are averages from data in refs 37 and 39, the former corrected by subtracting 0.07 eV as noted earlier.

These estimated values, placed beside the experimental data for **10** in Scheme III, assume an undistorted amide linkage. The experimental N1s value in **10** is 0.08 eV lower than the value calculated for the undistorted linkage, and while this difference is within the estimated errors in experiment and approximation, it is, at least qualitatively, consistent with resonance theory. If one employs the 1.06 eV amide/amine difference using *N,N*-dimethylformamide (Table IV) as a standard, the corresponding value for 1-pyrrolidinecarboxaldehyde would be about 0.98 eV. The O1s value is also slightly lower than the calculated value, but the uncertainties in O1s data are greater in magnitude, and this seeming inconsistency with resonance theory may be nullified once more precise O1s values become available.

In Figure 1 O1s core ionization energies are plotted vs N1s core ionization energies for the amides and lactams listed in Table I. Although there is a general trend toward lower values as molecules get larger, obviously the dependencies of O1s and N1s core energies will vary with the particular type of substitution. It is noteworthy that 1,3-di-*tert*-butylaziridinone (point A in Figure 1) is far removed from the other points. We feel that this is due to hybridization effects as well as reduced resonance. Some of these effects can also be seen 2-azetidinone (point B). The bridgehead lactam 1-azabicyclo[3.3.1]nonan-2-one (point C) shows a similar tendency toward a relatively low N1s with a relatively higher O1s due to reduced resonance. 1-*n*-butyl-2-pyrrolidone (point D) furnishes a counterpoint. Figure 1 indicates no loss of resonance in 1-pyrrolidinecarboxaldehyde, but one must be cautious about such a conclusion due to the limited amount of O1s data.

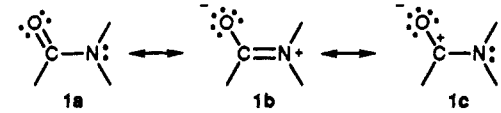
Canonical structures **1a** and **1b** both depict carbon in a double-bonded uncharged state. Thus, to a first approximation, one might anticipate that the carbonyl C1s ionization energies should vary relatively little as the balance between these two resonance contributors changes as a function of amide distortion. However, the data in Table I provide some striking disparities with this conventional viewpoint. First, it is noteworthy that the core ionization energies of the carbonyl carbons in amides and lactams are nearly 2 eV *lower* than those in the corresponding ketones (compare 3-pentanone and 2-pyrrolidone; compare 2-azetidinone and cyclobutanone). Second, the carbonyl C1s ionization energies in the distorted lactams 1,3-di-*tert*-butylaziridinone and 1-azabicyclo[3.3.1]nonan-2-one are both *lower* than those of other lactams in this study. Comparison of the C1s data for 2-pyrrolidone and 1-methyl-2-pyrrolidone suggest that this is not merely an effect of molecular size. Of particular interest is the fact that in 1-azabicyclo[3.3.1]nonan-2-one, both the N1s and the carbonyl C1s ionization energies decrease relative to standards while the O1s ionization energy increases. The same effect is seen in 1,3-di-*tert*-butylaziridinone, although a derivative of cyclopropanone is needed as a standard.

The carbonyl C1s ionization energy results are both clarifying and confounding. To a first approximation, one might anticipate that a ketone well represented by resonance contributor **13a** should not have a carbonyl C1s core



13a **13b**

energy much different from an amide well represented by **1a** and **1b**. If anything, the two electronegative atoms attached to C=O in the amide might raise its C1s ionization energy relative to that of the ketone. In attempting to understand these results, it is beneficial to refer to the recent publication of Wiberg and Brenneman.[14] They indicate that the carbonyl group in amides is best written as $C^+–O^-$. The strong implication of their conclusion is that, if one were to use resonance structures to represent an amide, then the dominant canonical contributors would be **1b** and **1c**. This would explain the significant C–N π



1a **1b** **1c**

bond order they calculate in the planar amide,[14] the high C–N rotational barrier, and the significant lengthening of C–N upon rotation of the amide linkage while C–O barely shortens. We too feel that the importance of the $C^+–O^-$ contributors has been overlooked previously. The high carbonyl C1s energy in a ketone suggests a very significant contribution from **13b**. This might rationalize the 0.5 eV decrease in the C1s energy in the comparison[39] of formaldehyde (294.5 eV) and acetaldehyde (294.0 eV) with methane (290.9 eV) and ethane (290.7 eV) which could reflect enhanced inductive stabilization in the carbocation-like aldehydes. In our view, while there may be a significant contribution from **1c** in amides, it should be smaller than the contribution of **13b** in ketones. This is sensible from the point of view that the positive carbon in **1c** is attached to one additional electronegative atom. The "loss" in the contribution of the $C^+–O^-$ canonical structure **1c** in an amide is compensated for by a strong, perhaps dominant, contribution from **1b**. Hence, the carbonyl C1s ionization energies in amides are lower.

Rotation of the amide linkage should decrease the contribution of **1b** due to poorer π overlap. This is consistent with the lower N1s in distorted lactams. If a small decrease in **1b** is compensated for by a small increase in **1a**, this would explain an increase in the O1s core energy. The fact that C1s is also lower in distorted lactams is not so simply explained. To a first approximation, the loss in **1b** compensated by the gain in **1a** upon distortion should not decrease the positive charge on the carbonyl carbon. However, if one were to invoke the increased electronegativity of the sp^2 N in the planar amide relative to the sp^3 N in the twisted structure,[14] then the relatively small decrease in the carbonyl C1s core energy upon twisting may be explained.

However, we must note that from a calculational point of view, both the "internal" and "external" approaches, described earlier, predict that twisting of the amide linkages produces opposite changes in the effective electronic populations of N and the carbonyl C.[14] This appears to contradict the results of the ESCA experiments which indicate that the core ionization energies of both carbonyl C and N decrease upon distortion. However, the comparisons differ in the experimental and calculational studies.

Conclusions

The N1s core ionization energies of two distorted lactams, 1-azabicyclo[3.3.1]nonan-2-one (**7**) and 1,3-di-*tert*-butylaziridinone (**6**) are significantly lower than those of model compounds. The N1s core ionization energy of 1-pyrrolidinecarboxaldehyde (**10**) is lower than that of the model compound but within the limits of uncertainty of the experimental data and approximations. These results are consistent with the predictions of classical resonance theory in which the nitrogens in distorted amides and lactams should be less positively charged than those in planar amides and lactams. It appears to be at variance with earlier predictions[10] of enhanced negative charge on

nitrogen in the planar structure. The O1s core energy in 1-azabicyclo[3.3.1]nonan-2-one is higher than that in 1-*n*-butyl-2-pyrrolidone, consistent with resonance theory. While the O1s value in the aziridinone is especially high, there are no cyclopropanone data to compare it with. The low N1s core energy in 1-pyrrolidinecarboxaldehyde is only 0.08 eV lower than the model value—very close to the combined experimental and estimation uncertainties. While this is consistent with its experimentally-known distortion, the O1s value is 0.04 eV lower than its model value. However, there are significant uncertainties and gaps in the O1s data.

The relatively high carbonyl C1s ionization energy in ketones suggests important contributions from resonance contributors such as **13b** which have C^+–O^- character. The relatively low carbonyl C1s ionization energy in amides suggests a much larger contribution from **1b**. The explanation of the reduced carbonyl C1s ionization energies in distorted lactams may rest with the electronegativity at nitrogen. However, it is clear that much more work must be done in order to observe the dependencies of experimental core ionization energies upon specific distortion modes and their relationships with different calculations of atomic charge.

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Registry No. $HCONH_2$, 75-12-7; $HCON(CH_3)_2$, 68-12-2; $CH_3CON(CH_3)_2$, 127-19-5; $(CH_3)_2NH$, 124-40-3; $CH_3NHC_2H_5$, 624-78-2; $(C_2H_5)_2NH$, 109-89-7; $C_2H_5NH(n\text{-}C_3H_7)$, 20193-20-8; $(n\text{-}C_3H_7)_2NH$, 142-84-7; $HCONHCH_3$, 123-39-7; $CH_3cONHCH_3$, 79-16-3; $CH_3CON(C_2H_5)_2$, 685-91-6; $CH_3CONHC_2H_5$, 625-50-3; $CH_3CON(CH_3)C_2H_5$, 38806-26-7; CH_3NH_2, 74-89-5; $(CH_3)_3N$, 75-50-3; $(CH_3)_2NC_2H_5$, 598-56-1; $(C_2H_5)_3N$, 121-44-8; 1-pyrrolidinecarboxaldehyde, 3760-54-1; *N*,2′-dimethylacetanilide, 573-26-2; 1,3-di-*tert*-butylaziridinone, 14387-89-4; 2-azetidinone, 930-21-2; 2-pyrrolidone, 616-45-5; 1-methyl-2-pyrrolidone, 872-50-4; 1-*n*-butyl-2-pyrrolidone, 3470-98-2; 1-azabicyclo[3.3.1]nonan-2-one, 74331-49-0; azetidine, 503-29-7; propanone, 67-64-1; cyclobutanone, 1191-95-3; 2-butanone, 78-93-3; 2-pentanone, 107-87-9; 3-pentanone, 96-22-0; piperidine, 110-89-4; pyrrolidine, 123-75-1; 1-methyl-2-piperidone, 931-20-4; *N*-methylpyrrolidine, 120-94-5; *N*-methylpiperidine, 626-67-5.

Specific Activation by Microwaves: Myth or Reality?

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Ene reactions involving carbonyl enophiles have been carried out under microwave irradiation at controlled temperature and atmospheric pressure. The reactions of diethyl mesoxalate with 1-decene and β-pinene and the cyclization of (+)-citronellal under homogeneous (neat liquid) or heterogeneous (clay catalyst) conditions have been studied. In each case the dependence of reaction yield on time and the stereoisomer ratios of the products are unaffected by the heating mode.

In the last few years there have been a growing interest in the use of microwave heating in organic synthesis[1-10] ("MORE chemistry": microwave oven-induced reaction enhancement). The use of such nonconventional reaction conditions reveals several features: (i) a reduction in the usual thermal degradation and/or better selectivity,[1,6,7] and (ii) for some reactions, especially under heterogeneous conditions,[1,3-5] there seems to be a marked rate enhancement compared to conventional heating. It should be noted however, that in most cases the reaction conditions (temperature, pressure, etc.) were not monitored with accuracy. In this respect, it appeared that organic solvents under microwave irradiation superheat by 13–26 °C above their conventional bp's at atmospheric pressure.[11] Thus, at this time, it is unresolved whether the use of microwaves provides specific activation. Accurate studies comparing the use of microwave to conventional heating are needed.

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