

Electronic energy levels of N-methyl derivatives of formamide and acetamide and their cation radicals

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Abstract. In view of the results from UV photoelectron spectra suggesting reversal of n and π levels in formamide and its N-methyl derivatives, INDO and STO-3G calculations have been carried out on N-methyl derivatives of formamide and acetamide in both neutral and cation radical states.

Keywords. Electronic energy levels; N-methyl derivatives of amides; cation radicals of N-methyl derivatives of amides.

1. Introduction

Electronic structures of simple amides continue to be of interest since these compounds represent the simplest model systems for the study of proteins and peptides. A number of studies on the electronic absorption spectra of amides have been carried out to elucidate the higher virtual electronic states involved (Hunt and Simpson 1953; Peterson and Simpson 1957; Kaya and Nagakura 1967; Neilson and Schellman 1967). The experimental observation that N-methyl substitution shifts the first $\pi \rightarrow \pi^*$ band towards longer wavelengths and C-methyl substitution leads to shift of this band to shorter wavelengths was explained by considering the intramolecular charge transfer and the hyperconjugation effect (Kaya and Nagakura 1967). Larson *et al* (1974), Glazer and Rosenheck (1962) and Momii and Urry (1968) have investigated the emissive properties of different types of amidic triplet states and discussed the important lower triplet as well as single excited states. A detailed *ab initio* study of the singlet as well as triplet electronic excited states and transitions in formamide has been reported by Stenkamp and Davidson (1977) who favour the following state ordering: $^3n\pi^*$ (5.34 eV), $^3\pi\pi^*$ (6.12 eV), $^1n\pi^*$ (5.63 eV), $^1\pi\pi^*$ (8.45 eV) in formamide. Similar treatment for N-methylacetamide has been reported by Nitzsche and Davidson (1978). There still seems to be uncertainty regarding the ordering of the highest occupied n and π molecular orbitals (MO) of the amides and their N-methyl derivatives. The narrow spacing between the n and π MO's in amides seems to be the main difficulty in an unambiguous assignment of the energy level ordering in these systems.

Since the Rydberg series observed in these molecules converge on the lowest ionization potential, they must involve the highest n and/or π levels as the terminal orbital. However, the lowest Rydberg series can still be assigned as either $n \rightarrow np$ or

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$\pi \rightarrow \pi p$ transitions, depending on which is uppermost. An early member of the *ns* Rydberg series has also been observed in acids and amides (Basch 1967, 1968) but again the question remains whether the originating orbital is of *n* or π type. Based on uv photoelectron spectroscopy and molecular orbital calculations, Brundle *et al* (1969) have proposed that the highest occupied MO of the formamide is of non-bonding (*n*) type centred on the oxygen atom and the next lower orbital is the π type MO. Ground state calculation on formamide using the double-zeta GTO basis set predicted a reversal of *n*, π ordering. However, vertical ionization potential calculated as the difference between the SCF energies of the neutral molecule and the positive ion, with allowance for correlation energy errors in both species, were opposite to the ordering based on Koopman's theorem, but in agreement with the experimental assignment. The spectra of mono- and di-N-methylated formamide were assigned to as the π uppermost MO, *n* being the next MO; no calculations were reported. Sweigart and Turner (1972) have made a detailed analysis of the uv photoelectron spectra of a series of carboxylic acids and their derivatives including amides. Again the crucial point about the *n*, π MO ordering for amides is not independently discussed, rather the assignment of Brundle *et al* (1969) is accepted for formamide.

A comparative study of analogous thioamides, ureas and thioureas using photoelectron spectroscopy has been carried out by Mines and Thompson (1975), but again the earlier assignment for formamide was accepted as given by Brundle *et al* (1969). One more paper on detailed CI calculations based on the iterative CIPSI algorithm (Huron *et al* 1973) which combines variation and perturbation techniques has appeared.

In the present paper, a detailed study of the neutral and the cationic open-shell species of formamide, acetamide and their mono- and di-N-methyl derivatives has been carried out. The electronic structures of the cationic species are analyzed in relation to those of the neutral molecules using the STO-3G SCFMO method at the *ab initio* level and the INDO method at the semiempirical level. The results are discussed in the light of experimental quantities where available.

2. Results and discussion

2.1 Energy level ordering

As can be seen from figure 1 *ab initio* STO-3G calculations on the six neutral molecules considered, show that there is apparently no energy level crossing involved in any of the species. This is in agreement with unambiguous experimental assignments shown in figure 2 (Sweigart and Turner 1972), except for the non-methylated parent amides, formamide and acetamide in which case the *n*, π ordering is reversed. The energy level ordering obtained from unrestricted open-shell calculations on the cation radicals of these systems is shown in figure 3. It is clear that there is considerable widening of the energy gap between the highest filled π and *n* type MO's in all the systems. It is interesting that the photoionization products except acetamide still maintain the same level ordering, namely π upper most, *n* next, as in the neutral molecules. It is clear at least in the case of formamide that the highest MO is of π type rather than of *n* type, and this order continues in its primary and secondary amides. Figures 4 and 5 give the results of semiempirical INDO calculations on neutral and cationic species. There is agreement between INDO and *ab initio* results for the neutral molecules of formamide series while for acetamide INDO predicts *n* higher than π . Open-shell calculations with INDO indicate

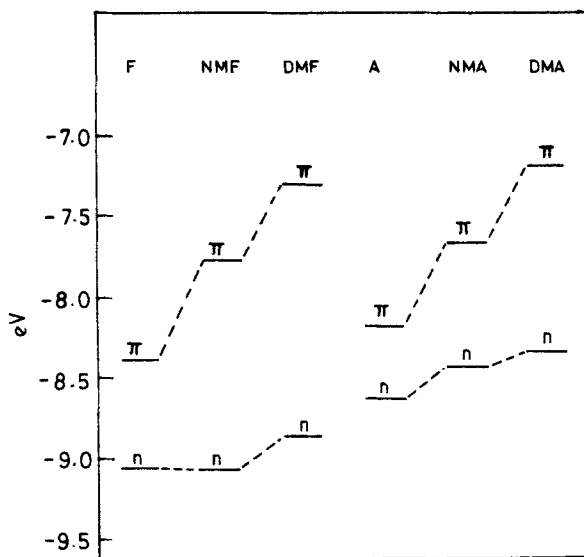


Figure 1. STO-3G energy levels of neutral amides.

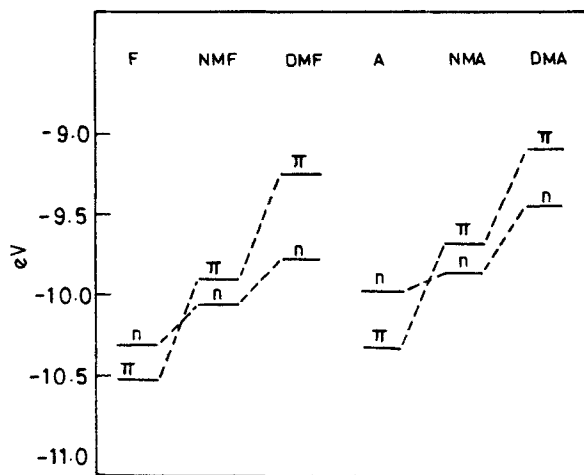


Figure 2. Experimental energy levels of amides (from Sweigart and Turner 1972).

a reversal of order for formamide and no reversal for acetamide. Considering the approximate nature of INDO method especially for open-shell systems not much weightage can be given to the INDO results.

Very recently a completely independent experimental study (Rao and Symons 1982) on the cation radicals of amides has been reported based on ESR studies in dilute solutions of the amides in freon (fluorotrichloromethane). The spectra of DMF and DMA have been shown to indicate that the highest MO from which the ionization took place is

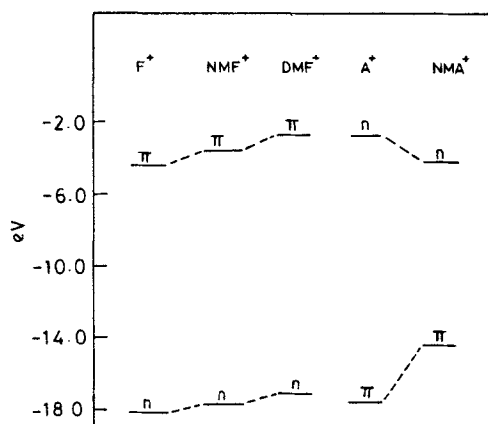


Figure 3. STO-3G energy levels of amide cations.

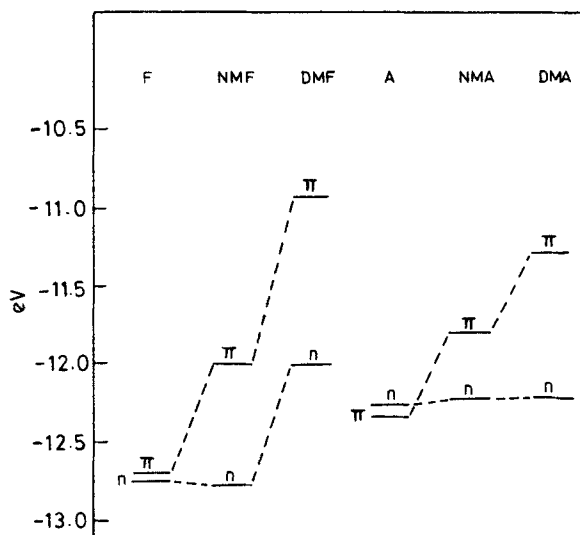


Figure 4. INDO energy levels for neutral amides.

of π type. The spectra of the mono methyl derivatives are reported to be poorly resolved and those of the parent primary amides (formamide and acetamide) could not be studied because they are insoluble due to their extensive inter molecular hydrogen bonding.

2.2 Geometries

Complete geometry optimisation was carried out for the neutral species as well as the cationic species. Table 1 shows the trends in C=O and C-N bond lengths from STO-3G, INDO calculations and experimental values. It is clear from both *ab initio* and INDO

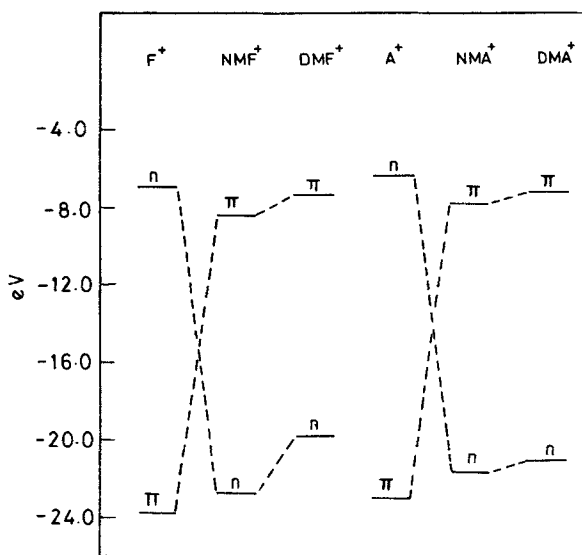


Figure 5. INDO energy levels for amide cations.

Table 1. C=O and C-N bond lengths (Å).

	Neutral species		Cations	
	$r(\text{C}=\text{O})$	$r(\text{C}-\text{N})$	$r(\text{C}=\text{O})$	$r(\text{C}-\text{N})$
STO-3G	~ 1.22	~ 1.405	~ 1.325	~ 1.36
INDO	~ 1.27-1.28	~ 1.37	~ 1.33	~ 1.34
Experimental	~ 1.22-1.28	~ 1.33-1.39	—	—

optimised geometries that there is an increase in the C=O bond length (~ 0.1 Å) while there is a shortening of the C-N bond length (~ 0.05 Å), in going from the neutral molecules to the cationic radical species. Experimental values of cation geometries are, however, not available for comparison. It is noted that these results are in agreement with previous calculations on neutral species (Peters and Peters 1978; Fogarasi *et al* 1979). Table 2 gives the optimised geometries for individual, neutral and cationic species. Table 3 shows the calculated total electronic energies of the neutral as well as the cationic amides.

2.3 Electron distribution

The electron distributions obtained from STO-3G and INDO methods are shown in table 4. It is clear that there is relatively little change in the electron density on the amide carbon atom in going from the neutral molecule to the cation. But the electron densities on the amide N and O atoms decrease sharply due to hole creation. This fact indicates that the hole created by the loss of an electron is almost entirely shared by the N and O atom centres of the amide unit. This observation also amounts to saying that the HOMO

Table 2. Optimised geometries for neutral and cationic amides.

	STO-3G		INDO		
	$r(\text{C}=\text{O})$ (Å)	$r(\text{C}-\text{N})$ (Å)	$r(\text{C}=\text{O})$ (Å)	$r(\text{C}-\text{N})$ (Å)	OCN (deg)
Formamide	1.218	1.403	1.268	1.365	125.5
Cation	1.311	1.389	1.326	1.312	127
N-methylformamide	1.219	1.405	1.269	1.375	124
Cation	1.322	1.405	1.301	1.373	120
N,N-dimethylformamide	1.219	1.405	1.267	1.368	125
Cation	—	—	1.288	1.358	124
Acetamide	1.220	1.410	1.276	1.373	120
Cation	1.358	1.325	1.277	1.336	122
N-methylacetamide	1.225	1.386	1.277	1.372	120
Cation	—	—	1.333	1.348	120
N,N-dimethylacetamide	1.225	1.386	1.277	1.378	120
Cation	—	—	1.312	1.357	120

Table 3. Calculated electronic energies of neutral and cationic amides.

System	Total Energy (a.u.)	
	STO-3G	INDO
Formamide	-166.68815	-37.74014
Cation	-166.46023	-37.37955
N-methylformamide	-205.26048	-46.16380
Cation	-205.05972	-45.79306
N,N-dimethylformamide	-243.84415	-54.36129
Cation	-243.66686	-54.02635
Acetamide	-205.27634	-46.17750
Cation	-205.07050	-45.84013
N-methylacetamide	-243.85458	-54.62929
Cation	-243.27462	-54.27765
N,N-dimethylacetamide	-282.42798	-63.07022
Cation	—	-62.73734

from which the electron is lost is not of non-bonding (n) type but is a delocalized π type MO. In the case of N-methyl acetamide (NMA), ionization from the HOMO leads to large electron loss on the O atom alone indicating that the HOMO is likely to be of n type rather than of π type.

3. Conclusions

(i) Unrestricted open-shell *ab initio* calculations do not predict n , π energy level crossing in the formamide series while such a crossing is predicted in the acetamide series. (ii) Changes in the electron distribution in going from neutral amides to their cation radicals indicate a π type MO as the highest occupied MO in all the cases except in acetamide. (iii) Both INDO and STO-3G results indicate that there is a lengthening of

Table 4. Effective charges on the N, C and O atoms from STO-3G results*.

	N	C	O
Formamide	-0.438 (-0.229)	0.254 (0.433)	-0.266 (-0.383)
Cation	-0.152 (-0.083)	0.284 (0.487)	-0.026 (0.025)
N-methylformamide	-0.365 (-0.194)	0.228 (0.422)	-0.266 (-0.383)
Cation	-0.092 (0.108)	0.252 (0.378)	-0.040 (0.060)
N,N-dimethylformamide	-0.303 (-0.127)	0.242 (0.407)	0.273 (-0.397)
Cation	-0.041 (0.173)	0.253 (0.327)	-0.057 (-0.105)
Acetamide	-0.440 (-0.242)	0.316 (0.410)	-0.283 (-0.408)
Cation	-0.648 (0.126)	0.415 (0.498)	0.073 (-0.004)
N-methylacetamide	-0.369 (-0.202)	0.303 (0.400)	-0.289 (-0.408)
Cation	-0.481 (0.455)	-0.241 (0.394)	0.859 (0.090)
N,N-dimethylacetamide	-0.305 (-0.172)	0.298 (0.394)	-0.291 (-0.405)
Cation	— (0.109)	— (0.350)	— (-0.116)

*INDO values are given in parenthesis.

the amide C=O bond (~ 0.1 Å) and slight shortening of the amide C-N bond (~ 0.05 Å) in going from the neutral to the cation radicals. (iv) The amide unit essentially retains its planarity after the removal of the electron.

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References

- Basch H, Robin M B and Kuebler N A 1967 *J. Chem. Phys.* **47** 1201
 Basch H, Robin M B and Kuebler N A 1968 *J. Chem. Phys.* **49** 5007
 Brundle C R, Turner D W, Robin M B and Bash H 1969 *Chem. Phys. Lett.* **3** 292
 Fogarasi G, Pulay P and Torok F 1979 *J. Mol. Struct.* **57** 259
 Glazer A N and Rosenheck K 1962 *J. Biol. Chem.* **237** 3674
 Hunt H D and Simpson W T 1953 *J. Am. Chem. Soc.* **75** 4540
 Huron B B, Malrieu J P and Ranourel P 1973 *J. Chem. Phys.* **58** 5745
 Kaya K and Nagakura S 1967 *Theor. Chim. Acta* **7** 117
 Larson D B, Arnett J F, Seliskar C J and McGlynn S P 1974 *J. Am. Chem. Soc.* **96** 3370
 Mines G W and Thompson H W 1975 *Spectrochim. Acta* **A31** 137

- Momii R K and Urry D W 1968 *Macromolecules* **1** 372
Neilson E B and Schellman J A 1967 *J. Phys. Chem.* **71** 2297, 3914
Nitzsche L E and Davidson E R 1978 *J. Am. Chem. Soc.* **100** 7201
Oliveros E, Riviere M, Teichteil C and Malrieu J P 1978 *Chem. Phys. Lett.* **57** 220
Peters D and Peters J 1978 *J. Mol. Struct.* **50** 133
Peterson D L and Simpson W T 1957 *J. Am. Chem. Soc.* **79** 2375
Ramakrishna Rao D N and Symons M C R 1982 *Chem. Phys. Lett.* **93** 495
Stenkamp L Z and Davidson E R 1977 *Theor. Chim. Acta* **44** 405
Sweigart D A and Turner D W 1972 *J. Am. Chem. Soc.* **94** 5592