On the Nature of Nitrogen–Nitrogen Bonding in Cyclic Aminimides

Shinji Tsuchiya * and Manabu Senō
Institute of Industrial Science, University of Tokyo, 7-22-1, Roppongi, Minato-Ku, Tokyo 106, Japan
Walter Lwowski
Department of Chemistry, New Mexico State University, Las Cruces, New Mexico 88003, U.S.A.

The bonding character of cyclic aminimides has been studied by *X*-ray photoelectron spectroscopy (XPS). The electron density on the quaternary nitrogen atom of cyclic aminimides is much higher than that of the corresponding salts, and the differences $\Delta(N^+-N^-)$ between the nitrogen 1*s* binding energies of the quaternary nitrogen(N^+) and the anionic nitrogen(N^-) are smaller than those in open-chain aminimides. These results indicate that the cyclic aminimides are considerably stabilized by displacements of σ electrons in the N–N bond toward the quaternary nitrogen. XPS and i.r. data also show the stabilization of the cyclic aminimides by amide resonance.

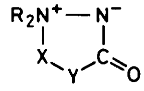
One of the more interesting aspects of the ylid bond is the mix between σ bonding, the coulombic interaction between the cationic and the anionic atoms, and d_π–p_π multi-bonding, and any other factors that might contribute to the nature of bonding of the ylid. Electrostatic stabilizing effects by coulombic interaction have been presented as the primary reason for the stability of ylids in which *d*-orbitals are not available.[1] We presented earlier another stabilizing effect in N–N ylids (commonly called aminimides).[2] This new stabilizing effect, found through *X*-ray photoelectron spectroscopic (XPS) measurements, is the displacements of bonding electrons between the two nitrogen atoms (N^+ and N^-), so that the σ electron cloud lies closer to the quaternary than to the anionic nitrogen atom.[2] This effect seems to be particularly important for the stabilization of ylids in which no *d*-orbitals are available for d_π–p_π multi-bondings. The cyclic aminimides used in this study are well suited for investigating the electron displacement effect in that only σ bonds are involved. XPS is also a suitable method by which to probe the electronic structure of ylids.[3,4] As our ylids contain two or three different kinds of nitrogen atom, two of which form the ylid bond, the XPS spectrum of the nitrogen 1*s* binding energies should show two or three peaks, and the energy differences between them should give the desired information.

A strong interaction between N^+ and N^- is expected for cyclic aminimides, since the interaction of the anionic nitrogen with the carbonyl group in the 3-position should be reduced, due to the deviation of the bond angle from the *ca.* 120° presumably present in the open-chain aminimides. Cyclic aminimides with carbonyl groups in both the 3- and 5-positions are quite stable and do not behave like other compounds containing a $-CO-N^+-$ linkage, but this stability disappears when the negative charge on N-2 is removed, upon which the molecules become strong alkylating agents.[5] This is in accord with partial neutralization of the positive charge on the quaternary nitrogen atom, presumably by the shift of electron density towards N^+, as described above.

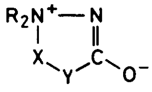
In this paper we report XPS and i.r. data for cyclic aminimides, all containing a carbonyl group adjacent to the anionic nitrogen atom, and we discuss the stabilizing factors and the nature of the bonding in these cyclic aminimides.

Results and Discussion

Methods for determining the binding energies in samples of insulating solids were described earlier.[2] Data using the difference in nitrogen 1*s* binding energy between nitrogen peaks in this paper are very accurate, because these values are not affected by surface potentials or the methods of sampling.



(IA)



(IB)

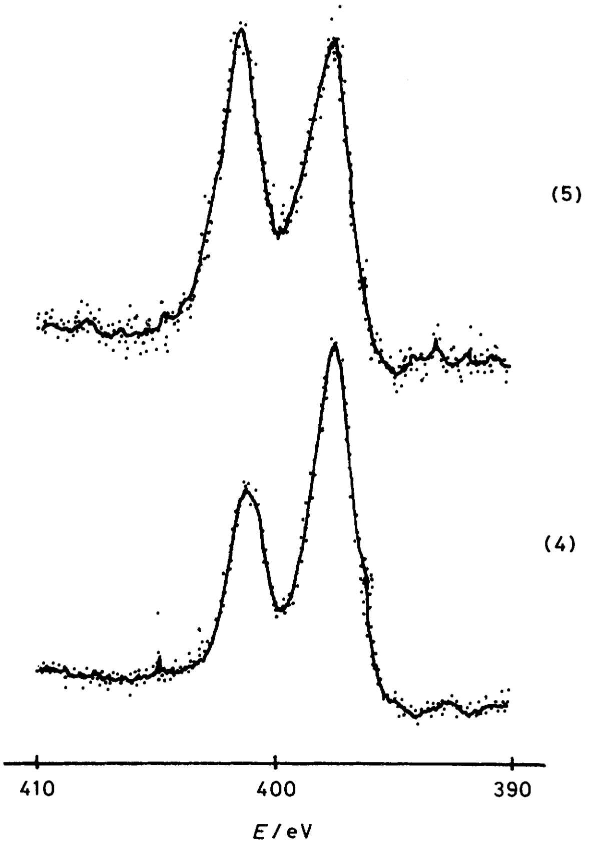
Thus, the electronic structure of the aminimides is discussed mainly in terms of the differences $\Delta(N^+-N^-)$ of the peaks for N^+ and N^- and those of uncharged nitrogen atoms in otherwise comparable structures. When the differences cannot be used, nitrogen 1*s* binding energies are referenced to the carbon 1*s* values of 284 eV.

The resonance structures (IA and B) are to be considered for these cyclic aminimides. The delocalization of electrons shown in (IB) will certainly contribute greatly to the stability of the aminimides,[6] but the displacements of bonding electrons in the N–N σ bonding might also be significant, and is explored here.

Typical spectra of cyclic aminimides are shown in the Figure. The peaks due to N^+ and N^- are separated clearly, and the aminimide (5), which contains just two nitrogen atoms, gives two peaks of equal height, each with a peak width at half-height of 1.5 eV, indicating one kind of nitrogen atom. On the other hand, the aminimide (4) contains three kinds of nitrogen atoms, bearing positive, negative, and no charge, respectively. The nitrogen 1*s* spectrum of (4) is different from that of (5); it shows a larger peak with a shoulder at lower binding energy and a peak width at half-height of 2.2 eV. This peak results from two overlapping peaks, those due to N^- and the nitrogen atom in the pyridyl substituent. The peak at higher binding energy is due to N^+. As shown in these examples, we can gain information about the electronic structure of aminimides by XPS, though we have to consider the contributions of the Madelung potentials and the reorganization energies.

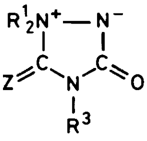
The nitrogen 1*s* binding energies of the cyclic aminimides are summarized in Table 1. Table 2 contains the differences $\Delta(N^+-N^-)$. As a correlation between the binding energy and the formal charge of the atom is established, $\Delta(N^+-N^-)$ can be regarded as a measure of the polarity of the cyclic aminimides. Our cyclic aminimides fall into two classes. Those of class (A) have three nitrogen atoms in the five-membered ring, in positions 1, 2, and 4. Those of class (B) have nitrogen atoms in the 1- and 2-positions (aminimide function) and a C=C double bond between positions 4 and 5, conjugated with the carbonyl group in the 3-position.

For comparison, Table 3 shows XPS and i.r. data of open-

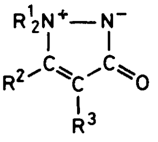


Nitrogen 1*s* spectra of cyclic aminimides (4) and (5)

Class (A)

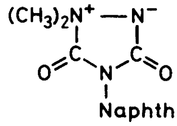
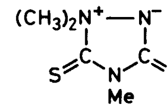
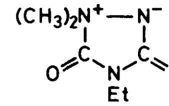
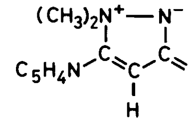
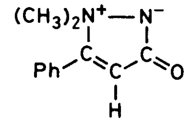
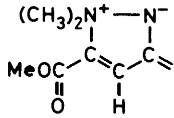
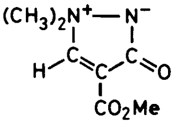
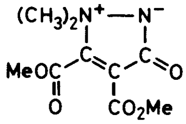
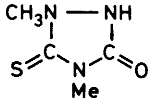
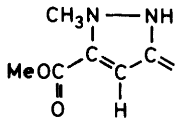


Class (B)



chain aminimides previously reported.[2] In the original publication, nitrogen 1*s* binding energies were referenced to the nitro-group nitrogen 1*s* binding energy value of 405.0 eV. In Table 3, the same data are corrected to the carbon 1*s* value of 284 eV to compare with the data for cyclic aminimides, but the differences between nitrogen atoms are the same. The nitrogen 1*s* binding energies of our cyclic aminimides are corrected to the carbon 1*s* value. This standard has been found, in some cases, to be less reliable. However, our measurements were performed repeatedly and good reproducibility of binding energy and peak shape was obtained. Thus, it seems that the effect of surface potentials such as the charge-up phenomenon is not serious. In addition, the electronic structures correlate exactly with each other by $\Delta(N^+-N^-)$.

Table 1. Nitrogen 1*s* binding energies of cyclic aminimides

		N 1*s* (eV)		
Compd.		N^+	N^-	N or NH
(1)		401.0	397.4	
(2)		400.6	397.4	
(3)		400.6	397.6	
(4)		400.8	397.0	
(5)		401.0	397.2	
(6)		400.6	396.8	
(7)		400.8	397.0	
(8)		400.6	396.7	
(9)				400.0
(10)				399.0

The values of $\Delta(N^+-N^-)$ are very accurate and give information on the nature of the bonds in aminimides. The values $\Delta(N^+-N^-)$ for the cyclic aminimides of class (A) are smaller than those for open-chain aminimides. This result suggests a larger displacement of the electron cloud of the N^+-N^- bond towards the quaternary nitrogen atom in the cyclic aminimides. This fact is supported by nitrogen 1*s* binding energies. That is, the nitrogen 1*s* binding energies (400.6—401.0 eV) of the quaternary nitrogens in cyclic aminimides are lower than those (401.0—401.5 eV) of the quaternary nitrogens of open-chain aminimides (Tables 1 and 3). This difference (*ca.* 0.5 eV) is essential. In addition, the contribution of the Madelung potentials and reorganization energies to the nitrogen 1*s* binding energies should be almost the same in cyclic and open-chain aminimides, because the arrangement around the quaternary nitrogen atoms are so similar. Thus, the data for the two kinds of aminimides can be compared directly. The observed lower nitrogen 1*s* binding energies indicate the electron density on N^+ to be higher in cyclic than in open-chain aminimides. Although another factor of high electron density is the difference in substituents at N^+, smaller $\Delta(N^+-N^-)$ values support the electron displacement effect strongly.

The $\Delta(N^+-N^-)$ values for class (A) depend on the ring substituents and correlate with the stretching frequencies of

Table 2. Differences $\Delta(N^+-N^-)$ between nitrogen 1*s* binding energy of N^+ and that of N^- in the cyclic aminimides and their ν(C=O) absorptions

Aminimides of class (A)	$\Delta(N^+-N^-)$	ν(C=O)/cm^{-1}
(1)	3.6	1 710, 1 810 [a]
(2)	3.2	1 700
(3)	3.0	1 680, 1 810 [a]
Aminimides of class (B)		
(4)	3.8	1 600
(5)	3.8	1 600
(6)	3.8	1 600, 1 730 [b]
(7)	3.8	1 600, 1 740 [b]
(8)	3.9	1 610, 1 730 [b]

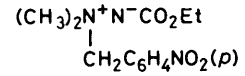
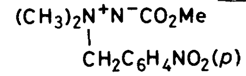
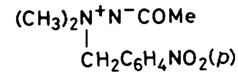
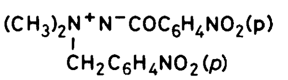
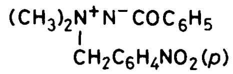
[a] This absorption band is assigned to the carbonyl group adjacent to the quaternary nitrogen and the tertiary nitrogen. [b] This absorption band is assigned to the carbonyl group of the ester substituent on the five-membered ring.

the carbonyl group at ring position 3, as expected by inspection of the applicable resonance structures, and as discussed in an earlier paper,[2] and shown in Table 2. Comparing (1) with (3), one sees that the stretching frequency of the carbonyl group next to N^+ remains the same (1 810 cm^{-1}), while that of the N^- conjugated carbonyl group is lower by 30 cm^{-1} for (3) compared with (1) owing to the substituents. The difference $\Delta(N^+-N^-)$ for (3) is also smaller. This correlation was found in open-chain aminimides,[2] as shown in Table 3. One must conclude from this relationship that the resonance contributor (IB) has considerable weight in the resonance hybrid (amide resonance). Evidence for amide resonance was also found in the carbon 1*s* spectra of cyclic aminimides.[7]

The nitrogen 1*s* binding energies of N^+ of the cyclic aminimides of class (B) are smaller than those of the open-chain aminimides. [For class (A), the range of nitrogen 1*s* binding energy is 400.6—401.0, for class (B) 400.6—401.0, and for open-chain aminimides 401.0—401.5 eV.] This indicates higher electron density at N^+ in all the cyclic aminimides, presumably due to the significant displacement of an electron along the N–N bond. The differences $\Delta(N^+-N^-)$ are smaller for class (A) than for class (B) and for open-chain aminimides [the ranges of $\Delta(N^+-N^-)$ are 3.0—3.6, 3.8—3.9, and 3.6—4.2, respectively]. In class (A), more electron density is removed from N^- by the carbonyl group, compared with class (B), where conjugation of the carbonyl group with the 4,5-carbon–carbon double bond impedes the amide resonance. The impediment due to this conjugation becomes clear when the values of $\Delta(N^+-N^-)$ of class (B) and the nitrogen 1*s* binding energies of classes (A) and (B) are compared with each other, *i.e.*, all the values of $\Delta(N^+-N^-)$ of class (B) are almost the same. The ranges of nitrogen 1*s* binding energies of the quaternary nitrogen (N^+) of classes (A) and (B) are the same (400.6—401.0 eV), while the values of the anionic nitrogen (N^-) for class (B) are lower than those for class (A) [the ranges of N^- for class (B) are 396.7—397.2, for class (A) 397.4—397.6 eV, respectively]. Thus, it is expected that cyclic aminimides of class (B) have the largest values of $\Delta(N^+-N^-)$, because carbonyl conjugation with the double bond impedes the amide resonance. However, the largest values (3.9 and 4.2) of $\Delta(N^+-N^-)$ are found in open-chain aminimides and the values of class (B) are almost 3.8. We consider that this observed result would be explained by stronger displacement effects in the aminimides of Class (B).

The difference in $\Delta(N^+-N^-)$ between class (A) and open-chain aminimides rests mainly in the nitrogen 1*s* values of N^+, which are smaller for class (A) than for the open-chain aminimides, while the range of nitrogen 1*s* values of N^- for open-chain aminimides contains those for class (A) (the ranges are 396.8—397.9 and 397.2—397.4 eV, respectively) and the average nitrogen 1*s* values of N^- are the same (average 397.3 eV).

Table 3. Nitrogen 1*s* binding energies and ν(C=O) of open-chain aminimides [a]

		E/eV			
Compd.		N^+	N^-	Δ (N^+-N^-)	ν(C=O)/ cm^{-1}
(11)	 $\underset{CH_2C_6H_4NO_2(p)}{\underset{\vert}{(CH_3)_2N^+N^-CO_2Et}}$	401.0	396.8	4.2	1 640
(12)	 $\underset{CH_2C_6H_4NO_2(p)}{\underset{\vert}{(CH_3)_2N^+N^-CO_2Me}}$	401.0	396.8	4.2	1 620
(13)	 $\underset{CH_2C_6H_4NO_2(p)}{\underset{\vert}{(CH_3)_2N^+N^-COMe}}$	401.5	397.6	3.9	1 580
(14)	 $\underset{CH_2C_6H_4NO_2(p)}{\underset{\vert}{(CH_3)_2N^+N^-COC_6H_4NO_2(p)}}$	401.3	397.4	3.9	1 580
(15)	 $\underset{CH_2C_6H_4NO_2(p)}{\underset{\vert}{(CH_3)_2N^+N^-COC_6H_5}}$	401.5	397.9	3.6	1 550

[a] All binding energies were correlated with the carbon 1*s* value of 284 eV.[2]

Only two non-ylid, but otherwise analogous, structures were available to compare with the cyclic aminimides (2) and (6). The value of the nitrogen 1*s* binding energy of (9) is closer to that of the neutral nitrogen atom in comparison with those of (2). Thus, it was expected that the average of the nitrogen 1*s* binding energies of N^+ and N^- in (2) corresponds with the nitrogen 1*s* binding energy of (9). However, the average is 399.0 eV, while the nitrogen 1*s* binding energy of (9) is 400.0 eV, 1 eV higher than the average. The same tendency is also observed in the case of compounds (10) and (6). This indicates the neutralization of positive charge by displacements of bonding electrons.

We conclude that cyclic (as well as open-chain) aminimides are stabilized by displacements of bonding electrons in the N^+-N^- bond, with addditional stabilization by delocalization of non-bonding electrons on N^- into the adjacent carbonyl group. The 'electron displacement effect' is particularly strong in aminimides of class (B), where the amide resonance is less than it is in aminimides (A) and in open-chain ones.

Experimental

The cyclic aminimides were synthesized as described previously.[5] I.r. spectra of cyclic aminimides were recorded for KBr disks using a Hitachi 260-10 spectrometer. XPS spectra were determined using a JASCO ESCA-1 photoelectron spectrometer or a McPherson ESCA-36 photoelectron spectrometer, using Mg-K_α radiation. The samples were ground in an agate mortar and dried under high vacuum for a few hours. The fine powder was dusted onto double-sided sticky tape or aluminium foil which was mounted on the sample holder. After the sample holder was placed in the sample chamber of the XPS spectrometer under high vacuum for 1 h, the XPS measurements were performed. To check for radiation damage, carbon 1*s* spectra were examined before and after measurements of nitrogen 1*s* binding energies. Changes in the carbon spectra were not observed. All spectra were run in both spectrometers and the same results were obtained. The carbon 1*s* line was taken as 284 eV for calibration purposes.

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