

Evidence for Amide Resonance observed in Cyclic *N*-Ammonio-imidates by X-Ray Photoelectron Spectroscopy

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Novel evidence for amide resonance of cyclic *N*-ammonio-imidates was found by means of X-ray photoelectron spectroscopy; the C 1s binding energy of the carbonyl group attached to the ylidic nitrogen is different from that of the ester group.

One of the stabilizing factors of carbonyl-stabilized ylides containing nitrogen is the amide resonance effect, in which an electron on the anionic nitrogen atom is delocalized into the π orbital of the carbonyl group. Amide resonance has been confirmed by means of i.r. spectroscopy;¹ the frequencies $\nu(\text{C}=\text{O})$ of the carbonyl group of ylides are much lower than those of the corresponding salts, and this is explained by a reduced contribution of the $\text{C}=\text{O}$ doubly bonded structure (I), and an increased contribution of structure (II). The i.r.

evidence for amide resonance is based on the strength of the bond between the carbon and oxygen atoms, which is a reflection of the electron density along the bond. It is also possible to obtain evidence for amide resonance from the electron density on the carbon atom which may be determined by means of X-ray photoelectron spectroscopy (X.P.S.).² This method gives more distinct evidence of amide resonance.

We previously investigated the stabilization effect in cyclic *N*-ammonio-imidates and clarified the importance of the

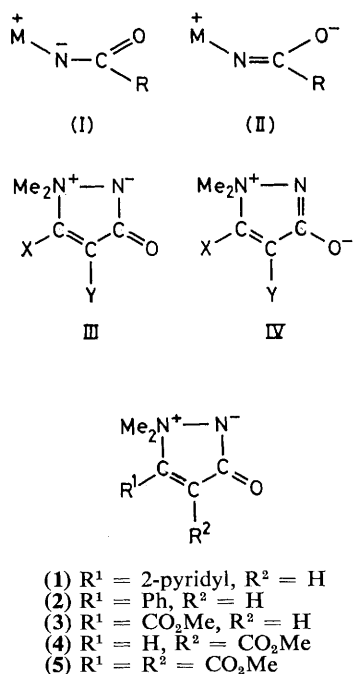


Table 1. Ratios of the height of the C 1s main peak to that of the C 1s shoulder peak and their differences (ΔE) in the *N*-ammonio-imidates (1)–(5).

<i>N</i> -Ammonio-imidate	Ratio	$\Delta E/eV$
(1)	No shoulder	—
(2)	No shoulder	—
(3)	9.5:2.0	3.4
(4)	9.0:1.5	3.3
(5)	9.0:4.0	3.3

electron displacement effect.³ It was also shown that amide resonance is one of the factors leading to the stabilization, because there is a good correlation between $\nu(C=O)$ and the N 1s binding energy determined by X.P.S. We have now found further new evidence from the measurements of C 1s spectra of cyclic *N*-ammonio-imidates.

The cyclic *N*-ammonio-imidates used in this experiment were prepared by published methods.⁴ X.P.S. spectra were determined using a JASCO ESCA-1 photoelectron spectrometer and powder samples were ground by an agate mortar and dispersed on double-sided sticky tape. Representative C 1s spectra of the cyclic *N*-ammonio-imidates are shown in Figure 1 and the binding energies are summarized in Table 1. The cyclic *N*-ammonio-imidates (1) and (2) in this study have only one type of carbonyl group, whereas (3)–(5) have two types: one is directly attached to the ylidic nitrogen (N^-) and the other is part of the ester group; only the former participates in amide resonance. The C 1s signals for compounds (1) and (2) containing only the carbonyl group showing amide resonance are single peaks, whereas compounds (3)–(5) with the two types of carbonyl group show a shoulder peak on the higher binding energy side. The intensity of the shoulder peak for compound (5) having two ester groups is greater than for compounds (3) and (4) with one. Hence, the shoulder peak for compounds (3)–(5) is assigned to the carbon atom of the carbonyl group of the ester group. As compounds (1) and (2) which do not have ester groups give a single C 1s line, the C 1s peak of the carbon atom of the carbonyl

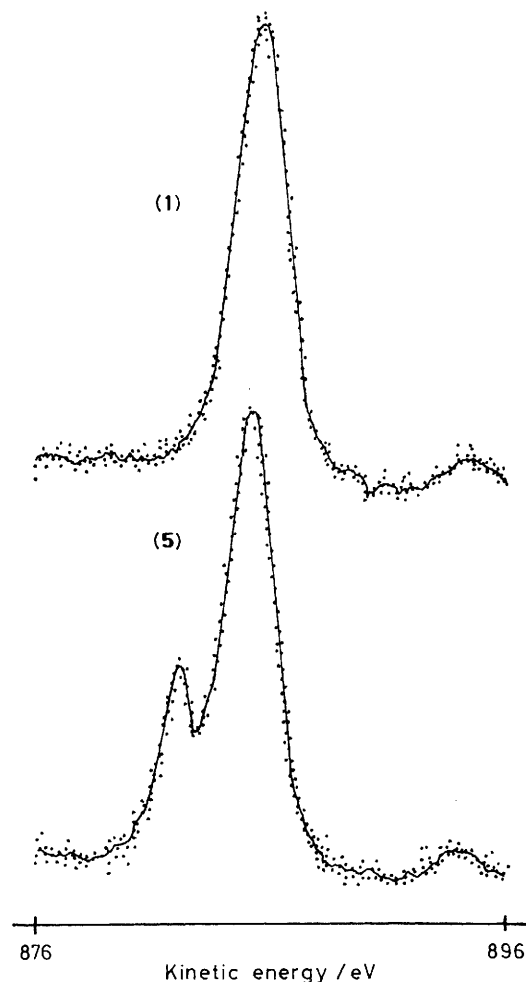


Figure 1. C 1s Spectra of the *N*-ammonio-imidates (1) and (5).

group showing amide resonance must be incorporated in the C 1s peaks of the other carbon atoms in the *N*-ammonio-imidate and impurities. The carbon atom of the carbonyl group participating in amide resonance is presumably almost neutral, as shown in canonical structures (III) and (IV). This is very different from the ester carbonyl group, in which the carbon atom bears a positive charge owing to the difference in the electronegativities of carbon and oxygen. The C 1s X.P.S. results thus may be explained by the neutrality of the carbon atom of the carbonyl group owing to amide resonance, thus providing distinct evidence for amide resonance in these compounds.

Received, 11th May 1982; Com. 528

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