Trans-annular Interactions in Morpholines: A Photoelectron Spectroscopic Study

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Received 2 May 1994

ABSTRACT

The He I and He II photoelectron spectra of 4-methylmorpholine, 4-morpholinecarbonitrile, and 4-morpholinepropionitrile have been measured. The electronic structure and heteroatom lone pair interactions, in particular, were analyzed with the aid of HeII/ HeI intensity variations, comparison with the spectra of related compounds, and AM1 semiempirical calculations. We present an example of combined inductive and resonance interactions operating in the morpholine ring system.

INTRODUCTION

Chemical reactivity of organic compounds can be rationalized (to a large extent) from the knowledge of functional groups present in the molecule. When several functional groups (substituents) are present, the possibility of mutual interaction (perturbation) arises. Such electronic structure perturbation has usually been treated on two levels: 1,2-interactions taking place between neighboring atoms [1] and proximity effects encompassing all $\geq$1,3-interactions [2]. UV photoelectron spectroscopy (UPS) can be used to probe the magnitude of interactions and perturbations, but often only ionization energy differences (ΔE_i) between interact-

ing functional group orbitals are considered. Additional insight which may be obtained from HeII/ HeI intensity variations and bandwidths is often not included in the final analysis. The purpose of this article is to study the propagation of the substituent effect of an N-cyano group across the morpholine ring.

EXPERIMENTAL

He I and He II photoelectron spectra were measured on a Vacuum Generators UV-G3 photoelectron spectrometer. The sample compounds were of commercial origin (Aldrich, purity >98%) and used without further purification. No hydrolysis or decomposition products were observed in the spectra. The resolution of HeI and HeII spectra was 25–30 meV and 50 meV, respectively. The sample inlet temperatures for 4-morpholinepropionitrile and 4-morpholinecarbonitrile were 120 and 110°C, respectively. The spectral calibration was achieved by adding small amounts of N_2 and Ar gas to the sample flow. AM1 calculations made use of the standard MOPAC 6 program, with full geometry optimization being performed during calculations. The optimization converged to the chair conformation with the N-substituent in the equatorial position. This conformation is preferred, as the dielectric constant measurements show [3].

RESULTS AND DISCUSSION

The He I and He II photoelectron spectra of 4-methylmorpholine (1), 4-morpholinecarbonitrile (2), and 4-morpholinepropionitrile (3) are shown in Figure 1. 1st, 2nd, and 3rd ionization bands are

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Dedicated to Prof. Shigeru Oae on the occasion of his seventy-fifth birthday.
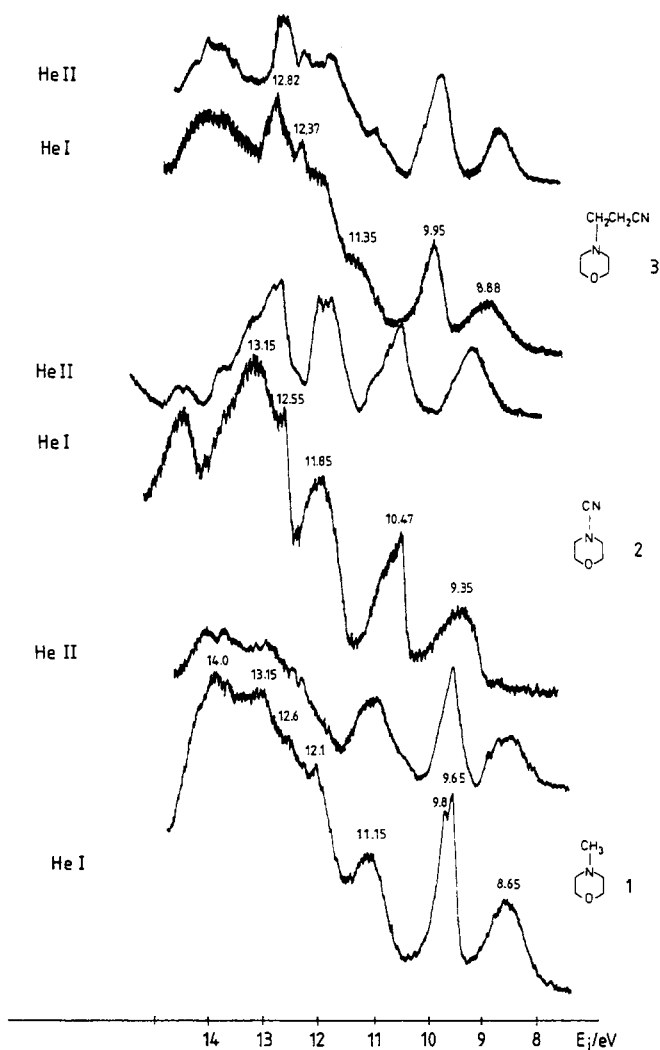
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FIGURE 1 He I and He II photoelectron spectra of morpholines.

FIGURE 2 Experimental energy level diagram for morpholines and alkyl cyanides.

clearly resolved in all the spectra, and their assignment may be obtained by comparison with the spectral assignment for morpholines [4,5] and AM1 calculations. 1st, 2nd, and 3rd bands correspond to ionization from nitrogen (n_N, a'), oxygen (π_O, a'), and oxygen (σ_O, a'') lone pairs, respectively (Figure 2). The sharpness of the 2nd band is a further indication of its pronounced oxygen lone pair character. We assumed C_s molecular symmetry in the analysis. 1 and 3 can be considered as reference compounds against which the influence of the–CN group in 2 may be assessed. The following trends are noticeable in Figures 1 and 2.

There is a pronounced increase of ionization energies in the sequence 4-methylmorpholine, 4-morpholinepropionitrile, and 4-morpholinecarbonitrile. The increase is uniform for all bands; 1st–2nd and 2nd–3rd band energy separations remain virtually unchanged.
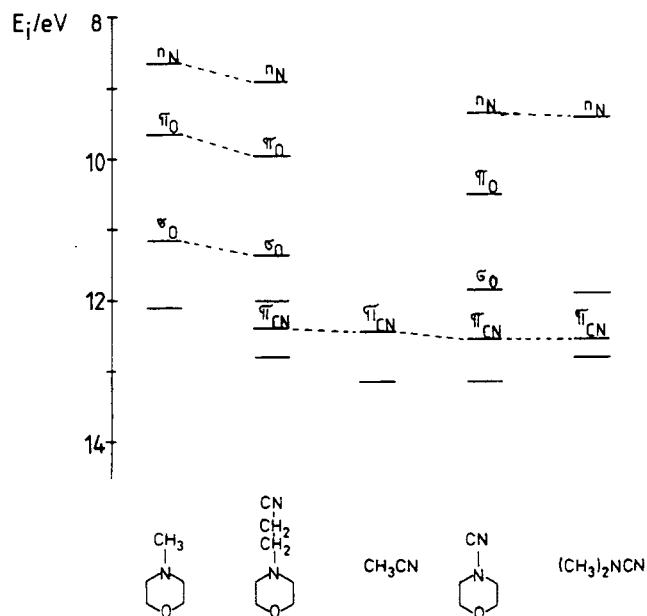
The ratio of 1st/2nd band intensity changes significantly on going from He I to He II excitation in the spectrum of 2. Also, the 2nd band profile broadens (when compared to the spectrum of 1), presumably indicating a geometry change during transition from the molecular to the cationic electronic state. The numerical data, related to these comments, are given in Table I.

When analyzing He I/He II intensities, it must be recalled that calculated He II/He I photoionization cross-sectional ratios for C2p, N2p, and O2p orbitals are 0.306, 0.449, and 0.639, respectively [6]. The π_O band, which decreases in relative intensity (on going from He I to He II), must have acquired additional C2p or N2p character. The broadening of the 2nd band's profile and He II/He I intensity variations both suggest a change in π_O character,

TABLE 1 Normalized Band Intensities and Widths for 1–3

| Molecule | Band | Relative Intensity | | Width (FWHM/eV; He I) |
		He I	He II	
1	1st	1.00	1.0	0.7
	2nd	1.17	1.28	0.35
	3rd	0.60	1.12	0.6
2	1st	1.00	1.00	0.85
	2nd	1.22	0.96	0.55
	3rd	2.01	1.56	0.75
3	1st	1.00	1.00	0.8
	2nd	1.36	1.22	0.4

which is brought about by through-bond interactions between N and O lone pairs. Such through-bond (trans-annular) interactions are facilitated by a molecular conformation whose "zig-zag" σ skeleton is a good conductor for this type of intermolecular interaction.

In **3**, the sole influence of a distant–CN group on the morpholine ring appears to be inductive, because the manifold of the first three bands is shifted to higher E_i (compared to the spectrum of **1**) without concomitant changes in band contours or He II/He I intensity variation.

The spectrum of **2** is interesting, not so much because of a strong E_i shift (which can at any rate be expected from the nearby–CN group), but because of the effect on the 2nd band. One must remember that, in the original assignment, the 2nd band corresponded to an oxygen lone pair ionization. The conclusion which follows is that the–CN group effect is strongly felt at the oxygen atom (presumably via intervening σ ring orbitals). This through-bond interaction between lone pairs at N and O atoms is supported by the results of AM1 calculation based on Koopmans' approximation. AM1 calculations are not given explicitly, however, because they do not add anything new to the empirical analyses, except confirming it.

Uniform E_i increase in **1–3** suggests a description in terms of a simple inductive effect: the closer the–CN group gets to the ring heteroatoms, the higher their E_i's become. Careful additional measurements of He II/He I intensities and band contours reveal that this picture is too simplistic. 1,2-(Truly inductive) and 1,4-(through-bond) interactions appear to be present, mimicking a simple inductive effect.

Very few photoelectron studies of morpholines with unsaturated acyclic substituents have been reported. Rademacher et al. [7] performed a UPS study of 4-butadiynylmorpholine and observed a strong interaction between butadiyne π and morpholine n_N orbitals of suitable symmetry. Their interpretation relied on observed E_i shifts and MNDO calculations to confirm the strength of the interactions.

Assignment of substituent, π_{CN} ionizations is tentatively given in Figure 2 on the basis of comparison with assigned spectra [8,9] of CH_3CN and $(CH_3)_2NCN$. Two final observations may be of interest concerning the morpholines. Compound **2** will probably have small gas-phase basicity (due to its high HOMO E_i) and ring inversion barrier. The reason for the latter assertion is that the height of the barrier in saturated six-membered rings decreases upon exocyclic conjugation [10].

In conclusion, we wish to emphasize the well-known, but often disregarded, caveat: inductive and resonance effects are separable only within the limits of a theoretical model. What appears to be an inductive effect is shown (after additional measurements of bandwidths and HeII intensities) to be an interplay of the two.

ACKNOWLEDGMENT

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