Study of electron densities of methyl acetate, *N*-methylacetamide and *N*,*N*′-dimethylurea by quantum mechanical investigations. Part 1. Gas phase

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The conformations and electron densities of a simple ester, amide and urea derivative have been studied with quantum mechanical methods at the Becke3LYP/6-31 + G* level. Discussions of electron densities use Natural Atomic (NAO) and Natural Bond Orbitals (NBO). The gas phase calculations indicate the importance of overall resonance stabilization for all molecules studied. It decreases in the series urea > amide > ester. The delocalization of one nitrogen lone pair into the $\pi^*_{C=O}$ bond is lower in the urea compared with the amide. This property is associated with a high flexibility of ureas.

Introduction

The structures and reactions of carboxylic acid derivatives such as esters, amides, acid halides and anhydrides have long been the subject of investigation. It is well known, that the properties of these compounds are mainly influenced by different degrees of inductive effects and resonance stabilization of the C(O)–X-bond. The dipole character of the carbonyl group along with π-electron-donating or σ-electron-accepting substituents is the source of the different reactivities of these substrates towards nucleophilic reactions at the carbonyl carbon.

It is of interest how derivatives of carbonic acid can be included in these rules. The most important compounds of this type are urea and its *N*-substituted derivatives. The effect of the existence of two nitrogen atoms at each side of the carbonyl group which can donate lone pair electrons is debatable. Already early structural studies[1] have indicated a significant longer C–N bond in urea than in similar amides. Measurements of ^{15}N chemical shifts[2] led to the conclusion that a nitrogen atom of urea is more shielded than that of a corresponding amide. Recent quantum mechanical investigations have shown that the barrier of rotation around the C(O)–N-linkage is much lower for ureas than for amides.[3,4] These results imply a lower delocalization of lone pair electrons in ureas than is found for amides. However, the reactivities of ureas towards nucleophilic attack on the carbonyl carbon lead to the opposite conclusion about resonance stabilization. The uncatalysed hydrolysis of urea in water at room temperature is not measurable.

N,*N*′-Disubstituted ureas undergo hydrolysis to give carbon dioxide and two amines only under very strict conditions.[5] A large number of enzymes are known to hydrolyse esters and amides by various mechanisms including hydrogen bonding at the carbonyl oxygen.[6] The hydrolysis of urea is catalysed only by ureases which always require transition metals.[7] This may be explained by a high resonance stabilization of urea derivatives, as has been assumed in empirical calculations of resonance energies.[8]

In order to show the usefulness of quantum mechanical methods to describe the difficult interplay between inductive and resonance effects in ureas the present study was undertaken. We compare conformations, rotational barriers and charge distributions of a methyl-substituted ester, amide and urea.

Computational details

The calculations were carried out with the GAUSSIAN94/DFT package[9] on IBM RS/6000 workstations at the University of Potsdam and on a CRAY Y-MP4E/464 at the Konrad-Zuse-Zentrum für Informationstechnik Berlin (ZIB). Final results were produced with the 6-31 + G* basis set[10] in conjunction with the Becke3LYP density functional (DFT) hybrid method.[11] The functional for the exchange-correlation energy used in this method is given by eqn. (1) where the individual

$$E_{XC} = (1 - a_O)E_X^{LSDA} + a_O E_X^{HF} + a_X \Delta E_X^{B88} + a_C E_C^{LYP} + (1 + a_C)E_C^{VWN} \quad (1)$$

energy terms are the Slater exchange (Local Spin Density Approximation), the Hartree–Fock exchange, Becke's 1988 exchange functional gradient correction,[12] the gradient-corrected correlation functional of Lee *et al.*[13] and the local correlation functional of Vosko *et al.*,[14] respectively. The coefficients derived by Becke are $a_O = 0.20$, $a_X = 0.72$ and $a_C = 0.81$.

Geometry optimizations of ground and transition states were made with no constraints, except molecular symmetry. We calculated force constants using analytic second derivatives of the potential energy. Vibrational frequencies are used unscaled. Thermal corrections of the total energies are based on standard formulae of statistical thermodynamics.[15]

Discussions of charge distributions are based upon analyses of Natural Atomic Orbitals (NAO), Natural Hybrid Orbitals (NHO) and Natural Bond Orbitals (NBO) (for a detailed description of these methods, see refs. 16–18). These calculations were performed with the GAUSSIAN94 implementation of the NBO 3.0 program.[19]

Results and discussion

Conformational analyses

The possible conformers of methyl acetate (MAC), *N*-methylacetamide (MAM) and *N*,*N*′-dimethylurea (DMU) correspond to rotational isomers produced by variation of the C1–O2–C3–C5, C1–N2–C3–C5 and C1–N2–C3–N2′-dihedral angles in steps of about 180°. Their relevant geometrical characteristics are summarized in Table 1. Differences between energies and enthalpies are shown in Table 2.

All the compounds studied prefer the common *trans*

Table 1 Gas phase geometries of stationary points

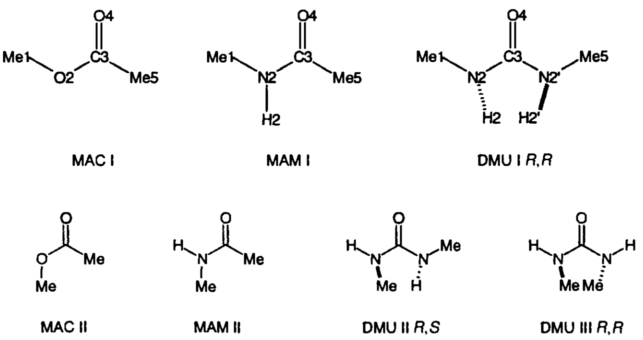
Compound		r(C3=O4)/Å	r(C3–X2)/Å	θ(H2–N2–C3–O4)/degrees
Preferred conformations				
MAC I	C_s	1.214	1.354	180.0[a]
MAM I	C_s	1.229	1.365	180.0
DMU I *R*,*R*	C_2	1.229	1.386	−156.2
Other conformations				
MAC II	C_s	1.209	1.362	0.0[a]
MAM II	C_1	1.229	1.371	−3.6
DMU I *R*,*S*	C_s	1.231	1.381	168.2/−168.2[b]
DMU II *R*,*S*	C_1	1.231	1.384/1.379[b]	−9.1/−162.9[b]
DMU III *R*,*R*	C_2	1.232	1.385	2.0
Transition states of rotation and inversion				
MAC TS	C_1	1.206	1.382	84.2[a]
MAM TS1	C_1	1.214	1.456	−61.3
MAM TS2	C_1	1.210	1.450	115.3
DMU TS1	C_1	1.226	1.451/1.355[b]	−60.4/178.4[b]
DMU TSi	C_1	1.231	1.378/1.384[b]	174.7/−163.3[b]

[a] θ(C1–O2–C3–C5). [b] First value: rotated or inverted part of the molecule; second value: unchanged part.

Table 2 Energies and enthalpies of activation and reaction

Reaction	ΔE(0 K)/kcal mol^{-1} [a]	ΔH(298 K)/kcal mol^{-1} [b]
MAC I→MAC TS	13.50	12.50
MAC I→MAC II	7.86	7.65
MAM I→MAM TS1	18.64	17.52
MAM I→MAM TS2	22.32	21.06
MAM I→MAM II	2.29	2.22
DMU I *R*,*R*→DMU TS1	8.11	7.56
DMU I *R*,*R*→TSi	0.77	0.04
DMU I *R*,*R*→DMU I *R*,*S*	0.76	0.63
DMU I *R*,*R*→DMU II *R*,*S*	0.78	0.83
DMU I *R*,*R*→DMU III *R*,*R*	4.79	5.10

[a] Difference of total energies. A conversion factor of 1 au = 627.5095 kcal mol^{-1} was used. [b] Difference of thermal corrected total energies. Activation enthalpies ignore the imaginary vibration of saddle points.



Atom numbering schemes and rotamers of the molecules studied. The chirality of N2 and N2′ in conformations of DMU is specified

conformation (rotamers I). MAC II is less stable than MAC I by about 8 kcal mol^{-1}.† Here the electrostatic interaction between O4 and the two lone pairs at O2 is repulsive. Both conformers of MAC are planar.

The ability of amide bonds to exist in planar *trans* and *cis* conformations is well known. It is explained by participation of the electrons of the nitrogen lone pair in the amide bond, yielding resonance stabilization of both conformations. However this behaviour is restricted by steric contacts and electronic substituent effects if the molecules are larger than formamide. These influences yield small to larger deviations from planarity of the amide bond. We obtain a planar nitrogen centre for MAM I, but an unsymmetric geometry for MAM II. The latter is caused by steric repulsions between the two methyl groups Me1 and Me5. It should be noted here that in particular the structure of conformer I depends on the method used for calculation. By using the 6-31G* basis set in conjunction with HF, Becke3LYP and MP2 methods a slight deviation from planarity is obtained [θ(HNCO) *ca.* −179°]. A symmetric structure is a saddle point in these cases. By using diffuse functions at heavy atoms a symmetric structure of MAM I exhibits a slight decrease in energy and no imaginary vibrations at the levels of theory used. These results are due to a slightly different description of the interplay between the electronic substituent effects at both sides of the carbonyl group by various methods. Since it should be clear that every quantum mechanical calculation is an experiment with a degree of error, we have to decide which results can be derived reliably. In the work presented here these are structural differences between the compounds we studied. In order to study deviations from planarity of the amide bond in detail, various substitution patterns have to be taken into account. Because of limited space this is not the aim of this paper.

All ground state conformers of DMU bear pyramidal NH groups, independent of the level of theory used. The high flexibility of DMU associated with this property yields conformers DMU II and DMU III with avoided steric repulsions. The pyramidal conformation of the nitrogen atoms induces two chiral centres in DMU. Two of the four possible stereoisomers are identical with respect to molecular symmetry. The remaining two isomers can be described by the positions of the two nitrogen lone pairs. The preferred stereoisomer of each rotamer is characterized by the location of the nitrogen lone pairs at different sides of the N–C(O)–N plane, yielding the DMU I *R*,*R* or *S*,*S*, DMU II *R*,*S* or *S*,*R*, and DMU III *R*,*R* or

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† 1 cal = 4.184 J.

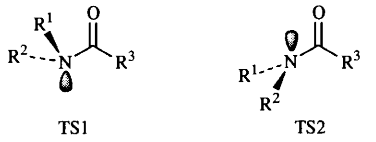

Fig. 1 Possible transition states of rotation around one C(O)–NH bond of amides and ureas

S,S conformers. The alternative DMU I *R,S* or *S,R* conformation shows a slight increase in energy in comparison with the DMU I *R,R* or *S,S* conformation (see Table 2), which is caused by repulsion of the two nitrogen lone pairs located at the same side of the molecule. Note that the nitrogen centres become more planar in the *R,S* conformation. This situation is coupled with a shortening of the C3–N2 bonds, but with a lengthening of the C3=O4 bond.

Properties of transition states of rotation, which separate the *cis* and *trans* conformers, are presented in Table 1. Energies and enthalpies of activation are included in Table 2. The transition state for the rotation in MAC is determined by interaction of one lone pair at O2 and the carbonyl oxygen, as assumed already in ref. 20. Two rotational transition states with pyramidal nitrogens may be possible for MAM and DMU (see Fig. 1). They can be transformed into each other by inversion of the nitrogen centre. Both are found for MAM. The structure TS1 has a lower energy than TS2 because the contact between the nitrogen lone pair and the carbonyl oxygen is avoided here. In the case of DMU, a structure like TS2 could not be characterized as a saddle point of first-order. Besides the usual imaginary vibration corresponding to rotation around one C–N bond, a second was found. It is located at the rotated methyl group and indicates a repulsion between the hydrogens of this group and the hydrogen located at the other NH group, which was not altered during these calculations.

The pyramidal conformation of the nitrogen atoms in the ground states of DMU implies barriers of inversion at these atoms. The transition state TSi studied here separates the DMU I *R,R* and the DMU I *R,S* stereoisomers. As assumed from the low reaction energy (see Table 2), the inversion barrier of one nitrogen atom in DMU is negligible and nearly disappears after thermal correction. The independence of inversions at the two nitrogen atoms is an interesting aspect of DMU. We attempted to calculate a transition state which involves simultaneous inversion of the two NH groups as has been done for unsubstituted urea.[3,4] The structures we obtained with C_{2v} symmetry are saddle points of second-order for various rotamers of the Me1 and Me5 groups.

The results shown in Table 2 are in good agreement with the interpretation of ^{15}N NMR measurements[2] and earlier studies of rotational barriers of amides and unsubstituted urea.[3] The experimental rotational barriers of ureas reported in the literature are based on ^{15}N-NMR chemical shifts, which are used in combination with formulae developed for rotational barriers in amides. Thus we avoid a quantitative comparison with our findings. Our results buttress the high flexibility of ureas in comparison with amides and correspond to the more single bond character of the C(O)NH linkages in ureas, which will be one subject of discussion in the following section. Interestingly, the energy barrier of rotation around one N2–C3 bond in DMU is lower than that around the O2–C3 bond in MAC. We explain this result in terms of intramolecular stabilization of TS1 in DMU by interaction between the lone pair of the nitrogen atom involved in rotation and the NH hydrogen of the unrotated amide function.

Charge distributions in the gas phase

The molecules studied here were selected with respect to near equal long-range substituent effects onto the carbonyl centre, so differences in electron densities at the –C(O)–X groups are mainly due to differences in X. The properties of the carbonyl group of these compounds are influenced mainly by inductive and resonance effects. We studied them with the aid of NAOs and NBOs. In order to guide you through our results, we give a brief description of it from a practical point of view. Molecular orbital (MO) calculations yield representations of a many-electron wavefunction of a molecule by a set of delocalized MOs which are built up by linear combinations of atomic orbitals (LCAO-MO methods). The practising chemist is often not familiar with this mathematical representation of molecular structure, so transformations of delocalized MOs into localized structure elements like atom centred atomic and hybrid orbitals or one-centre and two-centre bond orbitals are very useful to explain charge distributions.‡ The NBO approach we used yields sets of localized orbitals, which are designed to explain the electron density of a molecule to a maximal amount ('natural' localized orbitals[22]). The initial transformation of LCAO-MOs into a set of NAOs results in the optimal condensation of electron density in core and valence atomic orbitals. The full set of NAOs includes additional extra valence Rydberg orbitals, which are due to the existence of more basis functions in the input basis than is needed for the number of electrons (split valence basis sets, polarization and diffuse functions). The core and valence NAOs form a near minimal basis set, since they usually explain more than 99.5% of the total electron density. The sum of occupation numbers of all NAOs located at an atomic centre yields the natural electron population on this atom. The difference in the number of electrons of the isolated atom is the natural atomic charge. The NAO-based charges of the molecules we studied are summarized in Table 3.§ Their interpretation in connection with the other values shown in this table follows.

The density matrix represented in a set of NAOs is the basis for a subsequent transformation into a set of NBOs, which includes highly occupied core, lone pair and bonding orbitals, and anti-bond and Rydberg orbitals, which contain a minor amount of electron density. The highly occupied core, lone pair and bonding NBOs again form a minimal basis set, which is closely related to the Lewis structure. If this picture is valid in the case studied, these NBOs account for nearly 100% of the electron density. Deviations from this rule (lower occupancy of Lewis orbitals corresponding to significant electron density in anti-bonds) indicate electron delocalization. Then the structure cannot be described by the Lewis structure alone, leading to the concept of alternative Lewis structures to explain the same electron density. If the deviation from an ideal Lewis structure is small, perturbation theory in the sense of mixing occupied bonding orbitals with unoccupied anti-bonding orbitals leading to energetic stabilization[24] can be applied. This approach yields a picture of electron donor–acceptor interactions which is the basis for understanding effects like intramolecular conjugation, intermolecular charge transfer interactions, *etc.* Electron delocalization is the main source of the properties of the carbonyl group in acyl compounds, so we make extensive use of its description by analyses of NBOs.

Our NBO calculations led to the preferred Lewis structures expected for carboxylic acid derivatives. They include σ_{C3-O4}, $\pi_{C3=O4}$ and σ_{C3-X2} bonds, corresponding anti-bonds, two near localized lone pairs at the carbonyl oxygen O4 and delocalized

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‡ Most DFT methods which are based on the ideas of Hohenberg, Kohn and Sham use LCAOs to represent the electron density, which is the fundamental variable in DFT.[21] These 'LCAO-MOs' are not the same as MOs in the sense of the Hartree–Fock theory. A molecular wavefunction expressed in MOs does not exist in DFT, but if localization procedures handle the density matrix representation of MOs as is done in the NBO approach, they can be applied to DFT methods, too, presupposing that these methods yield reliable electron densities.

§ NAO-based charges are different from those obtained by the popular Mulliken population analysis,[23] since the NBO method handles overlap populations between atomic orbitals of the input basis set in another more rigorous way (for a discussion of this topic, see ref. 18).

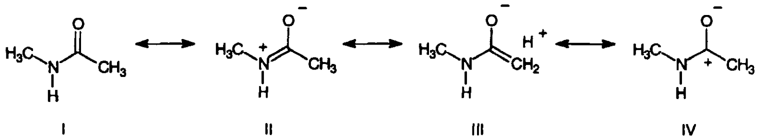

Fig. 2 Possible Lewis structures of MAM as indicated by NBO analyses

Table 3 Selected results from NAO–NBO analyses

	MAC	MAM	DMU
	Natural charges		
X2	−0.568	−0.674	−0.708
C3	+0.808	+0.668	+0.804
O4	−0.607	−0.646	−0.668
Percentage of total electron density in Lewis structures	98.658	98.540	98.465
	Occupancies of NBOs in electrons		
LP X2	3.760[a]	1.709	1.788[b]
LP O4[c]	3.828	3.846	3.832
$\pi^*_{C3{=}O4}$	0.221	0.295	0.373
$\sigma^*_{C3\text{-}X2}$	0.106	0.075	0.075[b]
$\sigma^*_{C3\text{-}C5}$	0.052	0.056	

[a] O2 of MAC contains two lone pairs, N2 of MAM and DMU only one. [b] Only one nitrogen centre counted. [c] Sum over occupancies of the two lone pairs at O4.

lone pairs at the X2 atoms (two for O2 of MAC, one for N2 of MAM and DMU). The Lewis structures found are able to account for about 98% of the total electron densities only (see Table 3), indicating the possibility of other Lewis structures. The remaining electron density rests in some anti-bonds. Its amount can be used as a first raw measurement of resonance effects, leading to an increasing overall electron delocalization in the series MAC < MAM < DMU.

A more detailed description of resonance can be given by the occupancies of bond orbitals. Selected values are presented in Table 3. Note that an ideal Lewis structure which describes 100% of the electron density is characterized by strictly double occupied bonding NBOs and lone pairs and zero-occupied anti-bonds. Deviations from this rule are a measure of electron delocalization from or into particular NBOs. The delocalization of electrons from the lone pair(s) at X2 into the $\pi^*_{C3{=}O4}$ anti-bond is shown to be the major resonance contributor. A second smaller contribution is associated with delocalization of electrons from the carbonyl oxygen lonepairs into the $\sigma^*_{C3\text{-}X2}$ anti-bonds. A third very small, but still measurable amount of electron delocalization is detected by determining the number of electrons found in the $\sigma_{C\text{-}H}$ bonds of the Me5 group in MAC and MAM. The three CH bonds of this group lose about 0.07 electrons, whereas the C–H bonds of Me1 lose about 0.03 electrons only. This particular result has to be interpreted in terms of hyperconjugation between the Me5 C–H bonds and the neighbouring carbonyl group. Comparing related NBOs, we observe an increasing occupancy of the $\pi^*_{C3{=}O4}$ anti-bond in the series MAC < MAM < DMU, which agrees with the assumed increasing amount of overall resonance stabilization. The corresponding electron loss at the electron-donating lone pair(s) of one X2 increases in the series DMU < MAC < MAM (−0.212 *vs.* −0.240 *vs.* −0.291). Note that DMU contains two nitrogen centres, which lose about 0.2 electrons each. These results show that the nitrogen lone pairs of DMU altogether are delocalized more than the single nitrogen lone pair of MAM. Looking at one lone pair only, it is less delocalized in DMU. Calculations of the associated stabilization energies by second-order perturbation theory yield 48 kcal mol^{-1} for the interaction of the two O2 lone pairs of MAC with its $\pi^*_{C3{=}O4}$ anti-bond, 65 kcal mol^{-1} in the case of MAM and 48 kcal mol^{-1} for one $LP_{N2} \rightarrow \pi^*_{C3{=}O4}$ interaction in DMU. The magnitude of these values must be handled with care, because a low order perturbation theory treatment of strongly delocalized charge distributions is not appropriate. Nevertheless, their ordering is consistent with the interpretation of occupation numbers of NAOs and NBOs.

The picture drawn by the NAO–NBO approach and the connection to the reported geometries and rotational barriers can be summarized by changing weights of alternative Lewis structures shown in Fig. 2. An increase in electron delocalization indicated by the rising occupancy of the $\pi^*_{C{=}O}$ anti-bond (structure II) corresponds to increasing single bond character of the C=O bond, an increasing double bond character of a C–X bond and a rising negative charge at the carbonyl oxygen. The calculated geometry differences (see Table 1) and rotational barriers (see Table 2) as well as the net atomic charges presented in Table 3 are consistent with this interpretation. Comparing MAC with MAM, the weight of structure II depends on the difference in polarizability between oxygen and nitrogen, which are able to donate different amounts of electrons to the electronegative carbonyl oxygen.

Structure III in Fig. 2 describes electron loss at the acid group of carboxylic acid derivatives. In acetic acid derivatives it may be called hyperconjugation. Its amount is small due to the low polarizability of methyl groups. Considering DMU as substituted MAM, conjugation to the carbonyl group can occur because of the greater polarizability of the introduced MeNH group, which replaces the acetic acid methyl group. Which of the two substituents of a carbonyl group is preferred for delocalization depends on the overall resonance stabilization energy only. From this point of view deviations from planarity of the nitrogen centres of ureas in comparison with amides can be explained by 'competitive resonance' in a general sense. These considerations might be extended to substituent effects on structures of other carboxylic acid amides. For example, they represent another viewpoint for the explanation of a non-planar structure of acetamide as presented in ref. 25. There the calculated geometry and obtained bond orders were explained by interactions between a hydrogen of the acetic acid methyl group and the nitrogen lone pair.

Finally, structure IV in Fig. 2 explains the polarity of the carbonyl group, which is influenced both by electron delocalization from substituents onto the carbonyl group and by electron-withdrawing effects of substituents. The charges of the carbonyl carbon reported in Table 3 can be explained mainly by electronegativities of the X-centres, leading to a decreasing electron density at C3 in the series MAM < MAC < DMU. If one remembers what is known about reactivities of acyl derivatives towards nucleophilic attack at the carbonyl carbon, then the electrophilic property of the carbonyl carbon expressed by its partial charge does not seem to be the source of the inertness of ureas towards such reactions. Similarly the inertness of ureas cannot be explained by the estimation of conjugation of one C1–N2 bond with the C=O group, as this is weaker than in amides. The reactivity of ureas deduced from the results shown here may be explained by (*a*) the high overall resonance stabilization of the reaction centre and (*b*) the high electron densities at electronegative atoms, which have to accept additional electron density introduced by a nucleophile.

Acknowledgements

This work was funded by the Deutsche Forschungsgemeinschaft, DFG-Gz. INK 16/A1-1. We thank Dr Steinke for his kind assistance in using the resources at ZIB.

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Paper 5/08360E
Received 28*th December* 1995
Accepted 19*th March* 1996