Conformations of Acetanilide and Related Compounds Studied by Ultraviolet Photoelectron Spectroscopy

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(Received October 19, 1979)

Conformations of acetanilides were studied by UPS in the vapour phase. The dihedral angle, θ, between the amide group and the phenyl group was evaluated from the difference in the vertical ionization energy, ΔE_{1v}, between the two MO's, the anti-bonding and bonding type combinations of the benzene ring $e_{1g}(S)$ orbital and the highest occupied π orbital of the amide group. The steric inhibition of conjugation due to N-methylation is larger than that due to ortho-methylation. For this series of compounds, ΔE_{1v} is directly proportional to $\cos\theta$ and this simple relationship is useful for the rough estimation of θ.

Ultraviolet photoelectron spectroscopy (UPS) is useful for the study of conformations of rather large molecules in the vapour phase. UPS has hitherto been used for the investigation of steric hindrance effects upon the conformations of various aromatic compounds such as nitrobenzenes, anilines, biphenyls, phenylethylenes, and so forth.[1-5] In this paper we report the conformations of some gaseous acetanilides studied by UPS, comparing the conformational data in the vapour phase with those in the crystalline state obtained by the X-ray diffraction method.

Experimental

The compounds studied are as follows: acetanilide (**1**), *o*-methylacetanilide (**2**), *N*-methylacetanilide (**3**), *N,o*-dimethylacetanilide (**4**), *N,2',6'*-trimethylacetanilide (**5**), and oxindole (**6**).
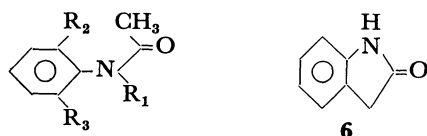
1: $R_1=R_2=R_3=H$
2: $R_1=R_2=H$, $R_3=CH_3$
3: $R_1=CH_3$, $R_2=R_3=H$
4: $R_1=R_2=CH_3$, $R_3=H$
5: $R_1=R_2=R_3=CH_3$

The photoelectron spectra of these compounds were measured with the photoelectron spectrometer described previously,[1] the 21.22 eV He I resonance line being used as the excitation source.

Results and Discussion

The photoelectron spectra of acetanilide and related compounds were measured with the results shown in Fig. 1. The vertical ionization energies, E_{1v}, derived from the spectra are listed in Table 1. In the region of 8—11 eV, the spectra of **1**, **2**, **3**, **4**, and **6** consist of four bands: two bands correspond to the two molecular orbitals, $\pi_-(S)$ and $\pi_+(S)$, which are interpreted approximately to be brought about by the antibonding and bonding type combinations of the benzene ring
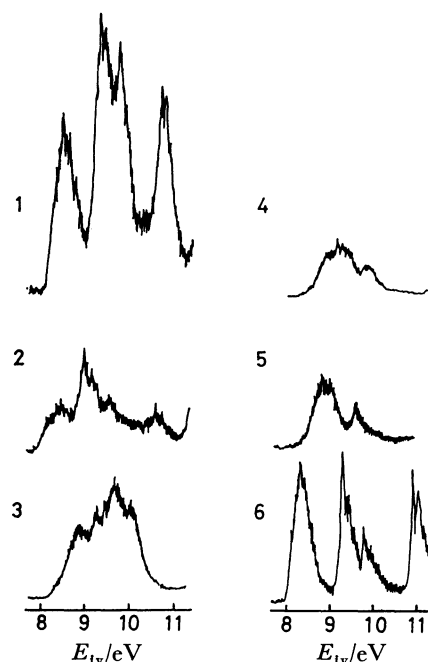
Fig. 1. Photoelectron spectra of acetanilide and related compounds.
1: Acetanilide, 2: *o*-methylacetanilide,
3: *N*-methylacetanilide, 4: *N,o*-dimethylacetanilide,
5: *N,2',6'*-trimethylacetanilide, 6: oxindole.

TABLE 1. VERTICAL IONIZATION ENERGIES

Compound	E_{1v}/eV			
	$\pi_-(S)$	$\pi(A)$	$\pi_+(S)$	$n(O)$
1	8.46	9.35	10.75	9.70
2	8.34	8.92	10.59	9.51
3	8.81	9.28	10.02	9.68
4	8.82	9.08	9.39	9.79
5	8.8		9.0	9.64
6	8.36	9.32	10.86	9.79

$e_{1g}(S)$ orbital and the highest occupied π orbital of the acetylamino group; the other two bands correspond to the a_2-like MO, $\pi(A)$, derived from the benzene ring $e_{1g}(A)$ orbital and to the non-bonding orbital of the carbonyl oxygen, $n(O)$.

The assignments of $\pi_-(S)$, $\pi_+(S)$, $\pi(A)$, and $n(O)$

bands of **1**, **2**, **3**, **4**, and **6** were made on the basis of the previous interpretation of the photoelectron spectra of anilines[1] and aliphatic amides.[6] The result is given in Table 1. The assignments of π(A) and n(O) bands were supported by the methyl substituent effect. Ortho-methylation is expected to decrease the ionization energy of π(A) MO, while N-methylation may have little effect on the value. The ionization energies of the n(O) MO's of **1**, **2**, **3**, **4**, and **6** are expected to vary only slightly by the alkylation on the ortho-position of the ring or on the nitrogen atom and to have the values similar to those of aliphatic amides, *i.e.*, 9.5—10 eV.[6] Comparative consideration of the E_{iv} values between **1** and **2** and between **1** and **3** leads us to the assignment given in Table 1. The UPS bands of the other compounds were assigned in a similar manner. In all cases except for **5** (see the later discussion) the first bands correspond to the ionization from the π_-(S) MOs.

The ionization energy difference between the π_+(S) and π_-(S) bands of acetanilides, $\Delta E_{iv}[\pi_+$(S), π_-(S)], is approximately given by the following equation[2] (the two-orbital model):

$$\Delta E_{iv}[\pi_+(S), \pi_-(S)] = E_{iv}[\pi_+(S)] - E_{iv}[\pi_-(S)]$$
$$= [(A_{Am} - A_{Ph})^2 + 4B_\theta^2]^{1/2}, \quad (1)$$

where $A_{Am} = \langle \psi_{Am}|H|\psi_{Am}\rangle$,

               $A_{Ph} = \langle \psi_{Ph}|H|\psi_{Ph}\rangle$,

and $B_\theta = \langle \psi_{Am}|H|\psi_{Ph}\rangle$.

ψ_{Am} and ψ_{Ph} are the wave functions of the acetylamino (Am) and phenyl (Ph) moieties, respectively, and A_{Am} and A_{Ph} are set equal to the negative of the first E_{iv}'s of the corresponding N-methylated acetamides[6] and those of the benzenoid molecules,[1b] respectively. The off-diagonal element, B_θ, depends on the dihedral angle, θ, between both moieties and is assumed to be represented by the following relation: $B_\theta = B\cos\theta$ where B is the matrix element for the completely planar molecule, oxindole ($\theta = 0°$). The dihedral angles evaluated by putting the numerical values into Eq. 1 are listed in Table 2 together with the ΔE_{iv} values.

In the case of the trimethylated anilide, **5**, the assignment of the first UPS band around 9 eV was not unambiguous because of the considerable overlap of the π_-(S), π(A), and π_+(S) bands. If the first peak is of π(A) nature, as for m-xylene,[7] the dihedral angle should be very close to 90°, and if it is attributed to the π_-(S) MO, the dihedral angle is calculated to be 85°. In either case the dihedral angle is surely larger than that of the dimethylated anilide, **4**.

The enhancement of non-planarity by N-methylation was also found by means of the X-ray crystal analysis technique.[8] In the crystalline phase the dihedral angles of **1** and **3** were reported to be 17.6°[8a] and 90°,[8b] respectively. It is interesting to note that the twisting of the amide group in **3** is not so extreme in the vapour phase as in the solid state, while those of **1** in both phases are comparable to each other.

From Table 2, it is concluded that N-methylation causes more drastic steric inhibition of conjugation than ortho-substitution. By considering the conformational change induced by N-methylation, the conspicuous

TABLE 2. DIFFERENCE IN IONIZATION ENERGIES, ΔE_{iv}, AND DIHEDRAL ANGLES, θ

Compound	ΔE_{iv}/ eV[a]	θ/° (gas)[b]	θ/° (crystal)[c]
Acetanilide (**1**)	2.29	23	17.6
o-Methylacetanilide (**2**)	2.25	27	
N-Methylacetanilide (**3**)	1.21	60	90
2′,6′-Dimethylacetanilide	1.10[d]	69	
N,o-Dimethylacetanilide (**4**)	0.57	77	
$N,2',6'$-Trimethylacetanilide (**5**)	(0.2)	85—90	
Oxindole (**6**)	2.50	0	

a) Experimental error of ± 0.05 eV. b) Uncertainty of $\pm 3°$ is estimated for θ values from the error of ΔE_{iv}. Numerical values used in the calculation of the dihedral angles were as follows: $A_{Am} = -9.68$ eV for the secondary amides, **1**, **2**, and **6**, $A_{Am} = -9.09$ eV for the tertiary amides, **3**, **4**, and **5**,[6] $A_{Ph} = -9.23$ eV for the benzene derivatives, **1** and **3**, $A_{Ph} = -9.13$ eV for the toluene derivatives, **2**, **4**, and **6**, and $A_{Ph} = -9.03$ eV for the m-xylene derivative, **5**.[1b] A virtual MO for toluene which results in the formation of acetanilide derivatives is estimated to have an orbital energy of -9.13 eV, which is the negative of the average ionization energy of the corresponding MO's for benzene and m-xylene: the benzene e_{1g} π orbital with E_{iv} of 9.23 eV and the m-xylene b_1 π orbital with E_{iv} of 9.03 eV.[1b] This averaging procedure is based on the additive nature of the methyl substituent effect on the lower π ionization energies of benzenes (see, for example, Ref. 1b). c) Determined by means of the X-ray diffraction[8]. d) From Ref. 5.
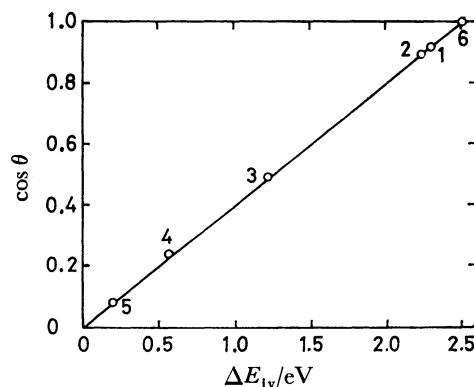

Fig. 2. Plot of $\cos\theta$ against the difference in ionization energy, $\Delta E_{iv}[\pi_+$(S), π_-(S)].

hypsochromic effect observed for the N-methylated anilides, **3** and **4**, can be explained in terms of reduced π conjugation.[9]

Finally, the $\cos\theta$'s estimated for the vapour phase are plotted against $\Delta E_{iv}[\pi_+$(S), π_-(S)]'s in Fig. 2. The plotted points fall on a straight line passing through the origin. This is because the $(A_{Am} - A_{Ph})$ term values in Eq. 1 are small for the compounds studied here. The linear relation in Fig. 2 may be useful for the rough estimation of the dihedral angles in acetanilides.

We are indebted to Dr. Michio Kondo, Central Research Laboratories, Sankyo Co. Ltd., for his kindness in giving us $N,2',6'$-trimethylacetanilide.

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