On the Bond Character of N-Containing Ylides

Shinji Tsuchiya*[1a] and Manabu Senō[1b]

Institute of Industrial Science, The University of Tokyo, 7-22, Roppongi, Minato-Ku, Tokyo 106, Japan

Received December 22, 1978

X-ray photoelectron spectroscopy measurements of N-containing ylides were performed to obtain the information about their charge distribution. It was clarified that the electron density of the quaternary nitrogen of aminimides is higher than that of their salts. This means that the stability of aminimides is largely effected by the electron withdrawing properties of the quaternary nitrogen. The electronic structure of sulfilimines having d orbitals available was compared to that of aminimides, and the large contribution of semipolar canonical structure is proposed for stabilized sulfilimines, since the contribution of the π interaction between the 3d orbital of sulfur (S^+) and 2p orbital of the ylidic nitrogen (N^-) is of little importance.

The typical chemical bond has been treated as primarily the interaction between the valence electrons of each atom. However, recent studies of X-ray photoelectron spectroscopy (XPS) have shown that the electronic energy of the core electrons is also affected greatly by the chemical bonds. For example, through the measurements of N 1s binding energy the large shift (8 eV) due to the difference of the bond character may be obtained.[2]

We have continued XPS studies of a series of organic and inorganic compounds[3] and found that, because the ylides contain many kinds of atoms bearing different charges, they are suitable compounds by which to probe the relationship of chemical bonds with core electrons by XPS measurements.[4] Hence, we became interested in the clarification of the bond character of especially stable representatives of these compounds. This paper reports XPS, infrared (IR), and nuclear magnetic resonance (NMR) data of a variety of nitrogen ylides, and the data are used to clarify the special electronic structures called ylide bonds.

Results and Discussion

Before discussing our XPS data, it is useful to outline the method for determination of the binding energies of samples of insulating solids. While some investigators correct all raw binding energies to the impurity, the C 1s line, and others use the value of the $4f_{7/2}$ of a thin gold film evaporated onto the sample, it has been noticed that these methods are not successful in all cases. A more reasonable method does not depend on a comparison between different materials but involves a comparison between nonequivalent atoms contained in one molecule. If the XPS spectra of compounds like this are measured, one can discuss exactly the electronic structure of individual compounds by the relative difference. Aminimides and sulfilimines used in the present investigation fit the condition described above. For example, the aminimides used in the present study have three kinds of nitrogen, and the spectra show distinct separation of peaks as shown in Figure 1. Through the measurements of a series of compounds, we also found that N 1s binding energies of the NO_2 group are not affected by the environment of nitrogen; namely, the peak width at half-height (PWH) of the N 1s peak assigned to the two kinds of nitro groups in the spectra of **4a** and **4b** is 1.5 eV as shown in Figure 1. This width indicates that the two nitro groups are essentially equivalent. In addition, the range of change for nitro groups is only 0.5 eV as shown in Table I These facts indicate that the nitro group is a good reference for the present compounds. These facts also indicate that it is possible to compare exactly the data of different compounds with each other, if we utilize a reference group incorporated in each molecule of interest. We tried the clarification of electronic structure of ylides by the method of the new reference and by the separation difference of N 1s peaks based on nonequivalent nitrogens. As each of a series of aminimides and sulfilimines has structures similar to each other, the Madelung potential and the relaxation effect are considered to contribute equally to the measured XPS data in this study. The data are therefore expected to give intrinsic information about the electronic structure of these compounds.

Table I. N 1s Binding Energies (eV) of the Nitro Group for Hydrazonium Bromides and Aminimides[a]

no.	compd	N 1s
1a	$\{(CH_3)_2\underset{\substack{\vert\\ CH_2C_6H_4NO_2\text{-}p}}{N^+}NHCOOEt\}Br^-$	404.9
1b	$(CH_3)_2\underset{\substack{\vert\\ CH_2C_6H_4NO_2\text{-}p}}{N^+}N^-COOEt$	404.9
2b	$(CH_3)_2\underset{\substack{\vert\\ CH_2C_6H_4NO_2\text{-}p}}{N^+}N^-COOMe$	404.7
3a	$\{(CH_3)_2\underset{\substack{\vert\\ CH_2C_6H_4NO_2\text{-}p}}{N^+}NHCOMe\}Br^-$	405.1
3b	$(CH_3)_2\underset{\substack{\vert\\ CH_2C_6H_4NO_2\text{-}p}}{N^+}N^-COMe$	405.2
4a	$\{(CH_3)_2\underset{\substack{\vert\\ CH_2C_6H_4NO_2\text{-}p}}{N^+}NHCOC_6H_4NO_2\text{-}p\}Br^-$	404.7
4b	$(CH_3)_2\underset{\substack{\vert\\ CH_2C_6H_4NO_2\text{-}p}}{N^+}N^-COC_6H_4NO_2\text{-}p$	404.7
5a	$\{(CH_3)_2\underset{\substack{\vert\\ CH_2C_6H_4NO_2\text{-}p}}{N^+}NHCOPh\}Br^-$	404.9
5b	$(CH_3)_2\underset{\substack{\vert\\ CH_2C_6H_4NO_2\text{-}p}}{N^+}N^-COPh$	405.0

[a] The binding energies were corrected to the C 1s value of 284 eV.

The ylides in which the heteroatoms (M) have available d orbitals have canonical structures as follows.

$$\underset{\text{Ia}}{M^+{-}N^-{-}X}\qquad \underset{\text{Ib}}{M{=}N{-}X}\qquad \underset{\text{Ic}}{M^+{-}N{=}X^-}$$

Two main factors have been suggested to account for the stabilities of ylides. The first is the delocalization of

---

[1] (a) Address correspondence to this author at the University of California, San Diego, Department of Chemistry, D-006, La Jolla, Calif. 92093. (b) University of Tokyo, Institute of Industrial Science, 7-22, Roppongi, Minato-Ku, Tokyo 106, Japan.

[2] D. A. Shirley, "Elecron Spectroscopy", North-Holland, Amsterdam, 1972. M. Senō and S. Tsuchiya, *J. Electron Spectrosc. Relat. Phenom.*, **8**, 165 (1976).

[3] M. Senō, S. Tsuchiya, and S. Ogawa, *J. Am. Chem. Soc.*, **99**, 3014 (1977); M. Senō, S. Tsuchiya, M. Hidai, and Y. Uchida, *Bull. Chem. Soc. Jpn.*, **49**, 1184 (1976); M. Senō, S. Tsuchiya, H. Kise, and T. Asahara, *ibid.*, **48**, 2001 (1975); M. Senō, S. Tsuchiya, and T. Asahara, *Chem. Lett.*, 405 (1974).

[4] M. Senō and S. Tsuchiya, *J. Chem. Soc., Dalton Trans.*, 751 (1977); S. Tsuchiya and M. Senō, *Chem. Phys. Lett.*, **54**, 132 (1978).

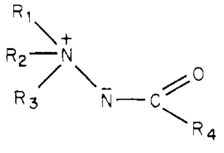
0022-3263/79/1944-2850$01.00/0

Table II. N 1s Binding Energies of Hydrazonium Bromides and Aminimides[a]

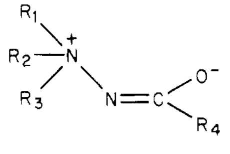
no.	compd	N 1s, eV			
		NO_2	N^+	NH	N^-
1a	$\{(CH_3)_2\underset{CH_2C_6H_4NO_2\text{-}p}{N^+}NHCOOEt\}Br^-$	405.0	402.3	400.0	
1b	$(CH_3)_2\underset{CH_2C_6H_4NO_2\text{-}p}{N^+}N^-COOEt$	405.0	401.1		396.9
2b	$(CH_3)_2\underset{CH_2C_6H_4NO_2\text{-}p}{N^+}N^-COOMe$	405.0	401.3		397.1
3a	$\{(CH_3)_2\underset{CH_2C_6H_4NO_2\text{-}p}{N^+}NHCOMe\}Br^-$	405.0	402.5	400.1	
3b	$(CH_3)_2\underset{CH_2C_6H_4NO_2\text{-}p}{N^+}N^-COMe$	405.0	401.3		397.4
4a	$\{(CH_3)_2\underset{CH_2C_6H_4NO_2\text{-}p}{N^+}NHCOC_6H_4NO_2\text{-}p\}Br^-$	405.0	402.1	400.0	
4b	$(CH_3)_2\underset{CH_2C_6H_4NO_2\text{-}p}{N^+}N^-COC_6H_4NO_2\text{-}p$	405.0	401.5		397.6
5a	$\{(CH_3)_2\underset{CH_2C_6H_4NO_2\text{-}p}{N^+}NHCOPh\}Br^-$	405.0	402.2	400.1	
5b	$(CH_3)_2\underset{CH_2C_6H_4NO_2\text{-}p}{N^+}N^-COPh$	405.0	401.5		397.9
7a	$\{(CH_3)_2\underset{CH_2C_6H_5}{N^+}NHCOPh\}Br^-$		402.3[b]	399.8[b]	
7b	$(CH_3)_2\underset{CH_2C_6H_5}{N^+}N^-COPh$		401.4[b]		397.5[b]

[a] All the binding energies were corrected to the N 1s value of the nitro group of 405.0 eV. [b] The binding energies of two compounds were corrected to the C 1s value of 284 eV.

negative charge in the dipole form, and the stabilities of ylides therefore are closely related to the electron-withdrawing characteristics of X and to the degree of interaction between the positive atom (M^+) and the negative atom (N^-). The interaction through a multiple bond between the heteroatom and the ylidic nitrogen (nitrogen anion) would be especially important, if the electron delocalization to X is small and the heteroatom (M) has available d orbitals.[5] Another stability factor is due to the high polarizability of the positive atom.[11] The aminimides used in the present investigation are stable in air, though the Wawzonek rearrangement occurs at high temperature.[6] Because aminimides do not have suitable d orbitals, this stability is described as arising from the delocalization of the nonbonded electrons on nitrogen (N^-) into the carbonyl group. In fact, the X-ray data on a single crystal of trimethylamine *p*-bromobenzimide and trimethylamine benzimide show that the geometry about the imide bond provides syn planarity of the N–C–O system. Further, the crystal structure bond lengths indicate that the electron pair in the p orbital of the ylidic nitrogen is delocalized to the π orbital of carbonyl.[7] However, our analyses on the bonding of aminimides by means of XPS suggest that these explanations should be improved.



IIa



IIb

Table III. The Differences $\Delta(N^+\text{-}N^-)$ between the Binding Energy of N^+ and That of N^- in Aminimides, the Differences $\Delta(N^+\text{-}NH)$ between the Binding Energy of N^+ and That of NH in Hydrazonium Bromides, and Their $\nu(C{=}O)$ Absorption

$(CH_3)_2\underset{CH_2C_6H_4NO_2\text{-}p}{N^+}N^-COR_4$ aminimide

$\{(CH_3)_2\underset{CH_2C_6H_4NO_2\text{-}p}{N^+}NHCOR_4\}Br^-$ hydrazonium bromide

R_4 =	$\Delta(N^+\text{-}N^-)$	$\nu(C{=}O)$, cm^{-1}	$\Delta(N^+\text{-}NH)$	$\nu(C{=}O)$, cm^{-1}
-OEt	4.2	1640	2.3	1740
-OMe	4.2	1620		
-Me	3.9	1580	2.4	1690
$-C_6H_4NO_2$	3.9	1580	2.1	1675
$-C_6H_5$	3.6	1550	2.1	1690

The sulfilimines in contrast to aminimides have available d orbitals. Much of the physical data on sulfilimines, including that from X-ray crystal structure determinations, have been interpreted as supporting the existence of dπ–dπ bonding in sulfilimines.[8] Semiempirical molecular orbital calculations on phosphonium ylides led to the conclusion that dπ–pπ interaction makes a significant contribution to the stabilization of ylides.[9] Recently, however, an X-ray crystal structure analysis of an azasulfonium betaine has shown that the nitrogen atom is sp^3 hybridized and not sp^2 hybridized as would be expected if dπ–pπ conjugation were important.[10] The problem of the exact nature of the bonding in sulfilimines thus remains open at present.

Aminimides. N 1s binding energies of aminimides were summarized in Table II and Table III contains the difference, $\Delta(N^+\text{-}N^-)$, between the binding energy of N^+ and that of N^- in each aminimide and $\nu(C{=}O)$ absorptions. In

---

(5) A. M. Johnson, "Ylid Chemistry", Academic Press, New York, 1966; H. L. Ammon, G. L. Wheeler, and P. H. Watts, Jr., *J. Am. Chem. Soc.*, **95**, 6158 (1973).

(6) S. Wawzonek and E. Yeakey, *J. Am. Chem. Soc.*, **82**, 5718 (1960).

(7) A. F. Cameron, N. T. Hair, D. G. Morris, and D. M. Hawleg, *Chem. Commun.*, 725 (1971).

(8) T. L. Gilchrist and C. J. Moody, *Chem. Rev.*, **77**, 409 (1977).

(9) R. Hoffmann, D. B. Boyd, and S. Z. Goldberg, *J. Am. Chem. Soc.*, **92**, 3929 (1970).

(10) R. S. Glass and J. R. Ducheck, *J. Am. Chem. Soc.*, **98**, 965 (1976).

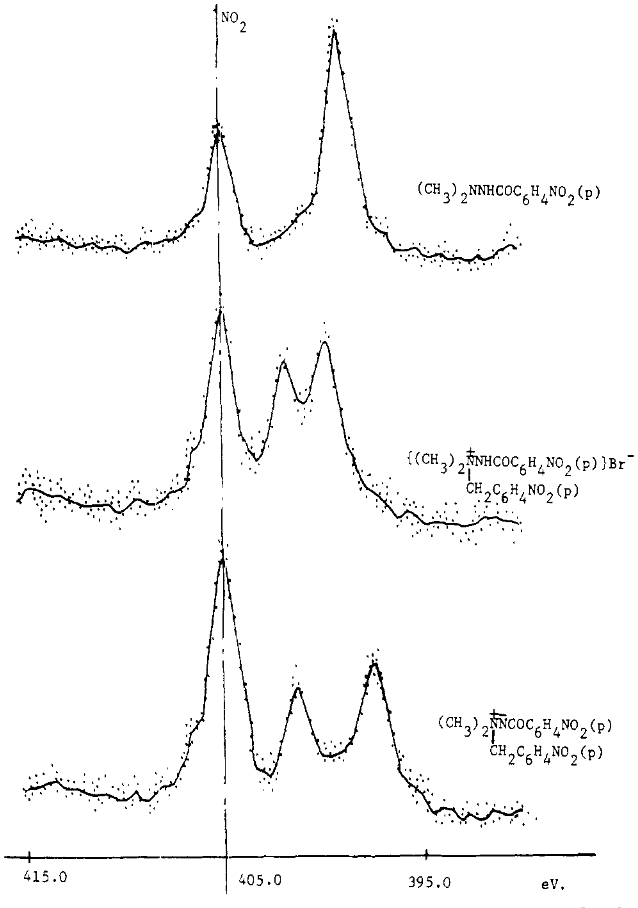
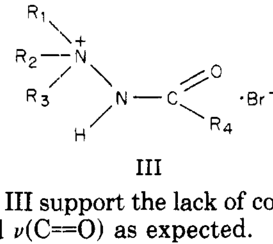


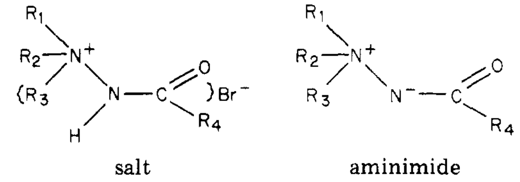
Figure 1. N 1s spectra of hydrazonium salt **4a**, aminimide **4b**, and a related compound.

previous studies, a correlation between the binding energy and the formal charge of the atom was established. In addition, these values of $\Delta(N^+\text{-}N^-)$ are the relative difference of binding energies of nonequivalent nitrogen atoms contained in one molecule (Figure 1). Hence, we could regard the value of $\Delta(N^+\text{-}N^-)$ as a measure of the degree of polarity on aminimides. As shown in the canonical structure of the aminimides IIa and IIb, these values of $\Delta(N^+\text{-}N^-)$ are closely related to ν(C=O); that is, we expect that the large contribution of a canonical structure (IIa) would give a large value of $\Delta(N^+\text{-}N^-)$ and a high value for ν(C=O); inversely, the large contribution of IIb gives a small value of $\Delta(N^+\text{-}N^-)$ and a low value of ν(C=O). For example, since ν(C=O) of compound **1b** indicates the highest frequency (1640 cm^{-1}) among all of the aminimides, we expect that the $\Delta(N^+\text{-}N^-)$ value of this compound is largest. In fact, Table III shows this tendency. We also found in Table III that there is a correlation between $\Delta(N^+\text{-}N^-)$ and ν(C=O) through the variation of the substituents. Table III also contains the values of $\Delta(N^+\text{-}NH)$ and the absorption of the salts. Since the salts of aminimide have the structure III, we cannot expect the relation described about aminimides. The experimental results in Table III support the lack of correlation between $\Delta(N^+\text{-}NH)$ and ν(C=O) as expected.



III

Table IV. The Differences ΔE between the N 1s Binding Energy of the Quaternary Nitrogen of the Salts and That of the Aminimides



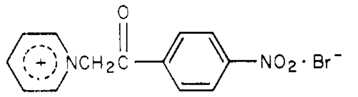
$R_1 = R_2 =$	$R_3 =$	$R_4 =$	ΔE
$-CH_3$	$-CH_2C_6H_4NO_2$	-OEt	1.2
$-CH_3$	$-CH_2C_6H_4NO_2$	$-CH_3$	1.2
$-CH_3$	$-CH_2C_6H_4NO_2$	$-C_6H_4NO_2$	0.6
$-CH_3$	$-CH_2C_6H_4NO_2$	$-C_6H_5$	0.7
$-CH_3$	$-CH_2C_6H_5$	$-C_6H_5$	0.9

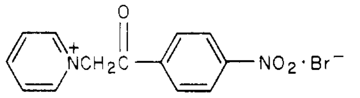
This close correlation between $\Delta(N^+\text{-}N^-)$ and ν(C=O) for aminimides and the large difference between ν(C=O) of the aminimides and that of their salts support the delocalization effect of the nonbonded electrons on N^- into the π orbital of the carbonyl group. However, we found other stabilization effects. The differences between the N 1s binding energies of quaternary nitrogen (N^+) for aminimides and those for the salts of aminimides were summarized in Table IV. As shown in Table IV, there is a large difference between the electron densities of the quaternary nitrogen of aminimides and those of the salts; that is, the quaternary nitrogen of aminimides shows extremely low N 1s binding energies, and the difference in N 1s binding energies of quaternary nitrogen between aminimides and their salts is 1.2 - 0.6 eV (1 eV $\approx$ 23 kcal/mol). This striking difference shows that the electron density of quaternary nitrogen of aminimides is considerably higher than that of their salts; that is, a strong interaction exists between the quaternary nitrogen (N^+) and the ylidic nitrogen (N^-) in aminimides. We presume that this interaction occurs through a σ bond; that is, the displacements of bonding electrons occur between the quaternary nitrogen and the ylidic nitrogen, or in other words, the electron cloud of the σ bond between N^+ and N^- lies closer to the quaternary nitrogen. Consequently, the electron density of the quaternary nitrogen increases, and the electron density of the ylidic nitrogen decreases. If this is the case, the displacements of bonding electrons would be an important factor in the stabilities of aminimides. The increase of electron density of the quaternary nitrogen is supported by NMR data, since the positions of all the peaks attached to the quaternary nitrogen of aminimides are at a higher magnetic field than those of their salts (Table V). For example, the ^1H NMR difference between the aminimides and their salts for the methyl attached to the quaternary nitrogen is 0.31–0.58 ppm. Also the difference of the methylene peak is 0.47–0.63 ppm. ^{13}C NMR data of methyl and methylene peaks also show the same tendency, and the differences are 1.0–4.00 and 2.00–7.00 ppm, respectively. The instability of aminimides could be canceled by some decrease of electron density on N^-. The Wawzonek rearrangement, which is the transfer of one substituent from the quaternary nitrogen to the ylidic nitrogen, is known to occur at high temperature. This means that the system of the molecules becomes unstable at high temperature and that rearrangement to a more stable system which does not have the formal charge in the molecule occurs. The effect of the carbonyl group and the coulombic effect have been presented as primarily explaining the stability of the nitrogen ylides which do not have $d\pi$–$p\pi$ interaction. However, the stability of nitrogen ylides would be explained definitely by the stabilization effect due to the displacements of bonding electrons.

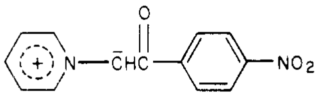
Table V. NMR and IR Data of Aminimides and Related Compounds

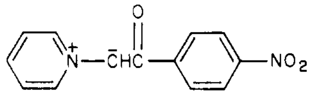
no.	compd	^{1}H NMR, δ			^{13}C NMR, δ		IR, cm^{-1}
		$(CH_3)_2N^+$	$-CH_2-$	$-CH_3$	$(CH_3)_2N^+$	$-CH_2-$	$\nu(C{=}O)$
1a	$\{(CH_3)_2N^+NHCOOEt\}Br^-$ $CH_2C_6H_4NO_2$-*p*	3.69	5.42	1.28			1740
1b	$(CH_3)_2N^+N^-COOEt$ $CH_2C_6H_4NO_2$-*p*	3.38	4.95	1.23			1640
2a	$\{(CH_3)_2N^+NHCOOMe\}Br^-$ $CH_2C_6H_4NO_2$-*p*						1740
2b	$(CH_3)_2N^+N^-COOMe$ $CH_2C_6H_4NO_2$-*p*	3.31	4.98				1620
3a	$\{(CH_3)_2N^+NHCOMe\}Br^-$ $CH_2C_6H_4NO_2$-*p*	3.77	5.50	2.14	58	72	1690
3b	$(CH_3)_2N^+N^-COMe$ $CH_2C_6H_4NO_2$-*p*	3.20	4.95	1.75	54	65	1580
4a	$\{(CH_3)_2N^+NHCOC_6H_4NO_2\text{-}p\}Br^-$ $CH_2C_6H_4NO_2$-*p*	3.85	5.60				1675
4b	$(CH_3)_2N^+N^-COC_6H_4NO_2$-*p* $CH_2C_6H_4NO_2$-*p*	3.45	5.10				1580
5a	$\{(CH_3)_2N^+NHCOPh\}Br^-$ $CH_2C_6H_4NO_2$-*p*	3.87	5.60				1690
5b	$(CH_3)_2N^+N^-COPh$ $CH_2C_6H_4NO_2$-*p*	3.40	5.10				1550
6a	$\{(CH_3)_2N^+NHCOMe\}Br^-$ $CH_2C_6H_5$	3.80	5.45	2.20	52	67	1700
6b	$(CH_3)_2N^+N^-COMe$ $CH_2C_6H_5$	3.22	4.92	1.83	51	65	1580
7a	$\{(CH_3)_2N^+NHCOPh\}Br^-$ $CH_2C_6H_5$	3.90	5.60		55	70	1700
7b	$(CH_3)_2N^-N^-COPh$ $CH_2C_6H_5$	3.35	4.97		53	68	1570

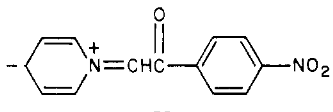
It is also interesting to investigate the pyridinium ylides having the quaternary nitrogen on a pyridinium ring and an ylidic carbon, in contrast to the aminimides which have a localized quaternary nitrogen and an ylidic nitrogen. The canonical structures of this pyridinium ylide are shown by IVa, IVb, Va, Vb, and Vc. The N 1s binding energy (400.8 eV) of N$^+$ of the pyridinium ylide is small compared to that of aminimides. It is expected that this indicates a strong interaction between the nitrogen on pyridinium ring and the ylidic carbon. However, the difference between the absorption of ν(C=O) of the pyridinium ylide and that of the pyridinium salt is very large (180 cm^{-1}), and the N 1s binding energy of N$^+$ of pyridinium salt is small compared to that of the salt of aminimides (Table VI). In addition, the difference (0.5 eV) between the binding energy of quaternary nitrogen of the ylide **8b** and that of the salt **8a** is small compared to those of aminimides. From these results, we presume that the small binding energy of nitrogen of pyridinium ylide is due not to the interaction between the nitrogen on pyridinium ring and the ylidic carbon, but to a large contribution from the canonical structure (Va) which shows the delocalization of positive charge on the pyridinium ring. In other words, since the positive charge of the pyridinium ylide does not localize on the nitrogen atom, the stabilization effect due to the displacements of bonding electrons is small compared to that of aminimides, and then the stabilization effect due to carbonyl group is large.


IVa


IVb


Va

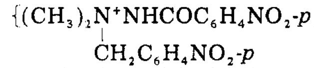
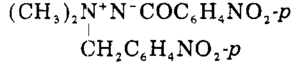

Vb


Vc

From these results of aminimides and pyridinium ylide, we suppose that the stabilization effect due to the displacements of bonding electrons operates strongly when the ylide has the large separation of charge or a large 1,2 dipole.

Sulfilimines. It is said that sulfilimines have the delocalization effect of nonbonded electrons on N$^-$ between S$^+$ and N$^-$ due to dπ–pπ interaction because the sulfur has d orbitals available. This point is very different from that from the case of aminimides. Hence, to probe the stabilization effect of ylides due to d orbitals, it is very interesting to compare the electron density on the ylidic

Table VI. N 1s and S 2p Binding Energies of Various Ylides and Related Compounds (eV)

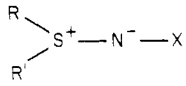
no.	compd	N 1s					S2p	IR, cm^{-1}
		NO_2[a]	N^+	NH	NH_2	N^-	SO_2 or S^+	$\nu(C{=}O)$
4a	 $\{(CH_3)_2\underset{CH_2C_6H_4NO_2\text{-}p}{\underset{\vert}{N^+}}NHCOC_6H_4NO_2\text{-}p\}Br^-$	405.0	402.1	400.0				1675
4b	 $(CH_3)_2\underset{CH_2C_6H_4NO_2\text{-}p}{\underset{\vert}{N^+}}N^-COC_6H_4NO_2\text{-}p$	405.0	401.5			397.6		1580
8a	$\{C_5H_5N^+CH_2COC_6H_4NO_2\text{-}p\}Br^-$	405.0	401.3					1710
8b	$C_5H_5N^+C^-HCOC_6H_4NO_2\text{-}p$	405.0	400.8					1540
9	$H_2NCOC_6H_4NO_2\text{-}p$	405.0			398.7			1680
10	$H_2NSO_2C_6H_4NO_2\text{-}p$	405.0			399.0			
11	$CH_3CONHCOC_6H_4NO_2\text{-}p$	405.0		399.3				
12	$(CH_3)_2S^+N^-COC_6H_4NO_2\text{-}p$	405.0				397.2	164.6	1570
13	$(CH_3)_2S^+N^-SO_2C_6H_4NO_2\text{-}p$	405.0				397.5	166.5 165.0	
14	$(CH_3)_2S^+N^-SO_2C_6H_4CH_3\text{-}p$[b]					397.7	166.6 165.4	
15	$(CH_3)_2S^+(O)N^-SO_2C_6H_4CH_3\text{-}p$[b]					397.9	167.2	
16	$(CH_3)_2S^+(O)C^-HCOPh$[b]						166.4	1530

[a] All raw binding energies were corrected to the N 1s value of the nitro group, 405.0 eV. [b] The binding energies were corrected to the C 1s value of 284 eV.

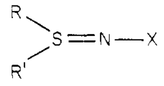
nitrogen of aminimides with that of sulfilimines. These sulfilimines were prepared from dimethyl sulfoxide and amides using a dehydrating agent. N 1s binding energies of N-containing ylides and related compounds are summarized in Table VI, together with IR $\nu(C{=}O)$ data. N 1s binding energies of amides **9**, **10**, and **11** show the tendency of chemical shift to increase with increasing electron-withdrawing capacity of the substituents. This result confirms the usefulness of the nitro group as a reference.

The sulfilimine **12** was prepared from dimethyl sulfoxide and *p*-nitrobenzamide (**9**), and the sulfilimine **13** was prepared from dimethyl sulfoxide and *p*-nitrobenzenesulfonylamide (**10**).[12] These reactions convert the nitrogen of amides **9** and **10** into the ylidic nitrogen of the sulfilimines **12** and **13**. Hence, it would be interesting to compare the N 1s binding energies of the amino group of the starting materials **9** and **10** with those of the ylidic nitrogen of the sulfilimines **12** and **13**. As shown in Table VI, the N 1s binding energies of the ylidic nitrogen of the sulfilimines **12** and **13** are lower than those of the amino group of corresponding amides, and the difference is 1.5 eV in both cases. This fact indicates that the electron density on ylidic nitrogen increases, and the amount of the increase is independent of the substituents like sulfonyl group and carbonyl group.

Comparisons of N 1s binding energies of the N^- of sulfilimines with those of aminimides are also evident. The difference in absorption $\nu(C{=}O)$ of the aminimide **4b** and the sulfilimine **12** is small as shown in Table VI, and this indicates nearly the same contribution of the carbonyl substituent to the delocalization of nonbonded electrons in both compounds. Hence, we can estimate the degree of interaction between S^+ and N^- in sulfilimine or N^+ and N^- in aminimide from N 1s binding energies of N^- of both compounds. As already described, while the sulfur of sulfilimine **12** has d orbitals available, the nitrogen of aminimide **4b** does not. Thus, we would expect a higher binding energy for the ylidic nitrogen of sulfilimine due to the interaction between the 3d orbital of S^+ and the 2p orbital of N^-. Nevertheless, it was found that the N 1s binding energy (397.6 eV) of aminimide **4b** is higher than that (397.2 eV) of sulfilimine **12**; that is, the electron density of N^- of the sulfilimines is higher than that of the aminimides. Since the difference (0.3 eV) between the N 1s binding energy of the amino group of the amide **9** and that of the amide **10** is the same as that between the N 1s binding energy of N^- of the sulfilimine **12** and that of the sulfilimine **13**, we could estimate the N 1s binding energy of (*p*-nitrobenzoyl)sulfoximine as follows. The difference between the stabilization effect of the *p*-toluenesulfonyl group and that of the *p*-nitrobenzoyl group (0.5 eV) is found from the N 1s binding energies of sulfilimines **12** and **14**. If this value is subtracted from the N 1s binding energy of the sulfoximine **15** to rectify the difference of stabilization effect, we could gain the value (397.4 eV) of (*p*-nitrobenzoyl)sulfoximine. This value is also lower than that (397.6 eV) of the aminimide **4b**. Though the sulfur attachment may affect the relaxation energy of the nitrogen atom, we presume that, because data indicate that the N 1s binding energies of the amides **9**, **10**, and **11** depend on only the electron-withdrawing capacity, the difference due to this effect is small. From these facts, it is suggested that the sulfur–nitrogen bond in sulfilimines has a large contribution from the semipolar canonical structure (VIa) rather than the covalent structure (VIb) containing the participation of d orbitals in bonding. Streitwieser suggested that the ability of the sulfur to stabilize a ylidic nitrogen (nitrogen anion) is due to the high polalizability of sulfur.[11] We do not have definite evidence about the degree of the contribution of the displacements of bonding electrons. If the S 2p binding energies of the salts of sulfilimines are measured, we could get some information about this.



VIa



VIb

Some information can be obtained from the S 2p binding energies. The S 2p spectra of carbonyl-stabilized sulfilimine **12** are shown in Figure 2. Each peak of the sulfonyl-stabilized sulfilimines **13** and **14** shows one large shoulder, while that of the sulfilimine **12** does not, and the position of the peak of sulfilimine **12** is close to that of the shoulder of sulfilimines **13** and **14**. Hence, the spectra of sulfilimines **13** and **14** should be assigned as follows: the main peak (166.5, 166.6 eV) is attributable to S 2p of the sulfonyl group, and the shoulder peak (165.0, 165.4 eV) is attributable to $(CH_3)_2S^+$. The sulfilimines **13** and **14** have

---

[11] A. Streitwieser and J. E. Williams, *J. Am. Chem. Soc.*, **97**, 191 (1975).

[12] T. E. Varkey, G. F. Whitfield, and D. Swern, *J. Org. Chem.*, **39**, 3365 (1974).

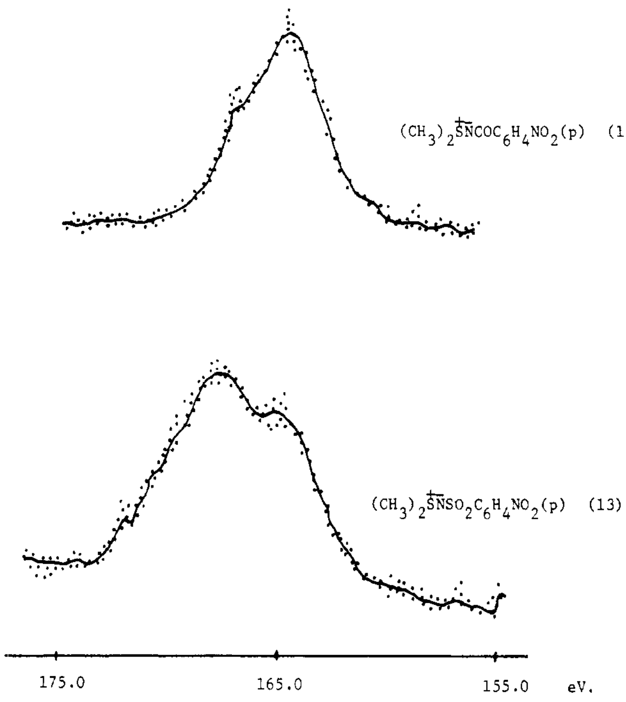


Figure 2. S 2p spectra of sulfilimines **12** and **13**.

two kinds of sulfur, and the chemical shifts between the imine sulfur and the sulfonyl sulfur are 1.5 and 1.2 eV, respectively. The S 2p peak of the sulfoximine **15** containing two nonequivalent sulfur atoms has a very small shoulder at the lower binding energy side, but we are unable to assign the cause of this shoulder. If we assign the two nonequivalent sulfur atoms to the main peak (167.2 eV), the introduction of an oxygen atom on the adjacent positive sulfur gives a large chemical shift (1.8 eV) to the adjacent positive sulfur; that is, the shift is the difference between the S 2p binding energy of sulfoximine **15** and that of sulfilimine **14**. However, the difference (0.2 eV) between the N 1s binding energy of N^- of sulfoximine **15** and that of sulfilimine **14** is small. This means that π interaction between the sulfur and the nitrogen is of little importance.

The XPS study of *N*-tosylsulfilimines has been reported by Mixan et al.[13] They compared the polarity of the S–N bond with that of the S–O bond of the sulfoxide and showed that the S–N bond is about 45% covalent.

If the difference between the S 2p binding energy of S^+ and the N 1s binding energy of N^- is inversely related to the polarity of the S–N bond, we should be able to obtain the information on the variation of the extent of polarity of sulfilimine with the substituent from these values. The values of compounds **12**, **13**, **14**, and **15** are 232.6, 232.5, 232.3, and 230.7, respectively. The extent of polarity of the sulfoximine **15** is large, and the S–N bonds of sulfonyl-stabilized sulfilimines **13** and **14** are more polar than that of carbonyl-stabilized sulfilimine **12**.

In conclusion, we have presented IR, NMR, and X-ray photoelectron spectroscopy data which clarify the charge distribution of unusual valence compounds, ylides, the extent of delocalization of nonbonded electrons due to resonance stabilizing group, and the effect of the electron-withdrawing properties by the adjacent quaternary nitrogen.

Experimental Section

Preparation of Samples. (A) The aminimides **3** and **6**, sulfur ylides **12**, **13**, **14**, and **15**, and nitrogen ylide **8** were prepared by published methods.[6,12,14] The aminimides **1**, **5**, and **7** were synthesized as described in the preceding reports.[4]

(B) The following procedure was used to prepare 1,1-dimethyl-1-*p*-nitrobenzylamine 2-*p*-nitrobenzimide (**4b**).

To 4.3 g of *p*-nitrobenzyl bromide in absolute ethanol, 1,1-dimethyl-2-(*p*-nitrobenzoyl)hydrazine (4.3 g) in absolute ethanol was added, and the mixture was refluxed for 5 h. 1,1-Dimethyl-1-(*p*-nitrobenzyl)-2-(*p*-nitrobenzoyl)hydrazonium bromide (**4a**, 4.5 g) was obtained by cooling. This salt (2 g) was dissolved in water and titrated to a phenolphthalein end point with 1 N sodium hydroxide. The precipitates were collected and recrystallized from benzene. The yield **4b** was 1 g (62%).

(C) The aminimide **2** was prepared by a similar procedure to that described for aminimide **4b**.

Physical Measurements. IR spectra were recorded for KBr disk using a JASCO IRA-2 spectrometer. ^1H NMR spectra were measured in deuteriochloroform with a Hitachi R-22 spectrometer operating at 90 MHz against Me_4Si as an internal standard at 37 °C. ^{13}C NMR spectra were obtained using a Hitachi R-26 spectrometer in the Fourier transform mode operating at 10 MHz. ^{13}C–H coupling was eliminated by using a broad-band ^1H-noise-modulated decoupler. The measurements were run in saturated deuteriochloroform solutions, and Me_4Si was used as an internal standard.

XPS spectra were determined using a JASCO ESCA-1 photoelectron spectrometer, using Mg Kα rays. The X-ray power supply was run at 8 kV and 40 mA. The samples were examined as fine powder dusted onto double-side sticky tape which was mounted on the copper sample probe. To correct for radiation damage, an attempt to examine the change of spectra during the time measurement was performed; the considerable changes of spectra were not observed, and the results of gas analyses by a mass filter (mass spectrograph) attaching the sample chamber also give no evidence for evolution of gases by decomposition. In the case of highly hygroscopic ylides, the samples were left under vacuum for 5 h before measurements were taken. All spectra were run in triplicate. The carbon C 1s line was taken as 284 eV and was used for calibration. For samples containing a nitro group, N 1s binding energies of other nitrogens were corrected by assigning the N 1s values of the nitro group as 405.0 eV.

Registry No. 1a, 63603-03-2; **1b**, 63603-01-0; **2a**, 70524-33-3; **2b**, 70524-34-4; **3a**, 58873-94-2; **3b**, 26377-98-0; **4a**, 70562-43-5; **4b**, 70562-42-4; **5a**, 63603-04-3; **5b**, 63603-02-1; **6a**, 63603-06-5; **6b**, 34025-17-7; **7a**, 63603-05-4; **7b**, 52723-43-0; **8a**, 25407-30-1; **8b**, 25357-54-4; **9**, 619-80-7; **10**, 6325-93-5; **11**, 51769-82-5; **12**, 55649-97-3; **13**, 31657-43-9; **14**, 31657-41-7; **15**, 70524-35-5; **16**, 20718-17-6; *p*-nitrobenzyl bromide, 100-11-8; 1,1-dimethyl-2-(*p*-nitrobenzoyl)hydrazine, 14908-42-0; methyl 2,2-dimethylhydrazinecarboxylate, 55741-07-6.

---

(13) G. E. Mixan and J. B. Lambert, *J. Org. Chem.*, **38**, 1350 (1973).

(14) P. K. Claus, W. Rieder, and P. Hofbauer, *Tetrahedron*, **31**, 505 (1975); L. Horner and H. Oediger, *Justus Liebigs. Ann. Chem.*, **627**, 142 (1959).