



# PHOTOELECTRON SPECTROSCOPIC INVESTIGATION OF THE ELECTRONIC STRUCTURE OF FUROXANS

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Disubstituted furoxans, 1,2,5-oxadiazole-2-oxides ( $X_2C_2N_2O_2$ , where X= H, Cl, Br, I, CH<sub>3</sub>, NC), have been investigated in the gas phase by He I and He II UV photoelectron spectroscopy. Ionization potentials have been determined and the electronic structures have been discussed within the frame of molecular orbital theory. The ground-state geometries of the neutral molecules have been obtained from quantum-chemical calculations using the B3LYP/cc-pVTZ method. Photoelectron spectroscopy, supported by quantum-chemical calculations at the SAC-CI/cc-pVTZ level, provides a detailed investigation into the electronic character of the molecules and an analysis of the effect of substitution on the orbitals of the parent furoxan.

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## 1. Introduction

Furoxans (1,2,5-oxadiazole 2-oxides) are important compounds in various fields of chemistry, in particular in synthetic organic chemistry<sup>1-3</sup> and medicinal chemistry,<sup>4</sup> due to their unusual structure and reactivity, and biological activity. They are important synthetic precursors and found applications as high energy materials.<sup>5</sup> A better understanding of the electronic structure of these compounds may help to find further applications.

Although the first furoxan derivative, dibromofuroxan, was synthesized (unknowingly) in the middle of the 19<sup>th</sup> century, the general structure of furoxans as planar five-membered rings with an exocyclic *N*-oxide group was confirmed only after a century of debate.<sup>1,2</sup> Furoxans having small substituent groups, such as hydrogen or halogen atoms and cyano or methyl groups, are key to understanding properties and chemistry of all furoxans. The structures of only the parent,<sup>6</sup> dibromo,<sup>7</sup> and dicyanofuroxans<sup>8</sup> were confirmed to date by X-ray crystallography. Vibrational and electronic properties of small furoxans were investigated recently by IR,<sup>8-13</sup> Raman,<sup>8,11,13</sup> and photoelectron spectroscopies.<sup>8-11,13</sup>

The furoxan moiety, due to its electronegative atoms, usually characterized as electron-rich, and thus its structural description by theoretical methods is challenging. It was pointed out that the description of electronic structures of furoxans were sensitive to dynamical correlation effects<sup>13-15</sup> and the HF wave function was found to be unstable for the parent furoxan; therefore early calculations based on HF and MP2 methods must be regarded as artefacts.

Calculations on the parent furoxan and substituted derivatives indicate that density functional theory using the B3LYP functional can provide a correct description of the furoxan geometry.<sup>8,13,15,16</sup>

In this paper we report a comprehensive photoelectron spectroscopic study of furoxans ( $X_2C_2N_2O_2$ , where X= H, Cl, Br, I, CH<sub>3</sub>, NC) and an investigation of their equilibrium structures using density functional theory. Our previous He I photoelectron spectroscopic studies<sup>8-11,13</sup> are reinvestigated using higher instrumental resolution and are augmented with He II measurements. The experimental work is assisted by high level SAC-CI *ab initio* calculations.

## 2. Experimental section

All furoxan derivatives were synthesized according to known literature methods: the parent furoxan and its dimethyl<sup>17</sup> and dichloro<sup>18</sup> derivatives were synthesized from glyoxime, dimethylglyoxime, and dichloroglyoxime by oxidizing with NO<sub>2</sub> gas, concentrated nitric acid, and anhydrous nitric acid, respectively, dicyanofuroxan<sup>19</sup> from cyanoacetic acid with anhydrous nitric acid, dibromofuroxan<sup>20</sup> from oximinoacetic acid with bromine and HgO, diiodofuroxan from silver fulminate with iodine. The purity of samples was checked by NMR and IR measurements.

The He I and He II ultraviolet photoelectron spectra (UPS) of gaseous furoxans were recorded using an Atomki ESA-32 photoelectron spectrometer described in detail elsewhere.<sup>21</sup> Photoelectron spectra were recorded using the constant transmission energy mode of the electron energy analyzer and were calibrated with the Ar<sup>+</sup>(<sup>2</sup>P<sub>3/2,1/2</sub>) spin-orbit doublet. The resolution of the analyzer was 30 meV in He I measurements (fwhm for the Ar <sup>2</sup>P<sub>3/2</sub> line). During the He II measurements the resolution of the electron energy analyzer was lowered to 80 meV (fwhm for the Ar <sup>2</sup>P<sub>3/2</sub> line) in order to gain higher electron count rates.

### 3. Computational methods

The geometries of the ground state neutral molecules were calculated using the B3LYP method and harmonic vibrational frequencies were obtained to identify them as real minima (zero imaginary frequencies) on the potential energy surfaces. The stability of B3LYP wave functions was checked, and B3LYP wave functions were found to be stable. We note that HF wave functions were found to be unstable (RHF-UHF instability) for all furoxan derivatives and so MPn calculations were rejected in this work. Vertical ionization energies (IEs) were calculated using the Symmetry Adapted Cluster/Configuration Interaction (SAC-CI) method using geometries obtained at the B3LYP level. Calculations were done using the cc-pVTZ basis set on C, H, N, O, Cl, and Br atoms and cc-pVTZ-pp on iodine.<sup>22</sup> Only valence electrons were correlated in post-HF calculations. All calculations were performed with the GAUSSIAN-09 quantum chemistry package.<sup>23</sup>

### 4. Results and discussion

#### 4.1. Equilibrium structure of furoxans

Calculated structural data of furoxans are presented in Table 1 and the structure and numbering of atoms are shown in Figure 1. The experimental X-ray structures of parent furoxan, dibromofuroxan, and dicyanofuroxan are also listed in Table 1 for comparison. Although the theoretical equilibrium structure cannot be compared directly with the crystallographic structure due to vibrational averaging and solid-state effects, we expect the differences for rigid molecules like furoxans to be small.

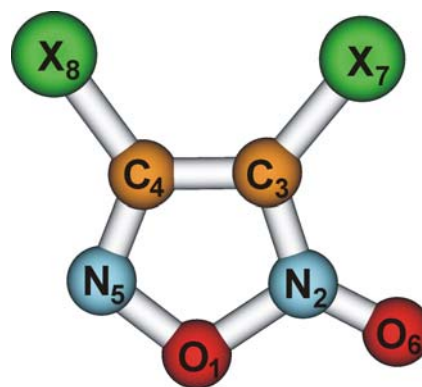


Figure 1. Structure of furoxans and numbering of atoms

According to calculations, all furoxans have a planar structure, not considering methyl group hydrogen atoms, and all molecules have  $C_s$  symmetry. Variation in bond lengths and especially in bond angles of the furoxan moiety due to substituent effects is relatively small, the largest is 0.028 Å and 1.9°, respectively. The  $O_1-N_2$  bond is the most sensitive, and its length is increasing with increasing electronegativity of the substituent atoms. This bond is the longest and weakest in all derivatives, suggesting a point of cleavage and ring opening in decomposition processes. Bond orders can be calculated using the Gordy's rule<sup>24</sup> and by comparing the calculated bond lengths of furoxans with those of molecules having typical single/double CC, CN, and NO bonds ( $H_3C-CH_3$ (1.527 Å)/ $H_2C=CH_2$ (1.324 Å),  $H_3C-NH_2$ (1.464 Å)/ $H_2C=NH$ (1.263 Å), and  $H_2N-OH$ (1.447 Å)/ $HN=O$ (1.198 Å), calculated at the B3LYP/cc-pVTZ level). C–N bonds, nominally double bonds, are between a single and double bonds (bond order 1.6–1.8), and  $C_3-C_4$

Table 1. Calculated<sup>a</sup> equilibrium geometry of furoxans ( $X_2C_2N_2O_2$ )

X=	H	Cl	Br	I	CH <sub>3</sub>	CN
$O_1-N_2$	1.464 (1.441)	1.458	1.458 (1.438)	1.458	1.445	1.472 (1.454)
$N_2-C_3$	1.325 (1.302)	1.329	1.329 (1.299)	1.330	1.326	1.340 (1.344)
$C_3-C_4$	1.408 (1.401)	1.417	1.418 (1.40)	1.422	1.419	1.425 (1.401)
$C_4-N_5$	1.302 (1.292)	1.297	1.296 (1.25)	1.297	1.305	1.306 (1.300)
$N_5-O_1$	1.360 (1.379)	1.370	1.371 (1.359)	1.370	1.367	1.346 (1.354)
$N_2-O_6$	1.210 (1.240)	1.207	1.207 (1.228)	1.208	1.218	1.195 (1.206)
$C_3-X_7$	1.073 (0.92)	1.693	1.852	2.061	1.486	1.406 (1.423)
$C_4-X_8$	1.077 (0.97)	1.706	1.868	2.079	1.489	1.420 (1.423)
$C_7-(H' \text{ or } N)$					1.087	
$C_7-H''$					1.091	
$C_8-(H' \text{ or } N)$					1.088	1.150 (1.134)
$C_8-H''$					1.091	
$O_1N_2C_3$	105.6 (107.2)	105.6	105.7	106.1	107.0	105.1 (105.4)
$N_2C_3C_4$	107.4 (107.2)	107.1	107.0	106.8	106.7	106.9 (106.8)
$C_3C_4N_5$	111.7 (111.9)	112.1	112.2	111.9	111.1	111.4 (112.1)
$C_4N_5O_1$	107.1 (106.6)	106.5	106.6	107.0	107.5	107.6 (107.2)
$O_1N_2O_6$	118.4 (116.4)	119.2	118.9	118.4	119.0	119.0 (118.2)
$C_4C_3X_7$	132.3 (130)	130.7	131.1	132.0	132.7	130.9 (131.3)
$C_3C_4X_8$	127.9 (128)	125.6	126.1	127.3	127.7	126.7 (126.8)
$C_3C_7(H' \text{ or } N)$					110.5	179.0 (179.0)
$C_3C_7H''$					110.9	
$C_4C_8(H' \text{ or } N)$					109.5	178.3 (178.0)
$C_4C_8H''$					111.1	

<sup>a</sup> Calculated at the B3LYP/cc-pVTZ level. Bond lengths are in Å and bond angles are in degrees. See Figure 1 for numbering of atoms. Experimental X-ray crystal structures from references [6,7,8] are in parenthesis.

and N<sub>5</sub>-O<sub>1</sub> bonds, nominally single bonds, are shorter than a C-C or N-O single bond (bond order 1.4–1.5 and 1.2–1.3, respectively). This tendency to bond order equalization is in agreement with the expected aromaticity of furoxans. The exocyclic N<sub>2</sub>-O<sub>6</sub> bond is short (bond order 1.9–2.0) and may be regarded as a double bond. Its length is decreasing with increasing electronegativity of the substituent atoms connected to the furoxan moiety.

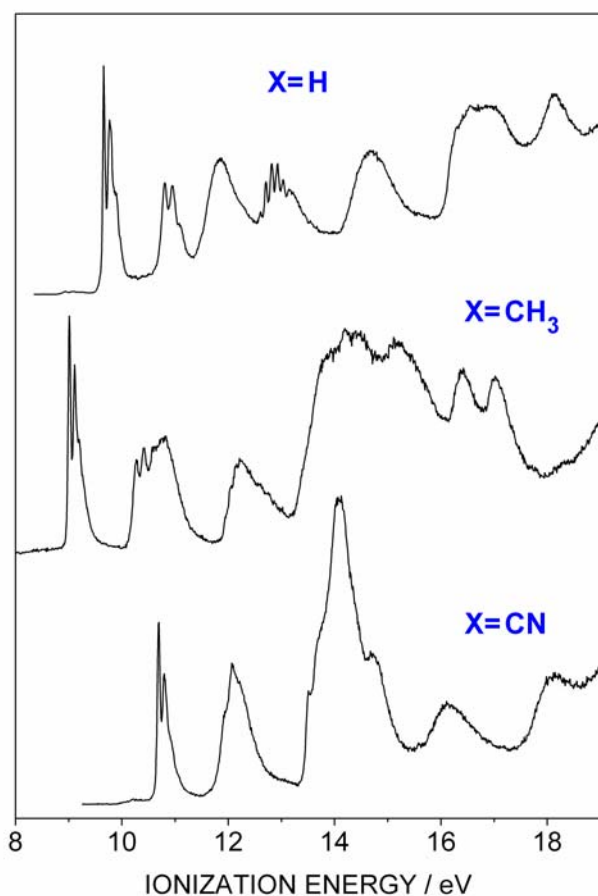
#### 4.2. Photoelectron spectra of furoxans

The He I and He II photoelectron spectra of furoxans are shown in Figures 2 and 3, and experimental and calculated ionization potentials are listed in Table 2. From the calculated IPs, from the comparison of the He I and He II spectra, and from the comparison of the spectra of substituted derivatives, the assignment is relatively straightforward.

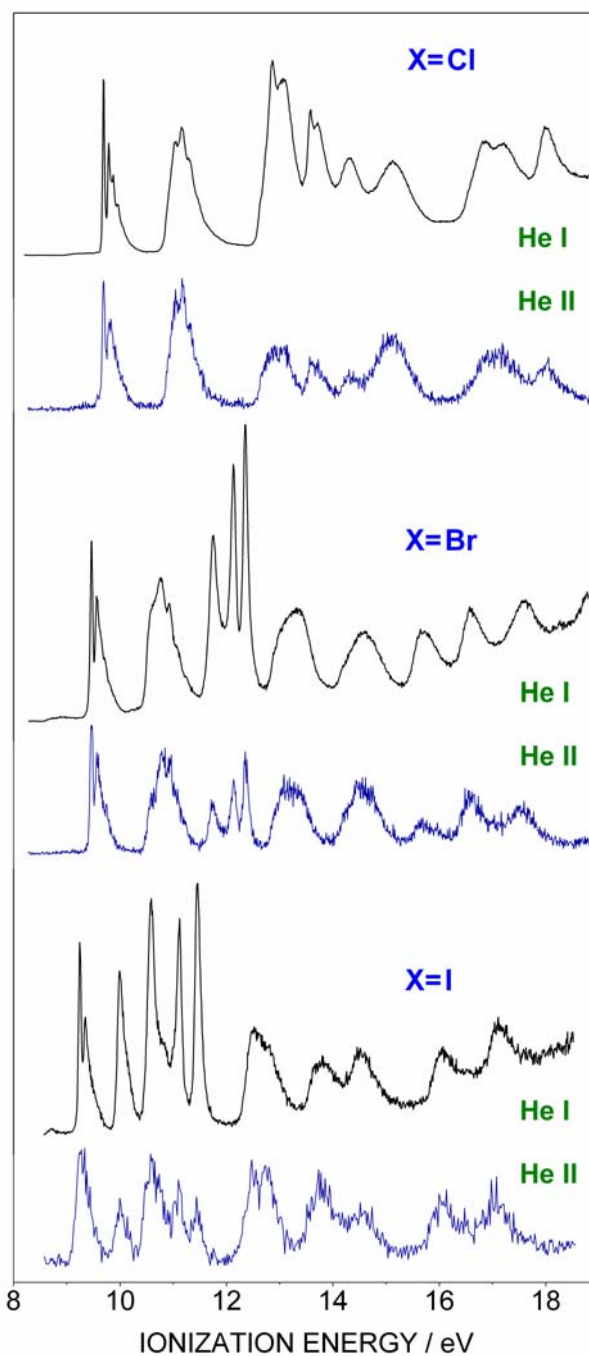
A possible starting point to describe the electronic structure of furoxans is to consider the MOs of a five-membered aromatic ring, modified with an exocyclic oxygen atom and two substituent atoms or groups. Three  $\pi$  orbitals, a nitrogen 'lone pair' orbital ( $n_{N,ring}$ ), an oxygen 'lone pair' orbital ( $n_{O,ring}$ ), and two oxygen 'lone pair' orbitals from the exocyclic oxygen atom ( $\pi(n_{O_6})$  and  $\sigma(n_{O_6})$ ) can be deduced from the furoxan moiety as low IP MOs. In addition, seven high IP orbitals can be deduced from the ring  $\sigma$  framework, including the terminal 'lone pair' of the exocyclic oxygen atom ( $n_{O,term}$ ). Ionization from some of

these orbitals will produce photoelectron bands in the investigated IP region. In addition to MOs of the furoxan moiety, MOs from the substituent groups are also expected. MOs in general are far from localized, but in order to keep discussion simple we use the notations above. MOs of the parent furoxan are shown in Figure 4.

According to calculations, the first band in spectra between 9 and 11 eV can be unambiguously assigned to the O<sub>6</sub> oxygen  $\pi(n_{O_6})$  lone pair with some contribution from the ring. These PE bands show vibrational fine structure with strong adiabatic transition. The band shape indicates a relatively small geometrical change due to ionization from the HOMO. The vibrational fine structure is not entirely resolved, but ionic vibrational frequencies of ground state



**Figure 2.** He I photoelectron spectra of the parent (top), dimethyl (middle), and dicyanofuroxan (bottom).



**Figure 3.** He I and He II photoelectron spectra of the dichloro (top), dibromo (middle), and diiodofuroxan (bottom).

**Table 2.** Experimental and calculated<sup>a</sup> vertical ionization energies of furoxans (X<sub>2</sub>C<sub>2</sub>N<sub>2</sub>O<sub>2</sub>)

X= H		Cl		Br		I		CH <sub>3</sub>		CN		orbital character and symmetry
Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	
9.66 <sup>b</sup>	9.27	9.69 <sup>c</sup>	9.35	9.40 <sup>d</sup>	9.22	9.24 <sup>i</sup>	8.90	9.01 <sup>j</sup>	8.50	10.69 <sup>l</sup>	10.20	$\pi(n_O)$ , a''
							9.99					$n_I$ , a''
							10.58					$n_I$ , a'
10.80 <sup>c</sup>	10.55	11.16 <sup>f</sup>	10.93	10.70 <sup>h</sup>	10.69	10.7	10.50	10.27 <sup>k</sup>	9.90	12.08	11.72	$\sigma(n_O)$ , a'
		11.16	11.13									$\pi(\text{ring})$ , a''
				10.70	10.77	11.12	11.08					$n_{Br}$ , $n_I$ , a''
		12.86	12.87	11.69	11.91	11.45	11.09					$n_{Cl}$ , $n_{Br}$ , $n_I$ , a'
		13.07	13.13	12.07	12.22							$n_{Cl}$ , $n_{Br}$ , a'
		13.58	13.53	12.29	12.48							$n_{Cl}$ , $n_{Br}$ , a''
11.85	11.80			(13.0)	13.77	12.5	12.71	10.80	10.64	12.08	12.15	$\pi(\text{ring})$ , a''
						12.9	12.84	12.23	12.06			$\sigma(n_{N,\text{ring}})$ , a'
						13.8	13.84					$\sigma(\text{ring, C-I})$ , a'
								13.5	13.30			$\pi(\text{ring})$ , a''
									13.70		13.64	CH <sub>3</sub> , $\pi(\text{cyano})$ , a'
									14.37	13.51	14.00	CH <sub>3</sub> , $\pi(\text{cyano})$ , a'
									14.84	14.08	14.14	$n_N(\text{cyano})$
										14.74	14.22	$n_N(\text{cyano})$
									15.22		14.21	CH <sub>3</sub> , $\pi(\text{cyano})$ , a''
12.91 <sup>d</sup>	12.96	14.31	13.75	13.3	13.24						14.42	$\sigma(n_{N,\text{ring}})$ , a'
									15.35			CH <sub>3</sub> , a'
		15.13	15.04					15.5	15.50		15.15	CH <sub>3</sub> , $\pi(\text{cyano})$ , a''
												$n_{Cl}$ , a''
14.68	14.24			14.5	14.67	14.5	14.24					$\pi(\text{ring})$ , a''
						14.5	14.58					$\sigma(\text{ring, C-I})$ , a'
14.68	14.74	15.13	15.18	14.5	14.67	16.1	16.31	16.41	16.29	16.14	16.52	$\sigma(n_{O,\text{ring}})$ , a'
16.3	16.46	16.86	17.07	15.65	15.97							C-X, a'
		17.20	17.02	16.53	16.77							$\sigma(\text{ring})$ , a'
16.5	17.23											C-H
16.9	17.54		18.09									$\pi(\text{ring})$ , a''
18.14	18.47	18.01	18.25	17.54	17.77	17.1	17.40	17.03	17.04	18.1	18.18	$\sigma(n_{O,\text{term}})$ , a'
			18.23									$\pi(\text{ring})$ , a''
												$\pi(\text{ring})$ , a''
												$\pi(\text{ring})$ , a''

<sup>a</sup> Calculated at the SAC-CI/B3LYP/cc-pVTZ level. <sup>b</sup> Cationic vibrational wavenumbers: 1130±50 and 810±50 cm<sup>-1</sup>. <sup>c</sup> Cationic vibrational wavenumber: 1210±50 cm<sup>-1</sup>. <sup>d</sup> Cationic vibrational wavenumber: 810±50 cm<sup>-1</sup>. <sup>e</sup> Cationic vibrational wavenumber: 800±50 cm<sup>-1</sup>. <sup>f</sup> Cationic vibrational wavenumber: 1050±100 cm<sup>-1</sup>. <sup>g</sup> Cationic vibrational wavenumber: 840±50 cm<sup>-1</sup>. <sup>h</sup> Cationic vibrational wavenumber: 1300±100 cm<sup>-1</sup>. <sup>i</sup> Cationic vibrational wavenumber: 800±50 cm<sup>-1</sup>. <sup>j</sup> Cationic vibrational wavenumber: 800±50 cm<sup>-1</sup>. <sup>k</sup> Cationic vibrational wavenumber: 1150±50 cm<sup>-1</sup>. <sup>l</sup> Cationic vibrational wavenumber: 840±50 cm<sup>-1</sup>.

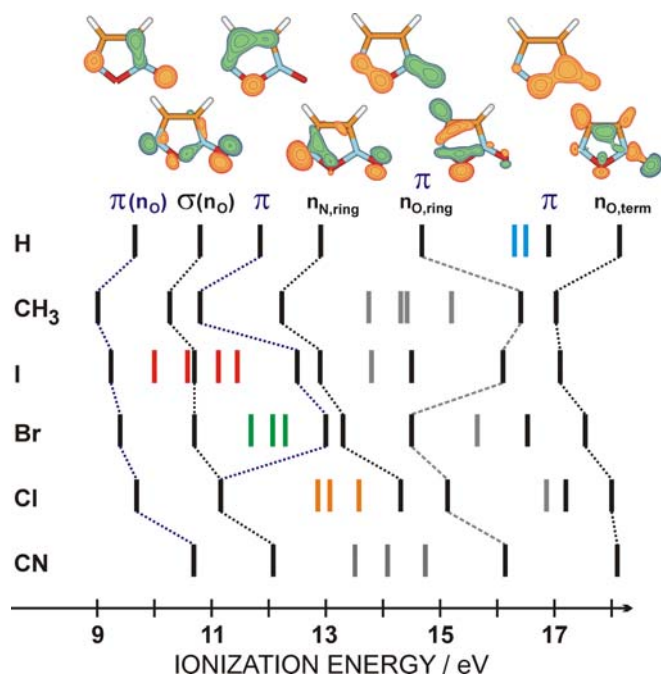
cations can be estimated with an accuracy of ca. 50 cm<sup>-1</sup> (see Table 2). The second band in all spectra, except that of the iodo derivative, is assigned to the in-plane O<sub>6</sub> oxygen  $\sigma(n_O)$  lone pair orbital, mixed some extent with the ring  $\sigma$  orbitals. The two exocyclic oxygen atom lone pair orbitals ( $\pi(n_O)$  and  $\sigma(n_O)$ ) are thus separated by 1.1–1.5 eV, which is similar to the ca. 1 eV separation observed in the spectra of simple aromatic N-oxides.<sup>25</sup> The third and the fourth bands in the spectrum of parent furoxan at 11.85 and 12.91 eV are unambiguously assigned to the ring highest lying  $\pi$  orbital and nitrogen 'lone pair' orbital ( $n_{N,\text{ring}}$ ), respectively. These PE bands are shifted toward lower IPs upon methyl substitution and can be unambiguously detected in the spectrum of dimethyl-furoxan. The second band in spectra of dichloro, dibromo, and dicyano derivatives, however, is assigned to two MOs, one is the in-plane O<sub>6</sub> oxygen  $\sigma(n_O)$  lone pair orbital and the other is a ring  $\pi$  orbital mixed to some extent with the CN group or halogen atoms. In the case of the bromo derivative the bromine lone pair character is dominant. The assignment of the sharp bands in the spectrum of diiodo, dibromo, and dichloro derivatives in the 10–11.5, 11.5–12.5, and 12.5–14 eV region, respectively, is

unambiguous as their relative intensity is strongly reduced in the He II spectra and they clearly originate from lone pair orbitals of halogen atoms. The intense broad feature in the spectrum of dicyano derivative between 13.5–15 eV is a result of the overlapping of seven PE bands assigned to the ionization of six highly localized cyano group based orbitals, four  $\pi(\text{cyano})$  and two terminal nitrogen lone pair  $n_N(\text{cyano})$ , and to the  $\sigma(n_{N,\text{ring}})$  orbital. A clear identification to individual orbitals is not possible, but calculation clearly show the clustering of the six cyano based MOs. Similar clustering of the relevant PE bands have been observed in the spectrum of 3,4-dicyano-1,2,5-thiadiazole in the same ionization energy region.<sup>26</sup> The assignment of PE bands in the high ionization energy region of spectra is less unambiguous. Our assignment (Table 2) is based on calculations and on comparing spectra of substituted derivatives.

It is interesting to compare the peak positions of PE bands corresponding to molecular orbitals of the furoxan moiety in substituted derivatives. The IE correlation diagram is shown in Figure 4. The dimethyl derivative has



the lowest ionization potential of all furoxans investigated and the dicyano derivative has the highest. Ionization potentials are gradually increasing in the order of  $\text{CH}_3 < \text{I} < \text{Br} < \text{Cl} < \text{CN}$  substituted derivatives, which can be explained by the electron donating and electron withdrawing effects of substituent groups. The shift of PE bands due to substituent effects indicates, in general, similar pattern and it is in agreement with the mesomeric and inductive effects of substituents attached to the furoxan moiety.



**Figure 4.** Experimental ionization energy correlation diagram for substituted furoxans and schematics of the corresponding molecular orbitals of the parent furoxan.

## 5. Conclusion

Structures of simple substituted furoxans have been investigated in the gas phase by photoelectron spectroscopy and by theoretical calculations using B3LYP and SAC-CI methods. According to calculations, furoxans have a planar ring structure with a short exocyclic N–O bond and a long endocyclic N–O bond. Photoelectron spectroscopy has provided information on the valence occupied levels of the neutral molecules and on the fundamental vibrations of the low-lying cationic states. Assessment of the sequence of cationic states has provided an assessment of substituent effects on ionization potentials and electronic structures. HOMOs of all furoxan derivatives have predominant exocyclic oxygen  $\pi$  lone pair character, therefore the lowest energy ionization potentials are assigned to ionizations from the out-of-plane oxygen lone pair orbitals.

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