

SUBSTITUTION EFFECTS IN ISOMERIC *para* AND *meta* DERIVATIVES OF BENZONITRILE REVEALED BY UV PHOTOELECTRON SPECTROSCOPY

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The UV photoelectron spectra of isomeric *para* and *meta* derivatives of benzonitrile with substituents NO₂, COCH₃, Cl, Br, CH₂I and NH₂ were measured. Their assignment was carried out with the aid of MNDO calculations. The splitting of the highest π orbitals $e_{1g}S$, $e_{1g}A$ is in all *para* derivatives greater than in their *meta* isomers, the greatest difference of splittings 0.25 eV being caused by the amino group. The level ordering $e_{1g}S$, A exists in all molecules except *meta* NO₂ and COCH₃ derivatives where it is believed to be reverse. The $\pi'_{CN} - \pi_{CN}$ splitting keeps nearly constant and it is close to that in benzonitrile. The ionization potentials of σ orbitals $e_{1u}S$, $e_{1u}A$, b_{2u} and b_{1u} in *meta* NO₂ derivative are, in agreement with our expectation, higher than in benzonitrile. It is not true for *para* isomer where on the contrary, they are lower and they differ from *meta* isomer by 0.7–1.8 eV.

Effects exerted by substituents upon the benzene ring have been studied extensively by UV photoelectron spectroscopy since this method enables the direct observation and at least qualitative or even semiquantitative evaluation of them. The resonance effect may be appreciated by the magnitude of splitting of the benzene e_{1g} orbitals while the inductive effect manifests itself most markedly by shifts of ionization potentials.

This paper aims to demonstrate substitution effects in some derivatives of benzonitrile and to compare them between series of *meta* and *para* isomers. In order to cover a relatively wide range of substituent donor–acceptor abilities (quantified by their σ constants) we chose following substituents: NO₂, COCH₃, Cl, Br, CH₂I and NH₂. Interpreting the photoelectron spectra we came from the assignment of the benzonitrile spectrum which was carried out with the aid of MNDO calculations and is in agreement with the *ab initio* assignment of Kimura and coworkers¹. It is worth noting, however, that other authors interpret the benzonitrile spectrum slightly differently^{2,3}. MNDO calculations were also made for the derivatives excluding those containing halogens Br and I since the parametrization was not available.

EXPERIMENTAL AND COMPUTATIONAL

The photoelectron spectra were recorded on the UVG 3 spectrometer with a resolution of 40 to 50 meV using the He I line for excitation. The inlet system temperature varied from 40° to 130°C depending on a type of the compound. The spectra were calibrated with argon/xenon mixture. All samples were prepared and characterized by methods described in literature⁴.

The calculations were carried out with an ICL 4-72 computer using the modified MNDO programme. The geometry of benzonitrile was taken from literature⁵ and was also applied to derivatives. They were assumed to be planar for substituents NO₂, COCH₃ and Cl and standard bond lengths and angles of substituents were taken into account. Considering the amino group to be more conjugated in *para* position than in *meta* position we used in *para* derivative the planar amino group having the ring-nitrogen bond length 0.137 nm (see *p*-nitroaniline⁶) and the H-N-H angle 120° while the aniline-like geometry⁷ was assumed in *meta* derivative.

RESULTS AND DISCUSSION

The PE spectra of *para* and *meta* substituted benzonitriles are shown in Fig. 1. Their assignment, together with that of the benzonitrile spectrum, is given in Table I and II. The estimated error of *IP*'s is 0.03 eV for values given to two decimal places and does not exceed 0.1 eV for those given to one decimal place. The *IP*'s are the vertical ones. The molecular orbitals except those belonging to substituents are classified in the C_{2v} group for *para* and in the C_s group for *meta* derivatives. Their benzene or C≡N character is given in parentheses.

It can be seen that the benzene *e*_{1g} orbitals are the highest ones excluding acetyl derivatives where they interfere with nonbonding C=O orbital whose peak is the most intense in this band group. The ordering of benzene orbitals is *e*_{1g}*S, A* in all *para* derivatives and is the same as in benzonitrile. This result can be expected since in *para* derivatives the *e*_{1g}*A* orbital is not influenced by the substituent resonance effect, due to its node in *para* position. The splittings of *e*_{1g} orbitals 0.41 and 0.40 eV in *para* derivatives with substituents NO₂ and COCH₃ possessing weak resonance effect are very similar to that in benzonitrile (0.46 eV). The *e*_{1g} orbitals are only inductively shifted to higher *IP*'s in comparison with benzonitrile. The stronger resonance effect is seen in *para* derivatives with substituents Cl, Br and CH₂I causing splitting 0.72, 0.75 and 0.75 eV respectively, while donor amino group increases the splitting to 1.34 eV.

The situation in *meta* isomers is rather different because here the resonance effect may influence both *e*_{1g} orbitals. This should lead to decrease of splitting comparing with *para* derivatives. The MNDO calculations indicate that the ordering *e*_{1g}*S, A* is kept in derivatives with donor substituents Cl and NH₂ while the reverse ordering is caused by acceptors NO₂ and COCH₃. The *e*_{1g} splittings in the series of *meta* derivatives are indeed lower than in *para* one and are following: NO₂ -0.40, COCH₃ -0.28, Cl 0.52, Br 0.56, CH₂I 0.61 and NH₂ 1.09 eV (negative sign denotes the *e*_{1g}*A, S* ordering). The assumed reversal of ordering for NO₂ and COCH₃ derivatives

is likely to be caused by inductive effect and it would be supported by finding such a substituent which would produce a negligible splitting when placed in the *meta* position.

The next remarkable effect is a drastic change of calculated e_{1g} electron densities occurring when going from *para* to *meta* isomer. The *para* derivatives possess exact or only slightly perturbed C_{2v} symmetry (with the axis lying in the $C\equiv N$ bond) which is, of course, obeyed by e_{1g} orbitals. In *meta* derivatives the C_{2v} symmetry is lowered to C_s and hence we would expect a substantial perturbation of e_{1g} orbitals

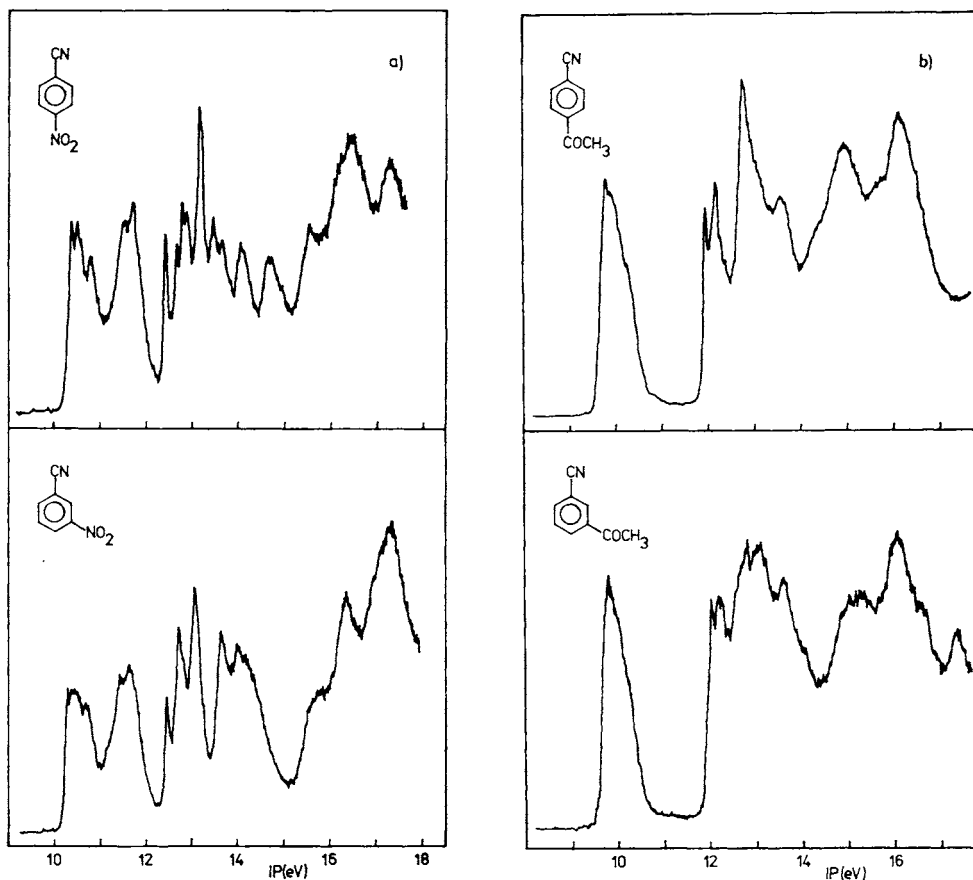
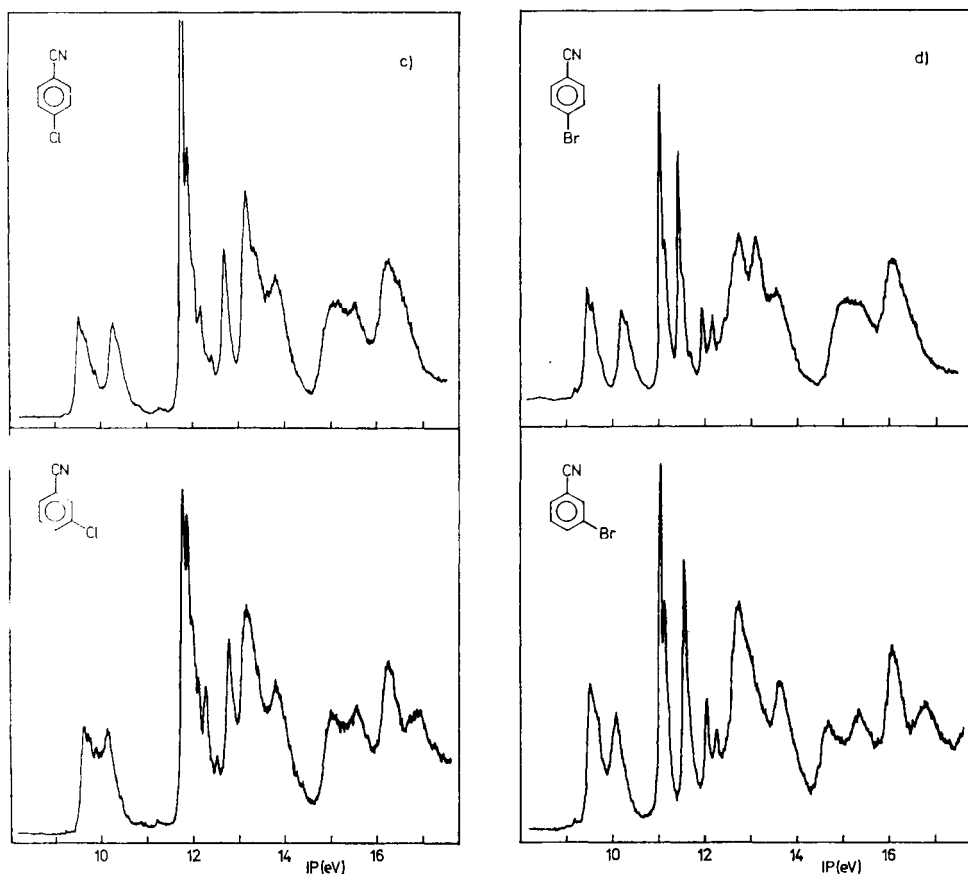


FIG. 1

He I photoelectron spectra of a) *p*- and *m*-nitrobenzonitrile, b) *p*- and *m*-acetylbenzonitrile, c) *p*- and *m*-chlorobenzonitrile, d) *p*- and *m*-bromobenzonitrile, e) *p*- and *m*-iodomethylbenzonitrile, f) *p*- and *m*-aminobenzonitrile

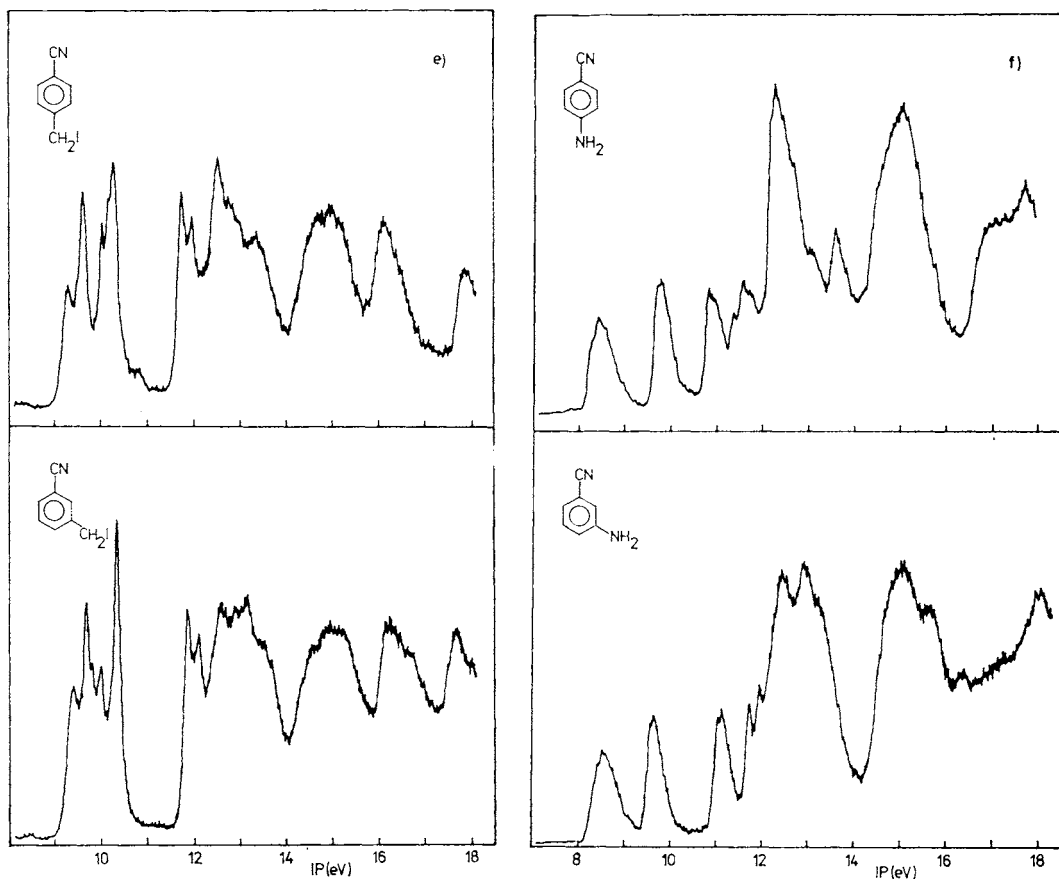
in a corresponding manner. However, the e_{1g} orbitals obey the slightly perturbed C_{2v} symmetry again but the axis lies now in the ring-substituent bond. So we may judge that the e_{1g} orbitals in *meta* derivatives are much more strongly affected by a substituent than by the cyano group. Their symmetry is likely to be controlled by substituent resonance effect because the perturbation increases from NH_2 to NO_2 . Moreover, no similar results exist for σ orbitals satisfying always C_s symmetry and thus making their description in terms of benzene orbitals sometimes difficult.

Rather unexpected result concerns the splitting of $C\equiv N$ orbitals π'_{CN} (in-plane) and π_{CN} (out-of-plane) which is always small and keeps nearly constant for both *para* and *meta* derivatives. The values range from 0.26 to 0.15 eV and are very close to that for benzonitrile (0.25 eV). Nevertheless, the *IP*'s are strongly dependent on a substituent and so we can derive that both $C\equiv N$ orbitals are influenced by the



substitution but to a very similar extent. This conclusion, however, is somewhat surprising since one would hardly suppose that *IP*'s of orbitals subjected to different interactions with a substituent will be equally shifted.

The highest benzene σ orbitals e_{2g} are nearly degenerate in benzonitrile. In the *meta* series it is true only for the bromo derivative while the others exhibit splittings from 0.27 to 0.57 eV and calculations predict $e_{2g}S, A$ ordering. The *para* derivatives are affected to a lower extent since the substituents COCH_3 , Br and CH_2I cause no splitting. The e_{2g} orbitals are split in NO_2 and NH_2 derivatives but substantially less than in *meta* isomers and the calculated ordering is reversed. There is a striking similarity between both Cl isomers manifesting itself by near e_{2g} splittings 0.46 and 0.38 eV and by identical $e_{2g}S, A$ ordering. The same is valid for Br isomers where, however, e_{2g} orbitals remain unsplit. So we can point out that in both series there is a remarkable difference between the behaviour of Cl and Br with respect



to e_{2g} orbitals. Looking at the spectra of Cl derivatives we observe an intense peak at 12.73 and 12.76 eV respectively which is assigned to $e_{2g}S$ orbital while this peak is missing completely in spectra of Br derivatives.

Some difficulties arise when interpreting the spectra of nitro derivatives in higher IP region, where benzene σ orbitals $e_{1u}S$, $e_{1u}A$, b_{2u} , b_{1u} and π and σ orbital of the nitro group should lie. The MNDO results are not reliable enough but in both cases they predict the IP's of benzene orbitals to be higher than in benzonitrile and other derivatives. This behaviour is seen in the spectrum of *meta* derivative where the band group between approximately 15.8 and 17.1 eV can be assigned to benzene σ orbitals though they interfere with orbitals of the nitro group. On the other hand the spectrum of *para* derivative exhibits two remarkable peaks at 14.03 and 14.66 eV which cannot

TABLE I

The assignment of PE spectra of *para* substituted benzonitriles. The substituent is given in the head of each column. The IP's of benzonitrile¹ are presented in the last column for comparison. The lower part of the Table presents the IP's of substituent orbitals

Orbital	IP, eV						
	NO ₂	COCH ₃	Cl	Br	CH ₂ I	NH ₂	H
$b_1(e_{1g}S)$	10.35	9.90	9.54	9.45	9.28	8.46	9.71
$a_2(e_{1g}A)$	10.76	10.30	10.26	10.20	10.03	9.80	10.17
$b_2(\pi_{CN})$	12.38	11.96	12.22	11.94	11.74	11.38	11.84
$b_1(\pi_{CN})$	12.63	12.18	12.45	12.17	11.97	11.61	12.09
$b_2(e_{2g}A)$	12.75	12.76	13.19	12.77	12.50	12.31	12.61
$a_1(e_{2g}S)$	13.13	12.76	12.73	12.77	12.50	12.70	12.61
$b_1(a_{2u})$	13.43	13.58	13.40	13.11	12.8	13.05	13.04
$a_1(n_{CN})$	13.62	13.58	13.85	13.54	13.35	13.61	13.46
$b_2(e_{1u}A)$	14.03	14.95	15.16	15.02	14.8	14.6	14.75
$a_1(e_{1u}S)$	14.66	15.7	15.58	15.40	14.8	15.1	15.36
$b_2(b_{2u})$	15.51	16.13	16.30	15.07	16.10	15.1	15.75
$a_1(b_{1u})$	16.40	16.13	16.60	16.07	16.10	16.9	16.55
n	11.30	9.80	11.79 11.91	11.04 11.45	9.60 10.27	10.86	
σ	11.50 11.68 16.40	13.15 14.4			12.8 14.8	17.3	
π	16.1	13.00 14.95					

be assigned to any orbital lying higher than e_{1u} orbitals. The alternative of assigning these peaks to nitro group π and σ orbital was rejected because the calculations in both derivatives confirm they lie much lower than e_{1u} orbitals. Moreover, these nitro group orbitals are known to have IP 's between 16 and 17.5 eV (see nitrobenzene⁸ or nitromethane¹) in agreement with positions in the *meta* derivative. Their shift to the region 14–15 eV when placing the nitro group to *para* position is not likely to occur. So we must conclude that peaks at 14.03 and 14.66 eV belong to split e_{1u} orbitals which are followed by b_{2u} and b_{1u} orbitals at 15.51 and 16.40 eV, respectively. These IP 's are lower than in benzonitrile and they differ from those in *meta* isomer by 0.7–1.8 eV. This effect was not observed in any other couple of isomers and is apparently characteristic only for the nitro group.

I would like to express my gratitude to Professor O. Exner for supplying the samples.

TABLE II

The assignment of PE spectra of *meta* substituted benzonitriles. The substituent is given in the head of each column. The lower part of the Table presents the IP 's of substituent orbitals

Orbital	IP , eV					
	NO ₂	COCH ₃	Cl	Br	CH ₂ I	NH ₂
$a''(e_{1g}S)$	10.71	10.27	9.61	9.53	9.38	8.53
$a''(e_{1g}A)$	10.31	9.99	10.13	10.09	9.99	9.62
$a'(\pi_{CN})$	12.46	12.04	12.27	12.05	11.86	11.71
$a''(\pi_{CN})$	12.72	12.19	12.51	12.27	12.10	11.93
$a'(e_{2g}S)$	13.07	12.79	12.76	12.72	12.59	12.41
$a'(e_{2g}A)$	13.64	13.06	13.14	12.72	13.11	12.90
$a''(a_{2u})$	14.01	13.59	13.30	12.89	13.11	12.90
$a'(n_{CN})$	14.30	14.0	13.79	13.64	13.46	13.20
$a'(e_{1u}A)$	15.8	15.2	14.97	14.68	15.0	15.0
$a'(e_{1u}S)$	15.8	16.04	15.52	15.33	15.0	15.0
$a'(b_{2u})$	16.34	16.04	16.21	16.06	16.23	15.0
$a'(b_{1u})$	17.10	16.6	16.84	16.79	16.61	15.60
n	11.30	9.79	11.76 11.84	11.04 11.55	9.67 10.32	11.11
σ	11.44 11.66 17.31	13.06 15.2			12.90 14.5	16.33
π	17.10	12.79 15.2				

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