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THE ELECTRONIC STRUCTURE OF GROUPS OF ISOMERIC HETERO-AROMATIC SYSTEMS

II—THE SPECTRA AND THE STRUCTURE OF THE N-OXIDES OF BENZOFURAZAN (BENZOFUROXANS)

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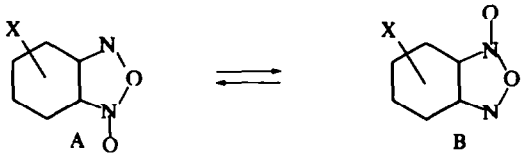
Abstract—The electronic spectrum of the benzofurazan-N-oxide and its - OR, --NH_2 and - - Cl 5-substituted derivatives has been calculated on the assumption that their structure should be on a charge-transfer ion pair (benzofurazane)$^+$-O^-. The agreement with the observed spectrum is very satisfactory; the first absorption band is assigned to an internal charge-transfer transition and the second band to a $\pi \rightarrow \pi^*$ transition.

The prediction of the more stable isomeric structure, based on the π-electron energy difference between 1-oxo- and 3-oxo-5-substituted benzofurazans, gives results opposite to the observations reported for —OMe and —Cl derivatives. Possible reasons of this failure are discussed.

IT HAS recently been established[1,2] that benzofuroxans (benzofurazan N-oxides) rearrange in solution by opening of the furazan ring at the N--O--N pair of bonds[3] and subsequent closure. The two isomeric forms* exist in equilibrium and the activation energy of this process is between 13 and 15 Kcal/mole:[1-3]



(I)

When a substituent is present in the benzenoid ring, the A ⇄ B equilibrium refers to two different isomers, and one purpose of the work was to predict which would predominate. Another reason for studying these isomers was to calculate the spectral shift resulting from the structure change and to determine whether the reported spectra[4] had been affected by the mixture of two isomeric forms. Finally, it should be possible to evaluate the influence of substitution on the benzofuroxan system and to

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* There is an ambiguity in the literature concerning the isomeric structures involved in this process, because the chemical name of benzofuroxan does not identify the position of the N-oxide group. When a fixed numbering for benzofuroxan is adopted A can be, and is, reported[1-3] as, e.g. 5- or 6-benzofuroxan depending on which N atom is given the number 1.

The ambiguity can be avoided if reference is made to the parent compound benzofurazane, so that the system (A, B) is defined as, e.g. (1-oxo-5-chloro-benzofurazan, 3-oxo-5-chloro-benzofurazan), and the rearrangement can then be described as the 1-oxo- to the 3-oxo-x-substituted benzofurazan.

compare these results with the available spectra, dipole moment and other data.

It was assumed that in equilibrium the n_A/n_B population ratio could be measured by the difference in the formation enthalpies of the two isomers,

$$\delta\Delta H = \Delta H_A - \Delta H_B \tag{1}$$

which implies that the entropy terms of the free energy of formation were nearly the same for both isomers.

The task of evaluating each of the ΔH terms is beyond the methods presently available. However, in this case A and B differ only in the position of the N-oxide group, and therefore the energy contribution of the core σ-electrons should be nearly the same for both isomers. Within the limits of this assumption, Eq. (1) can be directly related to the difference in the total π-electron energy, defined as:

$$\Delta E_\pi = E_{\pi A} - E_{\pi B} = \sum \{(I_{iA} - I_{iB}) + (\varepsilon_{iA} - \varepsilon_{iB})\} \tag{2}$$

with $\sum_i I_{iA}$ energy due to potential field of assumed core and $\sum_i \varepsilon_{iA}$ π-orbital energy including interelectronic repulsion, where ε_{iA} is the ith eigenvalue, $I_{iA} = (\psi_{iA}|H|\psi_{iA})$ of the isomer A, and likewise for the isomer B, the i summation being carried out over the MO's occupied in the ground state.

The assumptions made in relating ΔE_π to $\delta\Delta H$ are considered as acceptable for derivatives where the position, nature and dimensions of the substituents do not change greatly. Consequently, this work was restricted to benzofuroxan (BFX) and its chloro-, amino-, hydroxy- and methoxy-5-substituted derivatives.

RESULTS

The Pariser–Parr–Pople (P.P.P.) approximation of the ASMO method was used in the manner discussed previously.[5] The adopted geometry is shown in Fig. 1, and the details of its derivation are given in the appendix, together with other details which are relevant to the present case.

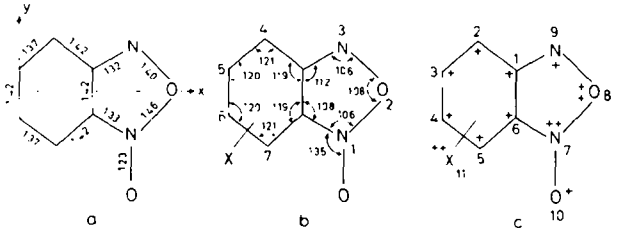

FIG. 1 Bond lengths *a*, bond angles *b* and molecular core *c*, for benzofuroxan. The X substituent is OH, OMe, NH_2 and Cl. The other bond lengths are: C—H, 1·05; O—H, 1·04; N—H, 1·02; C—O, 1·36; C—N, 1·42; C—Cl, 1·72 A. The bond to each substituent atom bisects the external angle. The numbering shown in *b* is the one conventional for benzofurazan, and the numbering shown in *c* is that here used for the atomic orbitals.

The results obtained for the ΔE_π are listed in Table 1. They show that 3-oxo-5-substituted benzofurazan (B) always gives a larger π-energy gain than the corresponding 1-oxo-isomer (A). These results disagree with the observations reported on the methoxy- and chloro-derivatives, where the isomer A is favoured and the equilibrium

TABLE 1. ΔE_π VALUES OF ISOMERIC SUBSTITUTED BENZOFURAZAN-N-OXIDES (eV)

Isomer	OBFX	MOBFX	ABFX	ClBFX
$-E_\pi$(A)	776·45	777·07	765·64	755·37
$-E_\pi$(B)	777·74	778·36	766·86	756·55
ΔE_π	1·29	1·29	1·22	1·18

constants are K(A/B) = 2·2 and 1·5, respectively.[1] Moreover isomer A is the stable form of Cl-BFX present in the solid, as has been established by X-ray diffraction on the crystal.[6]

These incorrect predictions are in line with the disagreement between the calculated total dipole moments of BFX and Cl-BFX, 3·25 and 2·95 D, and the observed values 5·29 and 3·90 D, respectively.[7] The reasons for this apparent failure of our calculations in the predictions of ground state properties are discussed later.

The calculated $\pi \rightarrow \pi^*$ electronic transitions (Table 2) do not show an appreciable dependence on the position of the substituent relative to the N-oxide group: the

TABLE 2. CALCULATED $\pi - \pi^*$ TRANSITION ENERGIES OF BENZOFURAZAN-N-OXIDES (BFX), eV

BFX	Cl-BFX		OH-BFX		MeO-BFX		NH_2-BFX	
	A	B	A	B	A	B	A	B
4·00	3·92	3·90	4·05	4·00	4·06	4·01	3·80	3·75
5·30	5·17	5·12	5·23	5·16	5·24	5·17	5·03	4·95

lowest transition energy of isomer A is nearly 0·05 eV higher than that of B. Our predictions indicate therefore that the observed spectra should not be affected by the position of the A ⇄ B equilibrium.

The spectral data are recorded in Table 3. All compounds have their lowest energy absorption band of rather high intensity, and very sensitive to the nature of the solvent: it is in general displaced to lower wavelengths in hydroxylic solvents, and

TABLE 3. UV ABSORPTION SPECTRUM OF 5-X-SUBSTITUTED-BENZOFURAZAN-N-OXIDES[a]

X	H	Cl	OMe	NH_2	NMe_2
CT	350 (7650)	356 (6800)	367 (41 0)	400 (2000)	≃450 (6300)
$\pi \rightarrow \pi^*$	~293 (1800)	~300 (2450)	~295 (4100)	~300 (4000)	310 (10700)
	~305 (2400)	314 (3600)	306 (6200)	315 (7900)	325 (12000)
	~320 (3450)	329 (4800)	320 (6200)	330 (8000)	340 (9300)
centre, eV	4·06	3·94	4·05	3·93	3·81

[a] Tabulated values give the λ_{max} (*nm*); measured in water, with the molar extinction in parenthesis. Data for amino- and dimethyl-amino-derivatives refer to neutral species in aqueous solution and are taken from ref. [4]. The other data are unpublished results kindly made available to us by Dr. A. J. Boulton of East Anglia University, Norwich, U.K.

similarly affected by polar solvents such as dioxan. This behaviour rules out a $\pi \rightarrow \pi^*$ assignment for the transition from which this band originates. The second band is only slightly affected by the change of solvent and shows, as a rule, a vibrational structure with three main components, resulting in a band-width of about 0·4 eV. We have assigned this absorption to a $\pi \rightarrow \pi^*$ transition approximately located at the centre of the band and compared it to our calculated transitions. The agreement is satisfactory and in line with that found in other cases.[5]

The first absorption band originates, in our view, from an internal charge transfer transition of the type discussed[8] possibly overlapped by an $n \rightarrow \pi^*$ transition. This assignment is based on the intensity and shape of the band, and on its behaviour in different solvents. An approximate prediction of this C.T. band was based on the method developed by Nagakura and applied to the following model. Benzofuroxan can be described as a charge transfer complex built up from a benzofurazan cation BFZ^+, (10 π-electrons, ψ_{BFZ+}) associated with a O^- anion, (2 π-electrons, ψ_{O-}), with the adjacent atoms in the valence state N^+ ($tr\ tr\ tr\ \pi$, V_3) and O^- ($tr^2\ tr^2\ tr\ \pi^2$, V_1). When their interaction at the equilibrium bonding distance is considered as purely electrostatic the wave-function of the complex is $\psi_{O-} \cdot \psi_{BFZ+}$.

After formation of the σ-bond by the joining of the trigonal orbitals a charge neutralization takes place and the wave-function of this electronic configuration is written $\psi_O \cdot \psi_{BFZ}$, with $O(tr^2\ tr^2\ tr^0\ \pi^2, V_1)$ in order to ensure that the π-electrons on oxygen negligibly interact with those on BFZ. The charge-transfer structure then develops through the ionization $O(tr^2\ tr^2\ tr^0\ \pi^2, V_1) \rightarrow e + O^+(tr^2\ tr^2\ tr^0\ \pi, V_1)$, and the π-electron interaction reaches its balance with the sharing of a π-electron pair between the orbitals of adjacent donor and acceptor. The wave-function of the structure derived from the ionization is $\psi_{O+} \cdot \psi_{BFZ-}$, with BFZ^- formed by the transfer of one π-electron from oxygen to the lowest antibonding orbital of BFZ.

The ground state of our system is approximated with the no-interaction π-configuration

$$\psi_G \simeq \psi_O \cdot \psi_{BFZ}, \tag{3}$$

and, accordingly, the locally excited configuration, identified as the lowest excited state of the non-interacting donor–acceptor π-system, is assumed

$$\psi_E \simeq \psi_O \cdot \bar{\psi}_{BFZ}, \tag{4}$$

where $\bar{\psi}_{BFZ}$ is the eigenfunction of the lowest excited state of BFZ. The charge-transfer configuration is

$$\psi_{CT} = a^{\frac{1}{2}} \psi_{O+} \cdot \psi_{BFZ-} + (1 - a)^{\frac{1}{2}} \psi_{O-} \cdot \psi_{BFZ+}. \tag{5}$$

The evaluation of the matrix terms corresponding to (3), (4) and (5) is discussed in the appendix. The calculated transitions, shown in Table 4 show a very satisfactory

TABLE 4. CALCULATED AND OBSERVED INTERNAL CHARGE-TRANSFER TRANSITIONS OF BENZOFURAZAN-N-OXIDES (BFX), eV

	BFX	Cl-BFX	MeO-BFX	NH_2-BFX
Calc.	3·53	3·51	3·46	3·05
Obs.	3·54	3·48	3·38	3·10

agreement with the maxima of the observed bands. We believe therefore that our assignment for the spectra of benzofuroxans is fairly well substantiated by the calculations which we have carried out.

DISCUSSIONS AND CONCLUSIONS

The description of the structure of benzofurazan-N-oxide as a charge-transfer ion pair (or electron donor–acceptor) complex $BZF^+ \cdot O^-$ has led to the correct prediction of the two lowest transitions and to the assignment of the corresponding bands as C.T. and $\pi \rightarrow \pi^*$.

It is also significant that the charge-transfer calculation correlates the N-oxide electronic transitions with those of the parent benzofurazan obtained from independent P.P.P. calculation. Its lowest calculated transition, 4·12 eV, compares almost exactly with the observed absorption maximum (4·17 eV in cyclo-hexane and 4·12 eV in water[4]).

The effect of the —OR, $—NH_2$ and —Cl substituents on the spectrum of the N-oxide is also correctly evaluated and its correlation with the spectrum of the correspondingly substituted benzofurazans is maintained.

This success of the spectral predictions is not matched by the calculated ground state energy differences, which give the wrong indication about the more stable isomers.

We shall consider two possible explanations for this disagreement. One is that our calculations deal with isolated molecules, whereas the equilibrium was studied with concentrated or saturated solutions in acetone. The effects of solvation and the solute–solute (dipole–dipole) interactions occurring with such polar molecules as benzofuroxans certainly affect the energy levels of the molecules[9] and might prevail on the contribution of the π-electron energy difference in stabilizing the different structures.

It is however equally possible that the present method is inadequate to deal with the ground state properties of these highly polarizable molecules. This view is supported by a brief analysis of the dipole moment components of BFX and Cl–BFX (isomer A) collected in Table 5. Chlorine substitution gives rise to a large increase in μ_π and a corresponding large decrease in μ_σ, and their combination results in a 10% decrease of the total dipole moment. This is much less than the decrease actually observed which is over 25%, i.e. 2·5 times larger. In these calculations the π-electrons were considered as moving in a σ-core, where the electron population of the non-bonding and σ-bonding orbitals is fixed and equated to the atomic valence state population. As a

TABLE 5. PARTIAL AND TOTAL DIPOLE MOMENTS (DEBYES)[a]

	BFX		Cl-BFX	
	D	(θ°)	D	(θ°)
μ_π	1·02	(130°)	2·45	(155°)
μ_σ	2·41	(170°)	0·95	(221°)
μ_t	3·25	(159°)	2·95	(172°)
observed	5·29		3·90	

[a] Angles refer to x-axis as in Fig. 1; charge convention is (−) → (+). Values in the 2nd column refer to the A isomer.

first consequence the penetration integrals were evaluated over an incorrect core-electron distribution and this strongly affected the α-*core* integrals. A measure of this influence is given by the μ_π component of BFX, which rises to 2·25 D (139°) when the α's do *not* include the penetration integrals. These integrals, however, are the only fraction of σ–π electronic interaction which can be included in the present approach. The method for studying molecules of this kind, with groups as polar as the N-oxide, must therefore be improved to account for the mutual σ–π polarization.*

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REFERENCES

[1] A. J. Boulton, A. R. Katritzky, M. J. Sewell and B. Wallis, *J. Chem. Soc.* B, 914 (1967), and literature
[2] F. B. Mallory, S. L. Manatt and C. S. Wood, *J. Am. Chem. Soc.* **87**, 5433 (1965), and literature therein.
[3] F. B. Mallory and A. Cammarata, *Ibid.* **88**, 61 (1966).
[4] A. J. Boulton, P. B. Gosh and A. R. Katritzky, *J. Chem. Soc.* C, 971 (1966), and personal communications by A.R.K. and A.J.B.
[5] M. Cignitti and L. Paoloni, *Theor. Chim. Acta* **7**, 383 (1967).
[6] D. Britton and W. E. Noland, *J. Org. Chem.* **27**, 3218 (1962).
[7] G. Tappi, *Gazz. Chim. Ital.* **71**, 11 (1941).
[8] S. Nagakura and J. Tanaka, *J. Chem. Phys.* **22**, 236 (1954); S. Nagakura, *Pure applied Chem.* **7**, 79 (1963) and literature therein.
[9] E. M' Kosower, G. S. Wu and T. S. Sorensen, *J. Am. Chem. Soc.* **83**, 3147 (1961).
[10] V. Luzzati, *Acta Cryst.* **4**, 193 (1951).
[11] H. H. Cady, A. C. Larson and D. T. Cromer, *Ibid.* **20**, 336 (1966).
[12] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron* **5**, 166 (1959).
[13] R. L. Miller, P. G. Lykos and H. N. Schmeising, *J. Am. Chem. Soc.* **84**, 4623 (1962).
[14] W. Gordy, *J. Chem. Phys.* **15**, 305 (1947).
[15] J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.* **84**, 540 (1962).
[16] C. R. Guerrillot, R. Lisillour and A. Botrel, *Theor. Chim. Acta* **3**, 111 (1965).
[17] M. Simonetta, V. Pierpaoli and G. Favini, *Rend. Accad. Lincei Sci. mat. fis. nat.* **24**, 58 (1958).

* *A Referee has made the following comments*: the calculations seem to confirm the expected greater stability of that isomer which permits of resonance. Thus

whereas the quinonoid form on the right is not possible for isomer A. Since this is contrary to observation, it would be reasonable to suppose that the long-range Coulomb interaction between oxygen and chlorine produces a destabilizing field effect in the case of B. Although this is apparently taken into account in the P.P.P. calculation through the Coulomb repulsion integral $(\mu\mu/\nu\nu)$ (μ = O, ν = Cl), the values for dipole moments in Table 5 suggest that the calculations are over emphasizing the quinonoid form, thus leading to a μ_π which is too large. The positive Hammett σ value for chlorine would seem to indicate that its overall effect should be electron withdrawing, making Cl the negative end of the dipole. This would produce an electrostatic interaction favourable to isomer A.

APPENDIX

1. *The geometry of the molecules.* The molecular structure of Cl–BFX, is the only one described[6] for the molecules here considered. This work was mainly intended to establish which isomer was present in the crystal and the bond lengths were regarded by the Authors themselves as rather inaccurate. Related molecules the structure of which had been studied are BFZ[10] and benzotrifuroxane.[11] A first trial of several averaged geometries indicated that significantly different charge distributions and spectral predictions were obtained without any evidence for a choice between them. The final criterion was to adopt for each bond type a relationship between bond order and bond length and modify the model geometry in such a way as to minimize the difference between the calculated and adopted bond lengths. The relationships used were the following (bond length d in Å, versus π-bond order p):

$$\text{C—C:}\quad d = 1{\cdot}511 - 0{\cdot}175\,p \qquad \text{Dewar (12)}$$

$$\text{C—N:}\quad d = 1{\cdot}478 - 0{\cdot}208\,p \qquad \text{Miller (13)}$$

$$\text{N—O:}\quad d = 1{\cdot}430 - 0{\cdot}230\,p$$

The last one is the linear equation obtained by taking for the pure single bond $d = 1{\cdot}43$, $p = 0$ and for the pure double bond $d = 1{\cdot}20$, $p = 1{\cdot}0$.[14]

The experimental molecular structure[10] was used for the calculations on BFZ.

2. *Valence state energies and γ_{pp} integrals.* The pertinent W_p data were the same as those used in the previous paper[5] or were calculated from the promotion energies given by Hinze and Jaffé.[15] The promotion energy $Cl(s^2p^5, {}^2P) \rightarrow Cl(tr^2\ tr^2\ tr\ \pi^2, V_1)$, which is not included in their paper, was calculated as a linear combination of the ^2P and ^2S spectroscopic term energies. When the energy of the state of the free atom is taken as zero, i.e. $E(J_{3/2}) = 0$, $E(^2P) = 0{\cdot}036$ and $E(^2S) = 10{\cdot}761$ eV,[15] then

$$E_{prom} = \tfrac{1}{3}[2E(^2P) + E(^2S)] = 3{\cdot}611 \text{ eV}$$

The γ_{pp} integrals were not calculated as in the previous paper[5] because the formula adopted does not apply to chlorine. The valence state electron affinities A_p were therefore calculated from the promotion energies and the γ_{pp} obtained according to the relationship $\gamma_{pp} = -W_p - A_p$. The calculated quantities are:

atoms	C	N-7(11)	N-9	O-8(11)	O-10	Cl
$-W_p$	11·16	28·72	14·12	34·12	17·70	26·67
A_p	0·03	11·96	1·78	15·30	2·47	13·73

3. *The core integrals.* The evaluation of the α^{core} integrals was carried out as before.[5] The required γ_{pq} integrals were calculated by the procedure described there as P.P. and the penetration integrals were included. The (C:Cl Cl) integral was taken from a tabulation by Guerillot *et al.*[16] made available to us by the authors. With $Z_{Cl} = 6{\cdot}45$, $Z_C = 2{\cdot}90$ and, $R = 1{\cdot}72$ Å, it is $\rho = 5{\cdot}85$, $\tau = -0{\cdot}194$; graphic interpolation of their tables gave

$$-(q:pp) = 0{\cdot}00113\,.\,Z_p a.u. = 1{\cdot}983 \text{ eV}$$

The (Cl:CC) integral was calculated as before as a combination of nuclear attraction and electron repulsion integrals. These latter integrals were calculated using the charged spheres approximation.[17] The 3p orbital spheres diameter was determined by multiplying R_{2_p} for the squared ratio of the quantum numbers $(3/2)^2$ and therefore

$$R_{3_p} = (10{\cdot}343/Z_{eff}),\ \text{Å}$$

Taking $Z_{eff} = 5{\cdot}75$ the 3$p\pi$ spheres diameter is 1·799 Å. The diameters of the trigonal orbital tr_1 along the C—Cl bond,

$$tr_1 = (2 \times 1{\cdot}92/15\pi)^{\frac{1}{2}}\,[\tfrac{1}{3} + (\tfrac{2}{3})^{\frac{1}{2}}\cos\theta]\,r^2 \exp(-1{\cdot}92r)$$

were obtained by imposing the condition $|tr_1| = |3p_z|$ when $\theta = 0$ and $= \pi$. Solving the corresponding equations it was found that $R^{\text{I}} = 1{\cdot}854$ and $R^{\text{II}} = 1{\cdot}498$ Å. The associated charges were obtained from the condition of equal charge density on the two spheres, or

$$q^{\text{I}} = R^{\text{I}3}/(R^{\text{I}3} + R^{\text{II}3}) \quad \text{and} \quad q^{\text{II}} = 1 - q^{\text{I}}$$

which gave $q^{\text{I}} = 0{\cdot}655$, $q^{\text{II}} = 0{\cdot}345$.

The evaluation of the repulsion integrals involving the $3p\pi$ and tr_t orbitals followed the simple electrostatic model[17] and the final value of the (Cl:CC) penetration integral was calculated as 0·62 eV.

The β_{pq}^{core} integrals were approximated

$$\beta_{pq}^{core} = \tfrac{1}{2} S_{pq}(W_p + W_q).$$

The overlap integrals were calculated from the usual development in terms of A_n and B_n functions.

4. *Eigenvalues and eigenfunctions.* Eigenvalues and eigenvectors were obtained through a SCF program developed in the Quantum Chemistry Laboratory at the Illinois Institute of Technology and kindly made available to us. The self-consistency was 10^{-4} in the eigenvectors. They are not given here in order to avoid printing numerical data which can be reproduced by any computer by using suitable programs and the numerical data reported in this appendix.

5. *Matrix elements and eigenvalues of charge-transfer transitions.* Diagonal matrix elements from the wave-functions Eq. (3), (4) and (5) were evaluated with reference to $H_{GG} = 0$. The H_{EE} term is therefore identified with the lowest $\pi \rightarrow \pi^*$ transition of BFZ or of the 5-substituted X-BFZ. The integral $H_{CT,CT}$ is compounded from the ionization potential of benzofurazan, the electron affinity of oxygen in its appropriate valence state, and the electrostatic interaction between the two ions:

$$H_{CT,CT} = I_{XBFZ} - A_O + q_O q_N \gamma_{ON}$$

where q_O and q_N are the net charges on the atoms of the N-oxide group of the corresponding X–BFX. The last term estimates the contribution coming from the electronegativity differences between oxygen and benzofurazan.

In evaluating the off-diaganol terms involving ψ_{CT} we considered $|(1 - a)|$ a measure of the charge transferred on oxygen in the ground state of X-BFX. Putting $|(1 - a)| \simeq |q_O|$ we have

$$H_{G,CT} = (1 - |q_O|)^{\frac{1}{2}} \langle \psi_O \cdot \psi_{BFZ} | H | \psi_{O+} \cdot \psi_{BFZ-} \rangle + (|q|)^{\frac{1}{2}} \langle \psi_O \cdot \psi_{BFZ} | H | \psi_{O-} \cdot \psi_{BFZ+} \rangle$$

Here the first integral involves nearly orthogonal functions and has been neglected. The second contains functions which differ in their core population and has been approximated by the product of the overlap between the adjacent orbitals times the average of two-centre one-electron and two-electron terms, neglecting the Z.D.O. integrals (zero differential overlap):

$$H_{G,CT} \simeq (|q_O|)^{\frac{1}{2}} S_{NO}[-(O:NN) - (N:OO) + \gamma_{NO}]$$

The evaluation of the integral

$$H_{E,CT} = (1 - |q_O|)^{\frac{1}{2}} \langle \psi_O \cdot \bar{\psi}_{BFZ} | H | \psi_{O+} \cdot \psi_{BFZ-} \rangle + (|q_O|)^{\frac{1}{2}} \langle \psi_O \cdot \psi_{BFZ} | H | \psi_{O-} \cdot \psi_{BFZ+} \rangle,$$

where now the second term is considered as negligible, is carried out along the same lines. The one-electron two-centre integrals are the same, but the two-electron two-centre contribution reduces to Z.D.O. integrals which are neglected. Therefore

$$H_{E,CT} \simeq (1 - |q_O|)^{\frac{1}{2}} 2S_{NO}^2[-(O:NN) - (N:OO)].$$

The numerical values which do not change with substitution are $S_{NO} = 0{\cdot}153$; $\gamma_{NO} = 9{\cdot}83$, $(O:NN) = 3{\cdot}56$, $(N:OO) = 1{\cdot}48$; $A_O = 2{\cdot}47$ eV. The other data required depend on the nature of the substituent and are, besides q_O and q_N, the H_{EE} and the ionization potentials. These are unknown and represent the most arbitrary choice: the same value 8·50 eV was used for all compounds, and it should be considered as an adjustable parameter in the calculations. The H_{EE} of BFZ is the calculated value; those of MeO- and NH_2-BFZ were identified with the respective lowest absorption band[4] and that of Cl-BFZ, whose spectrum is not known, assumed to be the same as BFZ.

The relevant data are given here together with the calculated eigenvalues ε_i:

X	:	H	MeO	NH_2	Cl
q_N	:	+0·606	+0·600	+0·591	+0·589
q_O	:	−0·428	−0·442	−0·461	−0·446
H_{EE}	:	4·12	3·90	3·10	(4·12)
ε_1	:	−0·06	−0·07	−0·07	−0·07
ε_2	:	3·47	3·39	2·98	3·44
ε_3	:	4·20	4·00	3·54	4·18