J. Am. Chem. Soc. **1991**, *113*, 5895-5896

Grignard or lithium derivatives.[15] Deuteriation can be accomplished smoothly and selectively. Reaction of carbonyl derivatives selectively produced the stereochemically homogeneous homoallylic alcohols.[16]

Acknowledgment. Financial support from the Ministry of Education, Science and Culture of the Japanese Government is gratefully acknowledged.

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(14) A representative experimental procedure for the synthesis of geranyltrimethylsilane is as follows: A mixture of freshly cut lithium (79 mg, 11.4 mmol), anhydrous magnesium chloride (543 mg, 5.70 mmol), and naphthalene (120 mg, 0.94 mmol) in 15 mL of THF was stirred at room temperature for 14 h. To the resulting black suspension of magnesium powder in THF was slowly added a solution of geranyl chloride (350 mg, 2.03 mmol) in THF (2 mL) below -95 °C (internal temperature[6]). After 20 min of stirring, the mixture was treated with a solution of chlorotrimethylsilane (0.25 mL, 2.0 mmol) in THF (1 mL) at -95 °C and stirred for an additional 1 h at this temperature. To the mixture was added a saturated NH_4Cl aqueous solution, and the organic material was extracted with ether. The combined extracts were dried and concentrated, and the product was purified by column chromatography on silica gel (hexane) to give geranyltrimethylsilane (0.033 g, 80% yield); the ratio of both α/γ and E/Z was determined to be >99:1 by GLC analysis.

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Mechanism of Cis-Trans Isomerizations of Amide and Peptide Excited States

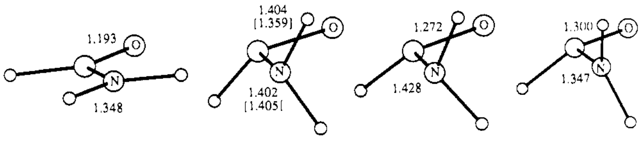
Yi Li,[†] Robin L. Garrell,[*,‡] and K. N. Houk[*,†]

Department of Chemistry and Biochemistry
University of California, Los Angeles
Los Angeles, California 90024-1569
Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

Received January 25, 1991
Revised Manuscript Received May 20, 1991

Peptides and simple amides such as *N*-methylacetamide (NMA) photoisomerize in aqueous solution to the less stable cis isomers during 220-nm ultraviolet resonance Raman (UVRR) experiments.[1,2] This observation has prompted us to reinvestigate the excited states of amides and peptides.[3] NMA in water has a weak $n-\pi^*$ transition at 210 nm and a strong $\pi-\pi^*$ transition at 188 nm.[2] Preresonance Raman enhancement of in-plane amide II and III modes and cis/trans isomerization led to the proposal that the amide $\pi-\pi^*$ excited state resembles the $\pi-\pi^*$ excited state of ethylene, which is known to have a single minimum, twisted 90° relative to the planar ground state.[4,6] However, we have found from ab initio calculations that the excited states of amides have pyramidal carbonyl and amine groups, as well as multiple energy minima.

Geometry optimizations of the singlet and triplet excited states of formamide and NMA were performed with the 6-31G* basis set and the unrestricted Hartree-Fock (UHF) method for triplets or with configuration interaction between all singly excited configurations (CIS).[7a] The molecular orbitals of formamide relevant to this discussion are given in Figure 1.[7b] The three π orbitals are typical of allyl systems. π_2 is concentrated more heavily on N than on O. π_3^* is a slightly perturbed carbonyl π^* orbital. CIS calculations predict the lowest vertical singlet state of formamide to be primarily $n_O-\pi_3^*$ in character. The higher energy $\pi-\pi^*$ singlet is nearly degenerate with a Rydberg transition. These results compare well with experimental assignments[8a] and other calculations.[9]



1 (Ground state) **2** (T_1) **3** (S_1) **4** (S_2)

Geometrical relaxation results in pyramidalization of both the carbonyl and amine groups. The T_1 and S_1 states (**2** and **3**) involve primarily excitation of the carbonyl. The pyramidal carbonyl group is a common feature of $n-\pi^*$ excited carbonyl compounds, and it results from the buildup of electron density on carbon.[10] The stabilizing interaction between the carbonyl and amine present in the ground state[11] now becomes repulsive. Consequently, the amine pyramidalizes, and the system resembles an aminomethyl anion, $R_2NCH_2^-$, in its conformational preferences.[12]

Both the S_1 and T_1 states have several staggered conformers, with rotational barriers of about 5 kcal/mol in S_1 and 3 kcal/mol in T_1. This is much lower than the ground-state barrier of 17-21 kcal/mol.[13] The most stable conformers of both T_1 and S_1 have the amine lone pair situated gauche to the carbonyl π^* orbital density on carbon and also directed away from oxygen, which is a region of high electron density.

The S_2 state, **4**, also has a pyramidal carbonyl group, but the amine group remains planar. The planarity of the amine in S_2 arises from the significant charge transfer from N to the carbonyl group. Consequently, the amine has some radical-cation character and the carbonyl group has some radical-anion character.[14]

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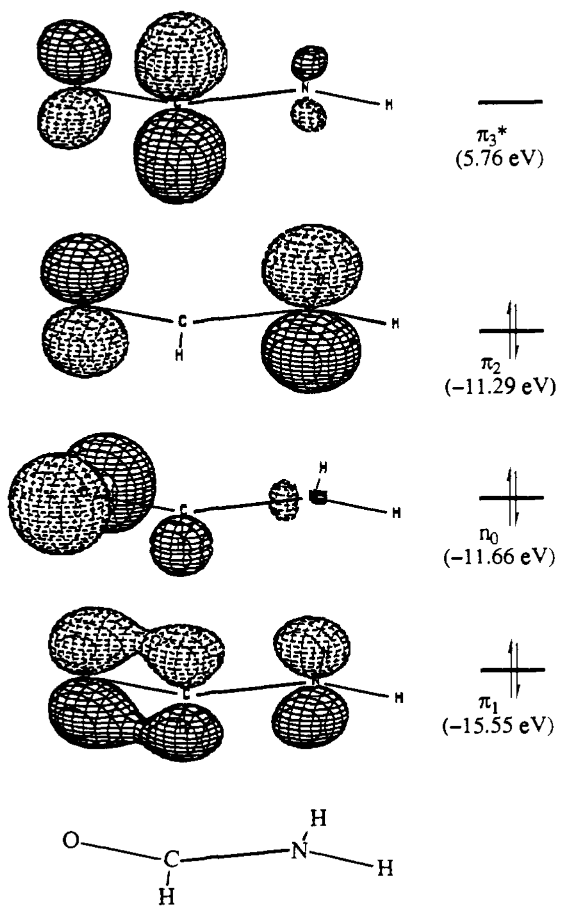

Figure 1. The 6-31G* n, π, and π^* orbitals of formamide.[7b]

The two lowest energy conformers of the S_1, S_2, and T_1 states of NMA are shown in Figure 2. The structures shown on the left side will form readily by relaxation of a vertical excited state of *trans*-NMA. Those on the right side resemble more closely the vertical excited states of *cis*-NMA. There are additional staggered energy minima, which are 4–6 kcal/mol higher in energy. Rotation about the CN bond requires 5–9 kcal/mol, while amine pyramidalization can occur with somewhat lower barriers.[15]

It is likely that cis–trans isomerization of amides occurs by excitation of the trans isomer to either S_1 or S_2, followed by rapid relaxation to the pyramidal and rotated S_1 state. Internal conversion of this state to S_0 or intersystem crossing to T_1 is fast, since no fluorescence is observed.[8] Rotation about the CN bond to form another staggered minimum requires about 5 kcal/mol, and relaxation to T_1 should be competitive with rotation. Isomerization via rotation may occur with higher efficiency in the triplet state, since the rotational barriers are lower, and the lifetime of the triplet should be longer than that of the singlet. Nevertheless, competing intersystem crossing to S_0 must be relatively rapid, since no phosphorescence is observed from amides. When staggered conformers of S_1 or T_1 with gauche methyl groups are formed, such as those on the right side of Figure 2, deactivation to the ground state will give *cis*-NMA.

Because of the significant barriers to rotation in the excited states, quantum yields are expected to be small and to decrease as temperature is lowered. Large substituents will hinder rotation and destabilize the cis excited-state conformers, effectively prohibiting isomerization. By contrast, an excited state with a single alkene-like perpendicular minimum should exhibit a $\Phi_{t\to c} + \Phi_{c\to t}$ of about 1.0, and these quantum yields (Φ) should not be influenced much by substituent bulk.[16]

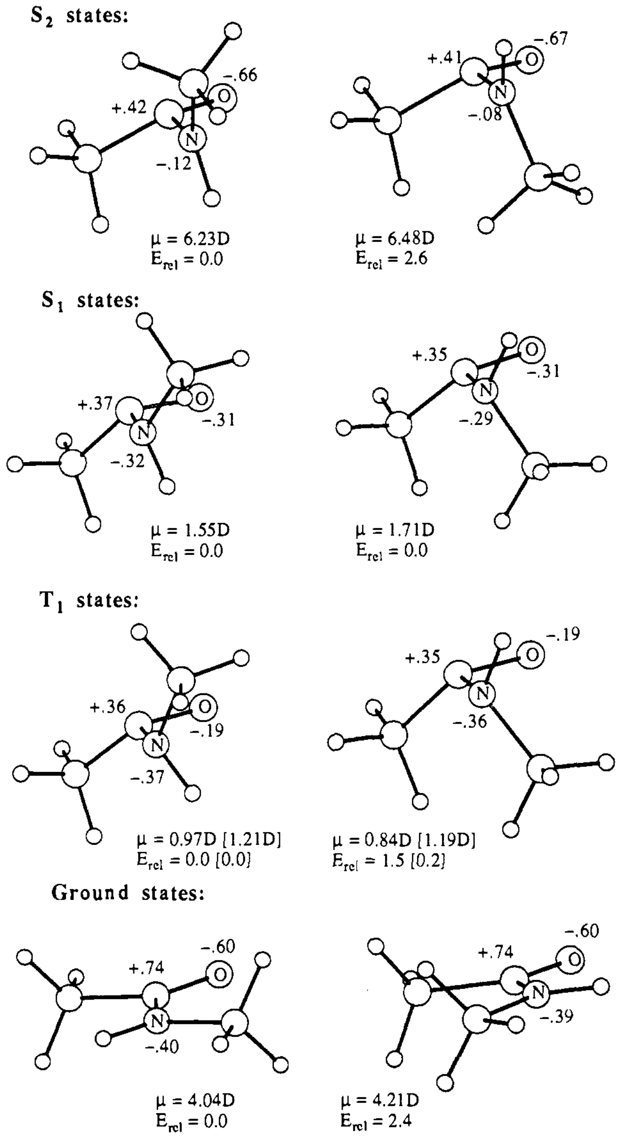

Figure 2. The 6-31G* optimized structures of NMA in the ground and excited states; RHF for the ground states; CIS [or UHF] for the excited states. Relative energies of conformers are given in kcal/mol. Mulliken charges with hydrogens included are given next to heavy atoms.

The geometries of the π^* excited states of the β carbonyl compounds were proposed to differ significantly from that of the π^* excited state of NMA, since a 1394-cm^{-1} band, assigned to amide V torsion, is found in the former.[4] However, we have calculated the geometries of the S_1 and S_2 excited states of (*N*-acetylamino)acetaldehyde (formyl-NMA); the π^* orbital shape and the geometry of the excited states are actually very similar to those of NMA. Computations of the influence of aqueous solvation on the excited states are in progress.

Acknowledgment. We are grateful to the National Institutes of Health (GM-42977 to R.L.G. and GM-36700 to K.N.H.) and the Pittsburgh Supercomputing Center (through National Science Foundation Grant DMR-8451962 to R.L.G.) for financial support of this research.

Supplementary Material Available: Figure 2 with geometry data added (1 page). Ordering information is given on any current masthead page.

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