Electronic structure of monosubstituted benzenes and X-ray emission spectroscopy

2.* Benzonitrile

V. D. Yumatov[a]* *and N. F. Salakhutdinov*[b]

[a]*Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences,*
3 prosp. Akad. Lavrent'eva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383) 235 5960
[b]*Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences,*
9 prosp. Akad. Lavrent'eva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383) 235 4752

The electronic structure of benzonitrile has been studied by X-ray spectroscopy. N-Kα and C-Kα spectra were recorded. The corresponding theoretical spectra were constructed on the basis of MNDO calculations. The molecular orbitals (MO) of benzonitrile have been compared with those of benzene and hydrogen cyanide. The p_π—p_π-interaction between the phenyl fragment and the cyano group has been studied. The contribution of the latter to the highest occupied orbitals of the molecule was shown to be small.

Key words: X-ray emission; N-Kα-spectra; C-Kα-spectra; MNDO; benzonitrile.

It has been shown previously[1] that the contribution of the formyl substituent to the highest occupied molecular orbital (HOMO) of benzaldehyde is insignificant. This compound is known to be a representative of $-M$ substituted benzenes. Benzonitrile also belongs to this class of compounds. In the present work we have studied the structure of this molecule by X-ray emission spectroscopy. The structure of the HOMO and the role of the atomic orbitals (AO) of the cyano group in its formation are of particular interest.

Experimental

The X-ray equipment has been described previously.[1] The N-Kα spectrum of benzonitrile was studied in the solid phase. An OHM crystal was used as the analyzer crystal ($2d$ = 2.35 nm).[2] The same crystal was used for recording the C-Kα spectrum of solid C_6H_5CN (C-Kα(OHM)) according to the known procedure.[3] To confirm te choice of the algorithm for correcting the experimental spectrum recorded for the gas phase using a NH_4AP analyzer crystal (C-Kα(NH_4AP)) an additional C-Kα spectrum was recorded. The procedure for correcting the spectrum that takes the efficiency of the crystal into account,[4] and the procedures for recording the spectra in the gas phase and for calibration[1] have been described previously. The use of OHM for the analysis of the emission of benzonitrile in the gaseous phase made no sense, because it caused a sharp decrease in the intensity with no substantial improvement of the resolution.

The spectra were calibrated (an OHM crystal) using the Al-K$\alpha_{1,2}$ line; in the case of the N-Kα spectrum, the third- and the fourth-order reflections were used, and for the C-Kα spectrum the sixth-order reflection was used. In the latter case, the C-Kα band of graphite was also used. The wavelengths of the calibration lines were taken from the literature.[5] The root-mean-square error in the energetic location of the N-Kα and C-Kα bands of benzonitrile in the solid state was ±0.5 eV; that in the gaseous phase was ±0.2 eV. The procedure for smoothing the spectra was reported previously.[1]

Results and Discussion

To understand the character of the electronic interactions in benzonitrile let us consider the structure of the MO of hydrogen cyanide, since it resembles the corresponding fragment of C_6H_5CN. HCN ($C_{\infty v}$ symmetry) has been investigated previously by photoelectron spectroscopy (PES)[6] and X-ray photoelectron spectroscopy (XES).[7] Quantum-chemical calculations were also carried out (for example, see Ref. 6). The HOMO 1π energy level is twice degenerate and is responsible for the π-bonds between the carbon and nitrogen atoms. The 5σ MO ($C2p_\sigma$—$N2p_\sigma$) is immediately adjacent to it. The 4σ and the 3σ MO consist predominantly of the C2s and N2s AO, and the 2σ and the 1σ MO are mostly built of the C1s and the N1s AO. The electronic structure of the benzene molecule (D_{6h} symmetry) has been described in detail previously.[6]

Benzonitrile (C_{2v} symmetry) has been studied by PES[6,8–10] and XES;[7] quantum-chemical calculations

---

* For part 1, see Ref. 1.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1251—1254, July, 1994.

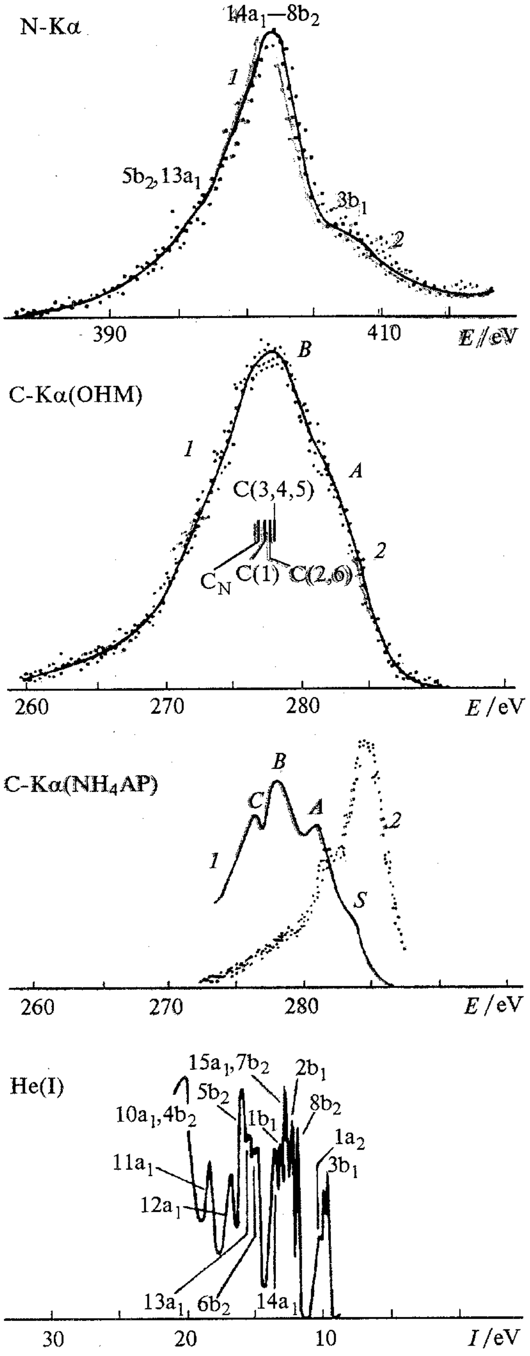

Fig. 1. The X-ray and photoelectron (He(I)) spectra of C_6H_5CN: the experimental spectrum (points (*1*)); the smoothed spectrum (the C-Kα(NH_4AP) spectrum corrected to allow for the efficiency of the analyzer crystal) (solid line (*2*)).

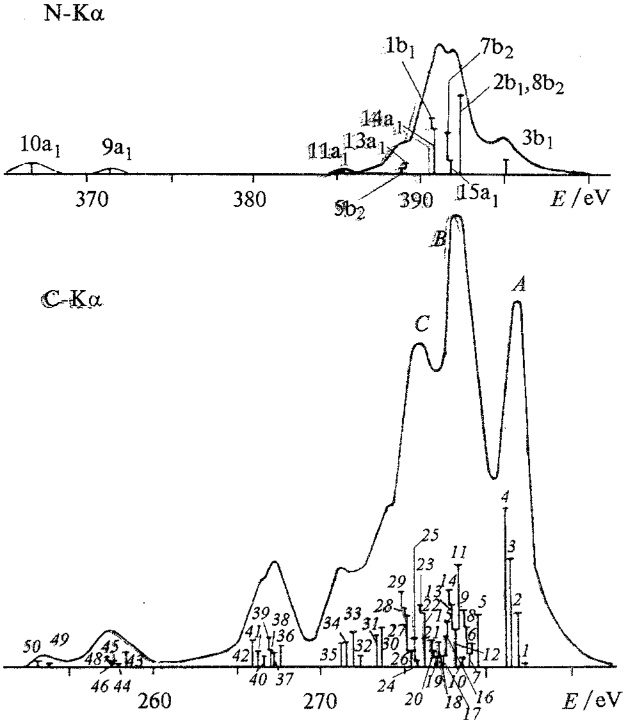

Fig. 2. Theoretical X-ray spectra of PhCN (identification of the lines is presented in Table 1).

have also been carried out.[6,8–11] The X-ray emisson spectra are presented in Fig. 1, along with the photoelectron spectrum.[6] All of the spectra were converted to a unified energy scale of ionization potentials (*I*) according to the standard procedure (see, for example, Ref. 12). The theoretical X-ray spectra of benzonitrile based on the results of MNDO calculations are shown in Fig. 2. The procedure for their construction has been reported previously.[1] The half-widths of the separate lines used in this procedure were selected empirically. They amounted to ~3 eV for the N-Kα spectrum and ~1.2 eV for the C-Kα spectrum.

As was noted previously,[1] in the analysis of the C-Kα spectra of monosubstituted benzenes, one should take into account the fact that the carbon atoms of the phenyl ring (C(1), C(2,6), C(3,5), and C(4)) have different energies of the 1s levels due to their nonequivalent location with respect to the substituent. In benzonitrile, the 1s level of the carbon atom of the substituent (C_N) can also be distinguished. Several values for all of the 1s levels have been reported; we used the average of these values. The mutual adjustment of the photoelectron and the C-Kα spectra was carried out relative to the C(4)1s level, which coincides in energy with the C(3,5)1s level. Hence, hereinafter, they will be referred to as C(3,4,5)1s and used to bring the theoretical spectra into coincidence with each other. The application of other C1s levels is also valid. The vertical lines in Fig. 1 correspond to the position of maximum *B* in the C-Kα spectrum, when the adjustment is carried out with various C1s levels of benzonitrile.

Let us interpret the experimental X-ray spectra using quantum-chemical calculations. Notice that the MO with symmetries a_1 and b_2 belong to the σ system, and the a_2 and b_1 MO belong to the π-system. Based on group-theory analysis, the following characteristic fea-

Table 1. The identification of lines in the theoretical C-Kα spectrum of benzonitrile shown in Fig. 2

Line	Transition	Line	Transition
1	$3b_1 \rightarrow C_N1s$	*24*	$13a_1 \rightarrow C(1)1s$
2	$3b_1 \rightarrow C(1)1s$	*25*	$5b_2 \rightarrow C(1)1s$
3	$3b_1, 1a_2 \rightarrow C(2,6)1s$	*26*	$13a_1 \rightarrow C(2,6)1s$
4	$3b_1 \rightarrow C(3,4,5)1s$	*27*	$5b_2 \rightarrow C(2,6)1s$
	$1a_2 \rightarrow C(3,5)1s$	*28*	$13a_1 \rightarrow C(3,4,5)1s$
5	$8b_2, 2b_1 \rightarrow C_N1s$	*29*	$5b_2 \rightarrow C(3,4,5)1s$
6	$8b_2, 2b_1 \rightarrow C(1)1s$	*30*	$12a_1 \rightarrow C(2,6)1s$
7	$15a_1 \rightarrow C_N1s$	*31*	$12a_1 \rightarrow C(3,4,5)1s$
8	$7b_2 \rightarrow C_N1s$	*32*	$11a_1 \rightarrow C_N1s$
9	$8b_2, 2b_1 \rightarrow C(2,6)1s$	*33*	$11a_1 \rightarrow C(1)1s$
10	$15a_1 \rightarrow C(1)1s$	*34*	$11a_1 \rightarrow C(2,6)1s$
11	$8b_2, 2b_1 \rightarrow C(3,4,5)1s$	*35*	$11a_1 \rightarrow C(3,4,5)1s$
	$7b_2 \rightarrow C(1)1s$	*36*	$4b_2 \rightarrow C(1)1s$
12	$15a_1 \rightarrow C(2,6)1s$	*37*	$4b_2 \rightarrow C(2,6)1s$
13	$7b_2 \rightarrow C(2,6)1s$	*38*	$10a_1 \rightarrow C_N1s$
	$1b_1 \rightarrow C_N1s$	*39*	$4b_2 \rightarrow C(3,4,5)1s$
14	$14a_1 \rightarrow C_N1s$	*40*	$10a_1 \rightarrow C(1)1s$
	$15a_1 \rightarrow C(3,4,5)1s$	*41*	$10a_1 \rightarrow C(2,6)1s$
15	$7b_2 \rightarrow C(3,4,5)1s$	*42*	$10a_1 \rightarrow C(3,4,5)1s$
16	$1b_1 \rightarrow C(1)1s$	*43*	$9a_1 \rightarrow C_N1s$
17	$14a_1 \rightarrow C(1)1s$	*44*	$3b_2 \rightarrow C(1)1s$
18	$1b_1 \rightarrow C(2,6)1s$	*45*	$9a_1 \rightarrow C(2,6)1s$
19	$14a_1 \rightarrow C(2,6)1s$	*46*	$3b_2 \rightarrow C(2,6)1s$
20	$1b_1 \rightarrow C(3,4,5)1s$	*47*	$9a_1 \rightarrow C(3,5)1s$
21	$14a_1 \rightarrow C(3,4,5)1s$	*48*	$3b_2 \rightarrow C(3,4,5)1s$
	$6b_2 \rightarrow C(1)1s$	*49*	$8a_1 \rightarrow C_N1s$
22	$6b_2 \rightarrow C(2,6)1s$	*50*	$8a_1 \rightarrow C(2,6)1s$
23	$5b_2 \rightarrow C_N1s$	*51*	$8a_1 \rightarrow C(3,4,5)1s$
	$6b_2 \rightarrow C(3,4,5)1s$		

tures of the conjugation of the phenyl ring with the substituent can be established: one of the π-orbitals of the CN group is antisymmetrical with respect to the reflection in the plane of the molecule (it correlates with the $1\pi_{\perp}$ MO of HCN) and can only interact with those π-orbitals of the phenyl ring whose structures are close to those of the $1e_{1g}$ and $1a_{2u}$ MO of benzene; the other π-orbital lies in the plane of the molecule (it correlates with the $1\pi_{\|}$ MO of HCN) and only conjugates with the antisymmetric σ orbitals of the phenyl group like the $3e_{2g}$As, $3e_{1u}$As, and $1b_{2u}$ MO of benzene; finally, the σ orbitals of the cyano group (they correlate with the 5σ-, 4σ-, and 3σ-MO of HCN) interact with the symmetrical σ-orbitals of the phenyl ring, which are, in turn, comparable with the $3e_{2g}$S, $3e_{1u}$S, $2b_{1u}$, and $3a_{1g}$ MO of benzene. Notice that π-conjugation can also be observed in the plane of the molecule, for example, between the 2p-AO of the cyano group and the MO with b_2 symmetry.

According to the quantum-chemical calculations, the $3b_1$ and $1a_2$ π-MO, which are mostly composed of the $2p_{\pi}$-AO of the carbon atoms of the phenyl ring, are the highest occupied orbitals. The nature of the $3b_1$ MO is close to the $1e_{1g}$S MO of benzene, and that of the $1a_2$ MO is close to the $1e_{1g}$As MO of benzene. According to MNDO calculations, the contribution of AO of the CN fragment to the $3b_1$ MO is small (≈8 %). Such low participation of AO of the substituent in the $3b_1$ MO may be explained by the fact that the interaction between the orbital of the phenyl fragment (like the $1e_{1g}$S MO of benzene) and the orbital of the substituent (comparable to the $1\pi_{\perp}$ MO of HCN) is insignificant owing to the great difference between their energies. Actually, as shown by PES,[6] the first ionization potential of benzene is 9.25 eV ($1e_{1g}$) and that of hydrogen cyanide is 13.6 eV (1π). The $1a_2$ MO, which is entirely composed of the $2p_{\pi}$-AO of the phenyl carbon atoms, does not interact with the π-system of the cyano group due to the difference in their symmetries. The two above-considered MO are responsible for the *A* band in the C-Kα spectrum (see Figs. 1 and 2). The *S* band is probably associated with the intrinsic fluorescence of the analyzer crystal.

The similarity of the C-Kα spectra of benzene and benzaldehyde has already been noted.[1] In the case of benzene, the line with the highest energy (the *E* scale of energy of transitions) corresponds to the $1e_{1g}$ MO level, which splits in the case of C_6H_5CN due to the decrease in the symmetry ($D_{6h} \rightarrow C_{2v}$): $1e_{1g} \rightarrow 3b_1 + 1a_2$. The *A* band in the C-Kα spectrum corresponds to the $3b_1$ and $1a_2$ MO; this is confirmed by the theoretical spectrum (see Figs. 1 and 2), and its high-energy part (scale *E*) most likely results from the $3b_1 \rightarrow C(1)1s(3a_1)$ and $3b_1 \rightarrow C_N1s(2a_1)$ transitions. However, the contribution of the C_N2p_{π} AO to the $3b_1$ MO is small (≈1 % according to MNDO), and, therefore, the intensity of the latter transition is rather low. In the N-Kα spectrum, the $3b_1$ MO must account for the small high-energy peak (see Figs. 1 and 2), which, after adjustment, coincides with the *A* band in the C-Kα spectrum and with the first broad band with a rather complex structure in the PES.

Thus, the X-ray spectroscopic experiment supports the statement inferred from the theoretical studies that the participation of the N2p-AO in the HOMO is small. In fact, a substantial proportion of the 2p-AO of the nitrogen atom in the $3b_1$ MO would have resulted in the appearance of an intense line, rather than a small maximum, in the N-Kα spectrum (see Fig. 1).

The next levels in order of increasing energy (the scale of ionization potentials *I*) are: $8b_2$, $2b_1$, $7b_2$, $15a_1$, $1b_1$, and $14a_1$ MO. All of these are responsible for the second broad band in the PES. After the adjustment this band coincides with the *B* band in the C-Kα spectrum and the dominant line in the N-Kα spectrum (see Figs. 1 and 2). The considerable intensity of the latter indicates that the contribution of the 2p-AO of the nitrogen atom to these MO is the greatest. The similar peaks in the photoelectron spectrum and in the C-Kα spectrum of benzene are due to the $3e_{2g}$ and $1a_{2u}$ MO. This group of MO in benzonitrile may arise due to the removal of degeneracy in going from C_6H_6 to C_6H_5CN and to the interaction of the orbitals of the phenyl fragment (similar to the $3e_{2g}$ and $1a_{2u}$ MO of benzene) with the orbitals of the cyano group, which are allowed in terms of symmetry.

The $2b_1$ and $1b_1$ MO reflect the conjugation of the π-orbital of the phenyl ring (it matches the $1a_{2u}$ MO of benzene) with the orbital of the cyano group (similar to the $1\pi_\perp$-MO of hydrogen cyanide). Figure 3 illustrates the results of the analysis of the π-orbitals of benzonitrile. The $8b_2$ and $7b_2$ MO belong to the π-system lying in the plane of the molecule. They are antibonding and bonding combinations of the MO of the phenyl fragment (similar to the $3e_{2g}$As MO of benzene) and the MO of the cyano group (similar to $1\pi_{\|}$-MO of HCN). The $8b_2$ MO is mostly concentrated at the CN fragment, while the $7b_2$ MO is localized at the benzene ring, as follows from *ab initio* calculations (see, for example, Ref. 6). However, according to the MNDO method, these two MO are approximately uniformly delocalized.[11] The $15a_1$ and $14a_1$ σ-MO result from mixing of orbitals of the phenyl ring with orbitals of the cyano group, which match with the $3e_{2g}$S MO of benzene and the 5σ-MO of hydrogen cyanide, respectively. The 2s-AO of the nitrogen atom significantly contributes to the $14a_1$ MO. This points to an admixture of a deeper orbital of the substituent (similar to the 3σ-MO of HCN).

The $6b_2$, $13a_1$, $5b_2$, and $12a_1$ MO of benzonitrile correspond to the third broad PES band, which coincides with the *C* line in the C-Kα spectrum and with the low-energy (the *E* scale) part of the N-Kα spectrum (see Figs. 1 and 2). Similar peaks in the photoelectron and the C-Kα spectra of benzene are attributed to the $3e_{1u}$, $1b_{2u}$, and $2b_{1u}$ MO. Thus, the following correlations have been established: the $6b_2$ MO correlates with the $3e_{1u}$As orbital of benzene, the $13a_1$ MO correlates with the $3e_{1u}$S-orbital of benzene, the $5b_2$ MO correlates with the $1b_{2u}$-orbital of benzene, and the $12a_1$ MO correlates with the $2b_{1u}$ MO of benzene.

According to nonempirical calculations,[6] MO of this group are predominantly localized at the phenyl fragment. Consequently, the low-energy constituent of the N-Kα spectrum corresponding to the transition from the above-listed MO to the N1s-orbital has low intensity (see Figs. 1 and 2). The deeper MO of benzonitrile, *viz.*, $11a_1$, $4b_2$, $10a_1$, $3b_2$, $9a_1$, $8a_1$, and $7a_1$ MO, comprise mainly the C2s and N2s AO and manifest themselves in the extended low-energy structure (the *E* scale) of the spectra, which is due to the presence of slight admixtures of N2p and C2p AO in these MO.

Thus, the π-system of benzonitrile (antisymmetric with respect to the reflection in the plane of the molecule) involves four MO: $3b_1$, $1a_2$, $2b_1$, and $1b_1$. The two higher MO correlate predominanly with the $1e_{1g}$ MO of benzene. The contribution of the AO of the substituent to the $1a_2$ and $3b_1$ MO is small. The $2b_1$ and $1b_1$ MO may be regarded as antibonding and bonding combinations of the π-orbitals of the phenyl fragment and the cyano group (see above). The $3b_1$ and $1a_2$ MO of benzonitrile are stabilized to a greater extent than the $1e_{1g}$ MO of benzene, which may be explained, as previously,[1] by the inductive effect. The electron density in this system is transferred from the phenyl ring to the more electronegative substituent. As a consequence, the C atoms of the phenyl fragment of benzonitrile are more positively charged than in benzene. Therefore, the energies of the C1s levels of the C atoms in the phenyl ring are greater than in benzene, and the N1s levels in the CN substituent are also less stabilized than in HCN (see Ref. 7).

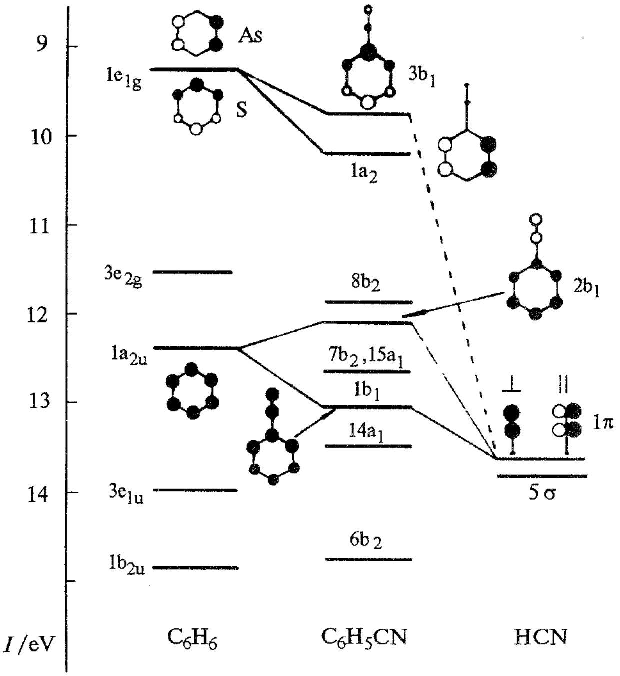

Fig. 3. The π-MO energy levels (for ionization potentials, see Ref. 6; the structure of the MO was determined by MNDO calculations).

In conclusion, the authors would like to thank Prof. D. S. Werch (Queen Mary College, London) who put the OHM crystals at their disposal.

References

1. V. D. Yumatov and N. F. Salakhutdinov, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1033 [*Russ. Chem. Bull.*, 1994, **43**, 968 (Engl. Transl.)].
2. I. W. Ruderman, K. J. Ness, and J. C. Lindsay, *Appl. Phys. Lett.*, 1965, **7**, 17.
3. V. D. Yumatov, Ph. D. (Chem.) Thesis, Inst. of Inorganic Chemistry, Siberian Branch, USSR Acad. Sci., Novosibirsk, 1976 (in Russian).
4. V. D. Yumatov, A. V. Okotrub, L. N. Mazalov, G. S. Belikova, and T. M. Okhrimenko, *Zh. Strukt. Khim.*, 1985, **26**, No 4, 59 [*J. Struct. Chem.*, 1985, **26** (Engl. Transl.)].
5. J. A. Bearden, *Rev. Mod. Phys.*, 1967, **39**, 78.

6. K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, and S. Iwata, *Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules*, Japan Scientific Societies Press, Tokyo, Halsted Press, New York, 1981, 270.
7. W. L. Jolly, K. D. Bomben, and C. J. Eyermann, *Atom. Data and Nucl. Data Tables*, 1984, **31**, 433.
8. J. W. Rabalais and R. J. Colton, *J. Electron Spectrosc. and Relat. Phenom.*, 1972/73, **1**, 83.
9. G. Bieri, L. Åsbrink, and W. von Niessen, *J. Electron Spectrosc. and Relat. Phenom.*, 1982, **27**, 129.
10. M. H. Palmer, W. Moyes, and M. Spiers, *J. Mol. Struct.*, 1980, **62**, 165.
11. V. V. Murakhtanov, L. N. Mazalov, and L. G. Bulusheva, *Zh. Strukt. Khim.*, 1989, **30**, No. 2, 31 [*J. Struct. Chem.*, 1989, **30** (Engl. Transl.)].
12. L. N. Mazalov and V. D. Yumatov, in *Elektronnoe stroenie ekstragentov* [*The Electronic Structure of Extragents*], Nauka, Novosibirsk, 1984, 26 (in Russian).

Received March 15, 1993;
in revised form February 15, 1994