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An ESCA Investigation of Ambident Ions and Tautomerism. *N*-Cyanobenzamides and Benzohydroxamic Acids

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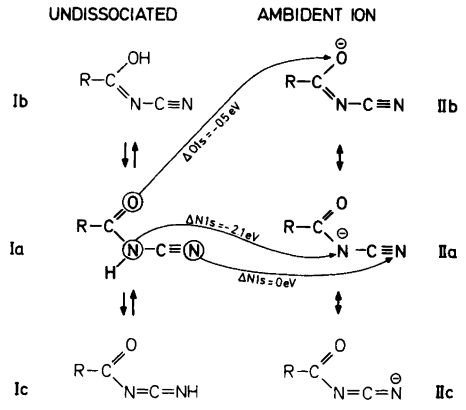
Solid state N1*s* and O1*s* electron binding energies have been measured by means of ESCA for some *N*-cyanobenzamides, their alkali salts, benzohydroxamic acids, their alkali salts and one hydrochloride, as well as for reference compounds. The electron binding energy shifts are discussed in terms of the electronic structure and tautomerism of the ambident ions. Similarities of shifts imply a similar charge distribution pattern in the anions of *N*-cyanobenzamide and 4-nitrobenzohydroxamic acid, indicating that the latter behaves as an N-acid. The data for the unsubstituted benzohydroxamic acid are compatible with O-acidity. The data for benzohydroxamic acid hydrochloride are consistent with O-protonation.

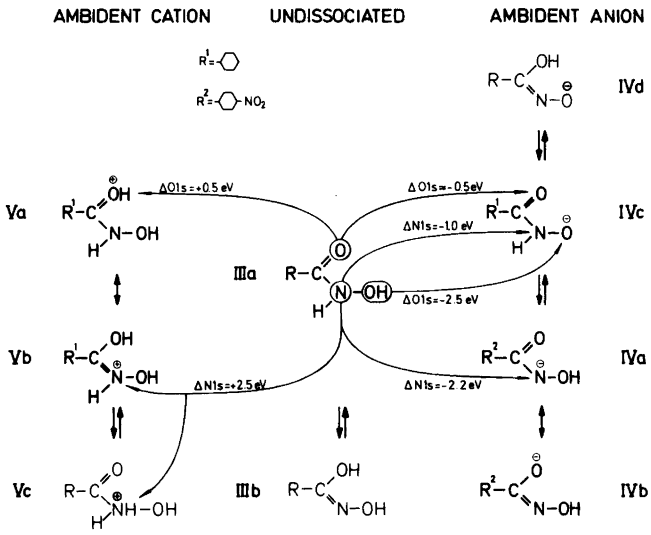
The structure of prototropic (tautomeric) molecules has been studied for over a century. While the structure of undissociated molecules, *i.e.* the position of the hydrogen atom, may now be established by a variety of methods,[1] there still remains the question of the electronic structure of the corresponding ambident anion, *i.e.* the distribution of the negative charge. The available methods are then more restricted, also owing to the unfavourable physical properties of the salts. Some of them can be investigated in the solid state only. For instance *N*-cyanoamides can easily be proven[2] to exist virtually in the structure Ia (Scheme 1). It is, however, more difficult to describe the electronic structure of their anions either in terms of the charges on individual atoms or in terms of the mesomeric formulae IIa–c. In particular the prevalence of Ia does not infer IIa to be the structure of the anion.

If a prototropic molecule bears more than one potentially acidic hydrogen, an additional problem arises. The anion has still at least one hydrogen and its position is to be determined in addition to the electronic structure of the molecule. For instance, the structure of hydroxamic acids was shown[3] to be IIIa (Scheme 2), and the anion may have three different structures, IVa⟷IVb, IVc or IVd. If we accept spectroscopic and other arguments in favour of the first structure,[3–5] the question of its charge distribution still remains. Similarly for the cation of hydroxamic acids[4] two structures are possible, Va⟷Vb or Vc, corresponding to O-protonation or N-protonation, respectively.

The present investigation is an attempt to apply ESCA to these problems. The experimental O1*s* and N1*s* electron binding energies of the structures



Scheme 1. N-Cyanoamides.



Scheme 2. Hydroxamic acids.

I–V and of reference compounds are compared and discussed in terms of chemical structure and charge pattern of the molecules. Owing to the involatility of the salts they were investigated in the solid state, and the lattice effects thus represent an inherent difficulty of the approach. However, one must take into account that many other methods are not at all applicable to non-volatile and slightly soluble compounds.

Since crystal lattice data are often lacking for organic salts their shifts can only be discussed on the level of "intuitive charges" used by chemists.[6a,7] It has been argued that the "intuitive charge" distributions are really reflexions of the potential at a given site of a molecule rather than of the actual charge distribution. This has received support by the finding that within a series of similar compounds, the core electron binding energies often correspond very well to those changes in charge distribution which would be predicted from the substituent effects on reactivity.[8]

EXPERIMENTAL

The samples were excited by Al$K\alpha$ radiation and the spectra recorded with a magnetic double-focussing spectrometer[9] equipped with a multichannel detector system.[10] The base pressure during the recordings was 1 mPa both in the sample and the analyzer compartments.

All the samples were studied in the solid state pressed on a silver backing. The C1*s* peak from the hydrocarbons ($E_b = 285.0$ eV), which coincides with the C1*s* peak from the phenyl groups, was used as a reference line to determine the binding energies.[11] This composite peak was so intense that it almost obscured other structures from chemically different carbon atoms. Thus no C1*s* binding energies were determined. Since the samples are insulators the irradiation may cause charging. The charging depends on sample thickness, geometrical arrangements in the sample compartment and the X-ray intensity (in our case the X-ray power was maintained at 40 mA/10 kV). In order to minimize the sample charging we made the samples thin. By recording spectra both from a grounded metal piece and the hydrocarbon layer on the sample surface we could compensate for the unavoidable charging. This is always possible since the hydrocarbon layer attains the same potential as the sample surface.[11] Inhomogeneous surface charging tends to broaden the electron lines, but thin and uniform samples will reduce this effect. We recorded spectra from several samples prepared from the same substance. The error in the absolute binding energies was estimated to ± 0.3 eV. However, the binding energy shifts are determined more accurately, since systematical errors do not enter.

Compounds *8*–*19* (Table 1) were characterized in previous works[2,3,5] and compounds *1a*, *b*, *2*, *4*, *5* and *7* were commercial laboratory reagents. Samples of compound *19*, which is very hygroscopic, were prepared in dry nitrogen atmosphere. In vacuum

the sample releases HCl. The resulting spectrum is thus a superposition of the spectra of compounds *9* and *19*, but chemical shifts of the N1*s* and O1*s* levels between the hydrochloride and the parent compound are large enough for the different chemical states to be easily identified in the electron spectrum.

In most cases the peaks in the spectra were sufficiently well-separated to allow a straightforward energy determination. For composite peaks we assumed that all components had the same line width. The number of components and their relative intensities are known from the chemical formulae. With these assumptions it is possible to make an analytical deconvolution using Voigt functions for the line profiles. For the deconvolution the narrowest observed line width for single peaks was used as a standard line width. This procedure was used for compounds *8*–*11*, *15*, *18* and *19*.

An attempt to run a spectrum of cyanamide in the vapour state failed due to polymerization when the sample was heated in order to evaporate it under vacuum.

RESULTS

The measured N1*s* and O1*s* electron binding energies are given in Table 1. The relevant shifts of the amidic nitrogen, cyano nitrogen, carbonyl oxygen and hydroxyl oxygen are graphically represented in Figs. 1–3.

Cyanobenzamides. Cyanamide (*4*) and cyanobenzamides (Nos. *9*–*11*) contain two types of nitrogen in the same molecule. (*N*-benzylcyanamide (*8*) exists as a trimer in the solid state.) For cyanamide the nitrogen peak is not broad enough to warrant a decomposition into two peaks of different binding energies, therefore the two nitrogen atoms are found to have about equal N1*s* binding energies in the solid state. The same is the case for the cyanobenzamide salts (*12*–*14*) but the N1*s* binding energy is shifted to a lower value compared to cyanamide (0.5 eV). In the undissociated cyanobenzamides there is a considerable internal nitrogen shift (2.1 eV). The lowest binding energy is assigned to the cyano nitrogen.

Table 1. Experimental N1*s* and O1*s* electron binding energies (eV).

	Compound [e]	N1*s*			O1*s*		
		N–H	C≡N	NO_2	C=O	O–H	Other
1a	Cl–C_6H_4–COOH [a]				532.3	533.6	
1b	C_6H_5–CO_2Na						531.6
2	C_6H_5–$CONH_2$	399.7			532.4		
3	H_3C–CN		399.8 [b]				
4	H_2N–CN	399.4	399.4				
5	NaO–CN		398.7				532.0
6	C_6H_5–CN		399.4 [c]				
7	O_2N–C_6H_4–CN		399.2	405.8			532.2
8	[C_6H_5–CH_2NHCN]$_3$	400.7	398.4				
9	C_6H_5–CONHCN	401.2	398.9		532.1		
10	H_3C–C_6H_4–CONHCN	400.6	398.7		532.5		
11	Br–C_6H_4–CONHCN	401.2	399.1		532.1		
	Mean value (*9*–*11*)	401.0	398.9		532.2		
12	C_6H_5–CONCN/Na	399.0	399.0		531.8		
13	H_3C–C_6H_4–CONCN/Na	398.9	398.9		531.5		
14	Br–C_6H_4–CONCN/Na	398.9	398.9		531.8		
	Mean value (*12*–*14*)	398.9	398.9		531.7		
15	C_6H_5–CONHOH	401.4			531.8	533.8	
16	O_2N–C_6H_4–CONHOH	401.0		405.8	——	532.6 [d]	——
17	C_6H_5–CONOH/K	400.4			531.3	531.3	
18	O_2N–C_6H_4–CONOH/Na	398.8		406.1	——	532.2 [d]	——
19	C_6H_5–$CONH_2$OH/Cl	403.9			532.3	534.7	

[a] The unsubstituted benzoic acid was too volatile in the vacuum of the spectrometer. [b] From Ref. 20 adjusted to solid state. [c] From Ref. 17. [d] Undeconvoluted O1*s* peaks. [e] Compounds *1a*, *7*, *10*, *11*, *13*, *14*, *16* and *18* are 4-substituted.

Table 2. Internal N1*s* electron binding energy shifts $\Delta(N^2-N^1)$, eV.

Compound	Calculated CNDO/2[a]		Found
	TPM	GPM	
$PhCON^2HCN^{1\,b}$	4.5	3.9	2.2
$H_2N^2CN^{1\,c}$	2.9	2.7	<0.5

[a] Geometrical data (bond angles and bond lengths) are estimated within the limits of standard values. [b] For the −CONH− group geometrical data from acetobenzohydroxamic acid were used [21]. [c] Data from Ref. 22.

In order to support this assignment of the N1*s* binding energies we performed CNDO/2 calculations on the two neutral compounds (*4* and *9*) using geometrical data based on the *Z*-conformation around the C−N bond as determined from solution dipole moments.[2] The lattice effects cannot be accounted for in a calculation unless the crystal structure is known. Especially for ionic salts these can be of great importance. Thus, we restricted ourselves to neutral compounds. We used both the ground state potential model (GPM)[6b] and the transition state potential model (TPM),[12-14] the latter accounting for relaxation energies. The results are given in Table 2 and both models give the same assignment. Our assignment is also supported by comparing the N1*s* binding energies with those of other compounds investigated, taking account of appropriate substituent effects.

The amide nitrogen in the neutral compound has a lower binding energy than that of the corresponding salt ("salt shift" of −2.1 eV), as would be expected for the creation of a formal negative charge on this atom (limiting structure IIa). The O1*s* binding energies situated in the carbonyl region also have lower values in the salts (−0.5 eV). The cyano nitrogen is unaffected by salt formation.

The experimental internal N1*s* shifts listed in Table 2 are about 2 eV smaller than the calculated ones. Levelling effects of this kind have previously been attributed to hydrogen bonding.[6c,15] Thus for acetic acid the binding energy difference of O1*s* between the =O and −OH groups is 1.8 eV in the vapour state but is not resolved in the solid state due to intermolecular $=O\cdots HO-$ hydrogen bonding.[6c] Similar levelling effects on anticipated internal shifts can be visualized for cyanobenzamides by intermolecular hydrogen bonding, involving either the cyano nitrogen or the carbonyl oxygen.

Benzohydroxamic acids. For 4-nitrobenzohydroxamic acid (*16*) the N1*s* salt shift is −2.2 eV, just equal to that in cyanobenzamides. The similarity of these salt shifts would be in agreement with structure IVa, b for the 4-nitrobenzohydroxamate (*18*). In the unsubstituted benzohydroxamic acid the N1*s* salt shift is much smaller, −1.0 eV suggesting structure IVc for the salt.

The highest O1*s* binding energies in the unsubstituted benzohydroxamic acid and its protonated form are assigned to the N−OH group, and the lower to the C=O group. This is done in analogy to the carboxylic acids where the −OH group has a binding energy about 1−2 eV higher than that of the >C=O group[6d,16] (in compound *1a*, 1.3 eV). In 4-nitrobenzohydroxamic acid and its salt the O1*s* spectra include components from the nitro group oxygens and could not be deconvoluted with any confidence. In the alkali salt of unsubstituted benzohydroxamic acid (*17*) the high binding energy

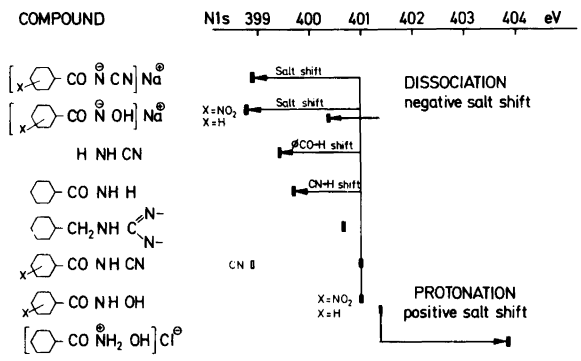


Fig. 1. Chart of N1*s* electron binding energies for amide nitrogen in a series of aromatic amidic compounds.

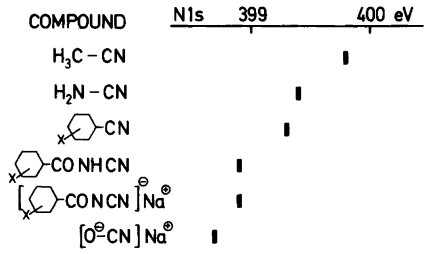


Fig. 2. Chart of N1*s* electron binding energies for cyano nitrogen in a series of cyano compounds.

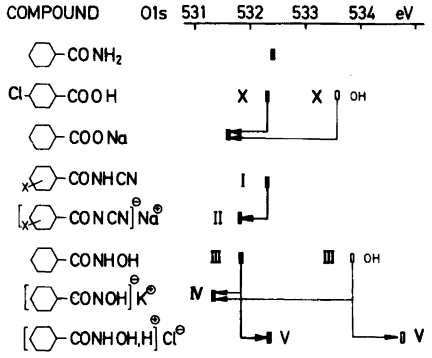


Fig. 3. Chart of O1*s* electron binding energies for carbonyl oxygen in a series of aromatic carbonyl compounds.

O1*s* component disappears. The narrowness of the O1*s* peak indicates that the two oxygen atoms have closely equal binding energies.

In the protonated benzohydroxamic acid (*19*) both the N1*s* and O1*s* salt shifts are in the opposite direction to those of the corresponding alkali salt and of a similar magnitude.

DISCUSSION

Amide nitrogen. With our assignment the substituent effects on the N1*s* binding energies of the cyanoamides indicated in Fig. 1 are consistent with previously known group shifts [17] for the substituents. The amide N1*s* electron binding energy for benzohydroxamic acids is about the same as for cyanobenzamides. The substituent effects of $-CN$ and $-OH$ are thus similar in these compounds.

Cyano nitrogen. For the cyano nitrogen (Fig. 2) there are significant substituent effects although effects from more distant atoms (second-order substituent effects) are usually small in ESCA.[18] However, in the present compounds the cyano nitrogen is a terminal atom in a conjugated structure. In such cases mesomeric electron displacements may cause significant second-order effects, and shifts up to 1 eV have previously been observed.[18,19] Also in this case the substituent effects cover a shift span of -1 eV from the acetonitrile (*3*) as a reference. This indicates strong $+M$ effects.

Carbonyl oxygen. For the cyanobenzamides we observe a small but significant O1*s* salt shift towards lower binding energy (-0.5 eV, Fig. 3). The shift is in the same direction as in going from carboxylic acid or benzamide to carboxylate, which indicates a delocalization of charge to the carbonyl oxygen in the salts (IIa↔IIb). For the unsubstituted benzohydroxamic acid there is a similar O1*s* salt shift (-0.5 eV) suggesting a similar charge delocalization pattern.

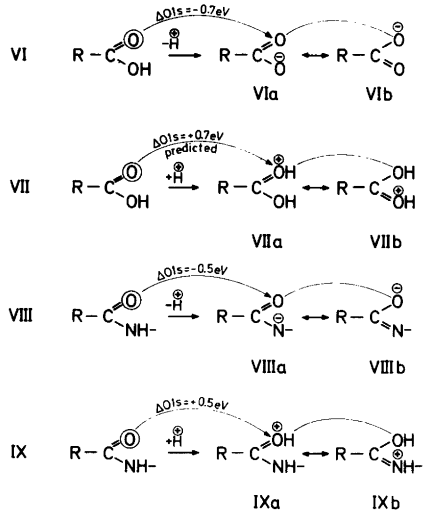
Hydroxyl oxygen. If we assume $N-H$ acidity for the benzohydroxamic acids we would expect to find the O1*s* $-OH$ component shifted according to the weight of the limiting structures IVa, b. Limiting structure IVa would require a slight shift towards lower binding energies due to a negatively charged adjacent nitrogen. For the unsubstituted benzohydroxamic acid, however, this component suffers a large shift (-2.5 eV), which is of the same magnitude as the salt shift for benzoic acid (-2.0 eV, Fig. 3). This is more consistent with $O-H$ acidity (IVc) which would be further supported by the smaller N1*s* salt shift (-1.0 eV) for the unsubstituted benzohydroxamic acid as compared with that of the 4-nitrosubstituted acid (-2.2 eV). This shift as well as the still smaller carbonyl shift (-0.5 eV) could well be explained as a potential effect caused by the neighbouring negative oxygen in IVc. These results indicate different tautomeric forms for 4-nitrobenzohydroxamate and benzohydroxamate in the solid state. Other spectroscopic and p*K* investigations indicate that in solution stronger hydroxamic acids are with certainty pure N-acids while in the weaker ones some O-dissociation may take place.[3,5] A more definite interpretation of the O1*s* as well as the N1*s* shifts in the salts would require knowledge of the crystal structure and a better understanding of the lattice effects on the ESCA shifts.

Benzohydroxamic acid. The protonated benzohydroxamic acid has previously been assumed to have structure Va↔Vb.[4] The N1*s* shift between the

acid and its protonated form (+2.5 eV) would in this case be consistent with a considerable weight of limiting structure Vb, *i.e.* O-protonation. A large N1*s* shift would, however, also be consistent with structure Vc, *i.e.* N-protonation. This is, however, less likely because of the loss of conjugation in this structure.[4]

The O1*s* component in the carbonyl region can be discussed in more detail on the basis of the carboxylic acid–carboxylate model VI (Scheme 3). Because of the symmetry of the anion VIa, b the carbonyl O1*s* salt shift (−0.7 eV) may serve as a standard salt shift for anions, where the limiting structures of type VIIIa↔VIIIb have equal weight. The smallness of this shift indicates a considerable counter ion effect. The creation of half a negative charge unit on oxygen would in a free ion be expected to cause a shift of about −3 eV.[6c] By analogy the O1*s* shift for a protonated carboxyl group (VII) would reasonably be expected to have the same magnitude but in the opposite direction. This may similarly serve as a standard salt shift for a protonation, where the limiting structures of the cations IXa↔IXb have equal weight.

The aromatic amidic compounds under investigation are of similar size and shape as the benzoic acid models Nos. *1a, b*. It thus seems reasonable to assume similar lattice effects. By analogy similar carbonyl O1*s* shifts would thus be expected for compounds of type VI/VIII and VII/IX, respectively. The difference of −0.5 eV between Ia and IIa, b (Scheme 1) may thus serve as a standard shift for VIII. We would thus expect a shift of about +0.5 eV for IX. Consequently the carbonyl shift of +0.5 eV for protonated benzohydroxamic acid would be consistent with structure Va↔Vb.



Scheme 3. Carbonyl groups.

SUMMARY

1. Cyanobenzamides and 4-nitrobenzohydroxamic acid have similar N1*s* and O1*s* salt shifts indicating similar structures with similar charge delocalization patterns for the corresponding anions.

2. *Cyanobenzamides.* The O1*s* salt shift indicates a delocalization of the negative charge in the anion to the carbonyl oxygen (IIa, b), similar to that occurring in carboxylate anions. The N1*s* shift of cyano nitrogen indicates negligible contribution of IIc.

3. *Benzohydroxamic acid.* The N1*s* salt shift for 4-nitrobenzohydroxamic acid is consistent with N–H acidity and delocalization of the charge to the carbonyl oxygen in the anion (IVa, b).

A smaller N1*s* salt shift for the unsubstituted benzohydroxamic acid could account for O–H acidity, which is also favoured by the O1*s* shift of the −OH group. For protonated benzohydroxamic acid the shifts are reversed when compared to the corresponding alkali salt shifts. The carbonyl O1*s* shift in conjunction with the N1*s* shift suggests O-protonation with a considerable delocalization of the positive charge to nitrogen (Va, b).

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