of active-site-directed irreversible inhibitors of zinc-containing proteases. The stereochemical effect of BEBA in the inactivation action and applications of this novel approach to the design of therapeutically useful inactivators are in progress.

Acknowledgment. We thank the Korea Science and Engineering Foundation and the Ministry of Education, Republic of Korea, for financial support.

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(15) We feel that pseudomechanism-based inactivator is a preferred terminology that properly reflects the mode of the inhibitory action: The oxirane ring of BEBA is *activated not by a chemical change but through coordination with the active-site Zn^{2+}* to form a covalent linkage with the carboxylate of Glu-270 (Figure 1). This inactivator is not an affinity label because the latter would not require such activation.

(16) The feature of the inhibitory mode of BEBA is consistent with the anhydride pathway. An alternative mechanism by which promoted water functions as a nucleophile may also be operational, but in this case no covalent modification of CPA is expected.

Dependence of *p*-*n*-Propylaniline Ionization Potential on Molecular Conformation: Comparison of Experiment with Theory

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Received September 13, 1990
Revised Manuscript Received February 11, 1991

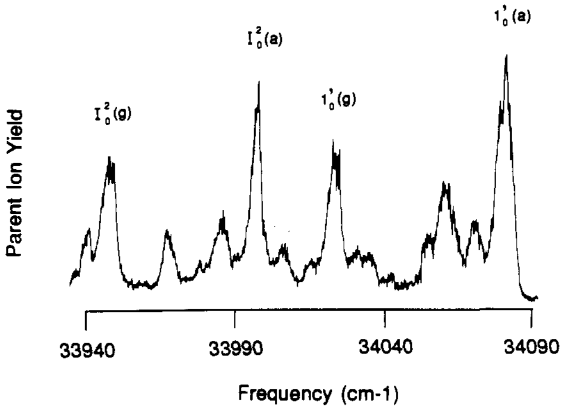


Figure 1. Wavelength dependence of the two-step ionization yield of *p*-*n*-propylaniline as recorded with a time-of-flight mass spectrometer. Peaks correspond to transitions between the vibrationless ground electronic state and various vibronic levels of the $^1B_2$ first excited singlet state of this molecule.

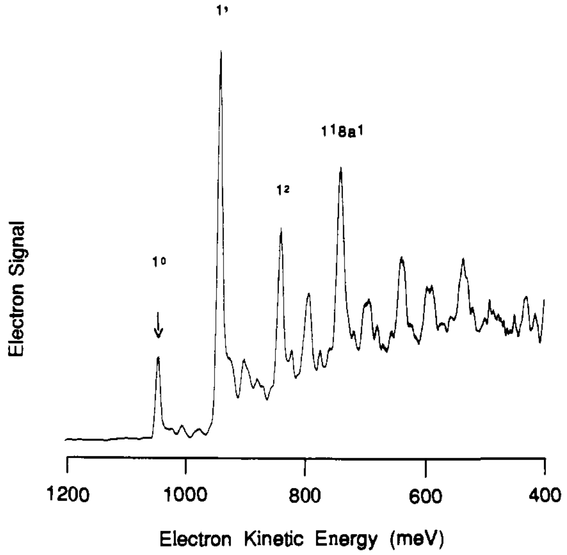
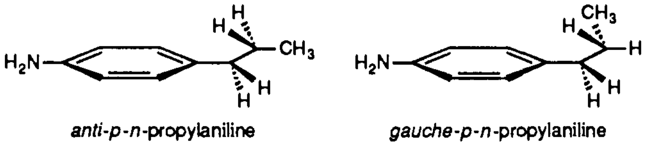


Figure 2. Photoelectron spectrum obtained by exciting the 1_0^1 transition of *anti*-*n*-propylaniline and photoionizing the electronically excited molecules with the same light pulse. Only *anti*-*n*-propylaniline ions are generated. The vertical scale corresponds to electron counts, in arbitrary units. A few ion vibrational assignments are indicated.

Cooling of molecules in supersonic jets often reduces the complexity of electronic spectra sufficiently that contributions from different molecular conformations can be clearly resolved. Some of the earliest cases demonstrating this involved the alkylbenzene and alkylaniline compounds studied by Smalley and co-workers.[1-3] They showed that when the alkyl substituent contains three or more carbon atoms, a splitting of sharp vibronic features occurs. Their generally accepted interpretation was that at least two molecular configurations exist: one with the alkyl chain folded back over the benzene ring and the other with it extended away from the ring. For substituent chains with four or more carbon atoms, further spectral splittings may imply the existence of additional conformations. The electronic spectrum associated with the folded (gauche) configuration is red-shifted relative to that of the extended (anti) configuration.[1-4] Although conventional photoelectron spectra of room temperature molecules exhibit such broadened and unresolved line shapes that conformational variations are barely discernible,[5-8] high resolution laser photoelectron spectroscopy makes it possible to directly measure the slight differences between ionization potentials of molecules in these two conformations. The present study involves gauche and anti conformations of *p*-*n*-propylaniline, which have the following structures:



Our pulsed supersonic beam photoelectron spectrometer, which cools aromatic molecules to approximately 8 K, has been thoroughly described.[9] Laser photoelectron spectra are recorded by exciting a particular vibronic level of a molecule with a pulse of tunable laser light and photoionizing the molecule from that initially selected level. To tune our laser to any desired spectral feature, we record the wavelength dependence of the two-step ionization yield, detecting the positive ions formed using a time-of-flight mass spectrometer. A typical wavelength dependence is displayed in Figure 1. At the low light intensities we used, little ion fragmentation was produced. A few spectral assignments that match those of Powers et al. are indicated in Figure 1. In this notation, X_0^n refers to a transition between the vibrationless ground electronic state and the $v = n$ level of mode

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0002-7863/91/1513-3202$02.50/0

Table I. Propylaniline Spectral Data

transition[a]	freq,[b] cm^{-1}	e^- KE, eV	IP, eV	ΔIP, meV
0_0^0 (g)	33210.2	0.816	7.419	9
0_0^0 (a)	33265.1	0.840	7.410	
1_0^1 (g)	34024.7	1.018	7.419	10
1_0^1 (a)	34081.3	1.042	7.409	
1_0^2 (g)	33948.3	0.999	7.419	9
1_0^2 (a)	33997.9	1.020	7.410	

[a] X_0^n corresponds to a transition between the vibrationless ground electronic state the $v = n$ level of mode X in the excited electronic state. [b] Experimental values of D. E. Powers et al. (ref 3).

X in the excited electronic state. 0_0^0 corresponds to a purely electronic transition involving no vibrationally excited levels. Modes X are labeled with numbers or letters historically associated with aniline.[10] With the frequency-doubled output from a picosecond dye laser tuned to the 1_0^1 transition of *anti-p-n*-propylaniline, the time-of-flight photoelectron spectrum displayed in Figure 2 was recorded. Note that this spectrum is associated with the anti conformation only. Although the largest peak in this spectrum corresponds to production of ions in their 1^1 vibrational level, some ions are formed vibrationally unexcited (peak 1^0). Assignments for most of the peaks in this spectrum have been derived as in our earlier aniline photoelectron study,[11] but only the 1^0 peak is relevant to the present discussion. It is so clearly resolved that a very precise measurement of the adiabatic ionization potential of the molecule in this conformation can be obtained with the relation

$$\mathrm{IP} = 2h\nu - \mathrm{KE}_{\mathrm{electron}}$$

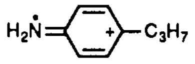
Photoelectron spectra similar to that displayed in Figure 2 were also recorded by exciting two other transitions of anti propylaniline along with corresponding gauche transitions. The first peak in each of these spectra corresponds to production of vibrationally unexcited ions and allows us to directly measure the adiabatic ionization potential for each conformation. As summarized in Table I, the difference between these ionization potentials is 9–10 meV, which is approximately 0.2 kcal/mol. Because we did not calibrate our spectrometer with a standard, the absolute accuracy of our ionization potential measurement is only ±40 meV. However, the differences between ionization potentials should be accurate to ±1 meV.

Theoretical ground-state conformations of propylaniline were estimated by AM1 calculations.[12] For the anti compound the three propyl carbons lie in a plane perpendicular to the aromatic ring. For the gauche compound the end carbon lies 73° on either side of that plane. Other orientations of the alkyl chain relative to the ring should be much higher in energy because of steric effects. At each conformation, STO-3G RHFSCF computations were performed to give relative energies. The ground state of the anti compound was calculated to be 45 meV (360 cm^{-1}, 1.0 kcal/mol) lower in energy than that of the gauche. Vertical ionization potentials were estimated by single-excitation configuration interactions for the ion. Although the absolute values obtained for the anti and gauche conformations, 4.637 and 4.658 eV, respectively, varied substantially from the experimental results indicated in Table I, their relative spacing of 21 meV was remarkably close to the experimentally measured 9–10 meV. Relative energies and IP's for rotational conformers should be fairly insensitive to electron correlation. There will be corrections for geometry relaxation in the ion, zero point energy changes, and basis set improvements. Although better calculations will be done, carbocation studies at this level of theory have produced the correct trends in stabilization energies.[13]

If we assume that interconversion of different molecular conformations is slow compared with the supersonic jet expansion process then the ratios of gauche and anti peaks in excitation spectra provide a measure of the relative abundance of the two conformations at the temperature of the stagnation zone of the nozzle. This in turn leads to an estimate of the relative energies of the two conformations. Because there are two equivalent gauche conformations for each anti conformation, the ratio of their absorptions should be given by

$$I_g/I_a = 2\exp[-\Delta E/kT]$$

Powers et al. found that anti propylaniline transitions are roughly 1.5 times more intense than their gauche counterparts. Our data displayed in Figure 1 are in basic agreement with this. For a gas sample temperature of 343 K, this implies that the anti conformation is approximately 260 cm^{-1} (0.74 kcal/mol) lower in energy than the gauche. This is in reasonable agreement with the 360-cm^{-1} result obtained by calculation. It seems clear that the lower steric repulsion of the anti compound stabilizes it relative to the gauche conformer. This repulsive interaction between the alkyl chain and the ring is apparently magnified in the ion. Hyperconjugation stabilizes the important carbocation resonance structure



more when the propyl group is in an anti rather than gauche orientation.

In conclusion, we have demonstrated that ionization potentials of two differing molecular conformations of *n*-propylaniline can be precisely measured and thereby easily distinguished with laser photoelectron spectroscopy. Hartree–Fock calculations lead to remarkably accurate relative energies for the ground and ionic states of these conformations in contrast with their estimates for the absolute energies of these states. Future experiments and calculations will focus on aromatic compounds having somewhat longer side chains and a correspondingly larger number of stable conformations.

Acknowledgment. This work was supported by the National Science Foundation.

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Halocarbonyl Cations[†,1]

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Received January 10, 1991

Even though alkyl acylium ions (acyl cations) have been prepared and characterized under long-lived stable ion conditions in solution as well as in the solid state,[2] the corresponding halocarbonyl cations, XCO^+ (**2** X = F, Cl, Br, I) have not been observed. The acylium cation structures **1** are rationalized by the contributions from resonance hybrids of the oxocarbenium ion **1a** and oxonium ion **1b** forms, with the latter being the dominant contributor. In halocarbonyl cation **2** an additional resonance interaction involving a halogen nonbonded electron pair (structure **2c**) is possible (back-donation, p–p interaction).

[†] Dedicated to Professor Horst Prinzbach on the occasion of his 60th birthday.

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