# 12. Consequences of Substitution in the Photoelectron Spectra of [2, 2]Paracyclophanes:

## Separation of 'Through-space' and 'Through-bond' Interactions as a Consequence of Fluorosubstitution

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*Summary*. The PE. spectra of [2,2]paracyclophane (**1**), 4-amino[2,2]paracyclophane (**2**) and 1,1,2,2,9,9,10,10-octafluoro[2,2]paracyclophane (**3**) are presented. The bands corresponding to ejection of the photoelectron from the five highest occupied $\pi$-orbitals have been assigned. The 'observed' orbital energies (*i.e.* the negative ionization potentials) are discussed in terms of 'through space' and 'through-bond' interactions between the semi-localized $\pi$-orbitals ($e_{1g}$) of the benzene moieties and the C, C-$\sigma$-orbitals of the ethylene bridges.

The PE. spectrum of **3** shows that the fluorine-induced lowering of the C, C-$\sigma$-orbital energy effectively 'turns-off' the 'through-bond' interaction. The resulting pattern of the first four bands confirms the assignment given for **1**.

Finally the band shifts induced by an amino group in position 4 are again in agreement with this assignment. Attention is drawn to the phenomenon of 'orbital switching' as a consequence of substitution in loosely coupled systems such as **1**.

The photoelectron (PE.) spectrum of [2,2]paracyclophane (**1**) was first described by *Pignataro, Mancini, Ridyard & Lempka* [1] who attributed the broad peak at 8 eV to two ionizing transitions only. *Boschi & Schmidt* [2] have shown that in agreement with the theoretical predictions of *Gleiter* [3] this feature should be assigned to the three transitions of **1** to its radical cation **1**$^+$ in the states[1]) $^2B_{2g}$, $^2B_{3u}$, $^2B_{3g}$. The second band at 9.5 eV was assigned to a transition to the $^2B_{2u}$ state of **1**$^+$.

In the present contribution we wish to confirm and extend this assignment of the $\pi$-bands of **1**, by making use of the information contained in the PE. spectra of the derivatives 4-amino[2,2]paracyclophane (**2**) and 1,1,2,2,9,9,10,10-octafluoro[2,2]-paracyclophane (**3**).



**1**          **2**          **3**
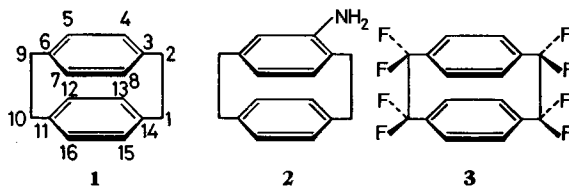
The analysis of these spectra leads to the recognition of a novel consequence of the 'fluoro-effect' [4] concerning the competition of 'through-space' and 'through-bond' interactions [5] in molecules such as **1**. Furthermore, attention is drawn to the phenomenon of 'orbital-switching' which has to be taken into consideration when a qualita-

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[1])   The labels refer to the coordinates as defined in [3] (*cf.* (**2**)). Note that in ref. [2] the x and y axes are interchanged relative to this convention.

tive discussion of the effect of substituents on loosely coupled $\pi$-systems (*e.g.* in **1**) is attempted.

**PE.-Spectra.** – In Fig. 1 are shown the He I PE. spectra of **1**, **2** and **3** which have been recorded on a spectrometer built according to the specifications given by *Turner* [6]. This incorporated a $\pi/\sqrt{2}$ cylindrical condenser analyser of 10 cm radius and the source of excitation was He I radiation. The spectra were recorded at elevated temperatures ($\sim 100°$ to $200°$) with an effective working resolution of $E/\Delta E \approx 250$. The ionization potentials were determined by an internal calibration procedure by a rare gas mixture. The data are collected in Tab. 1, together with previous results for **1** and with the proposed assignment of the $\pi$-bands. This is also displayed graphically in the correlation diagram of Fig. 2.

**Theoretical Model.** – Detailed molecular orbital calculations for **1** have been carried out repeatedly [3] [7]. However, for the purpose of this communication we shall use an almost qualitative, stripped-down ZDO LCMO model which yields a transparent rationalization of the observed effects rather than optimally adjusted values for the band positions.

As a basis we chose the benzene $e_{1g}(\pi)$ orbitals, which are symmetric (S) or antisymmetric (A) relative to a reflexion in the x, z-plane (see (2)), *e.g.* for the upper phenylene unit

$$\Phi(u, S) = \frac{1}{\sqrt{12}} (2\,\phi_3 + \phi_4 - \phi_5 - 2\,\phi_6 - \phi_7 + \phi_8)$$

$$\Phi(u, A) = \frac{1}{2} (\phi_4 + \phi_5 - \phi_7 - \phi_8)$$

(1)

the numbering of the $2p_z$-atomic orbitals $\phi_\mu$ corresponding to the convention shown in formula **1**. The phases of the corresponding orbitals $\Phi$ (l, S) and $\Phi$ (l, A) of the lower ring relative to those given in (1) are defined in (2).



(2)
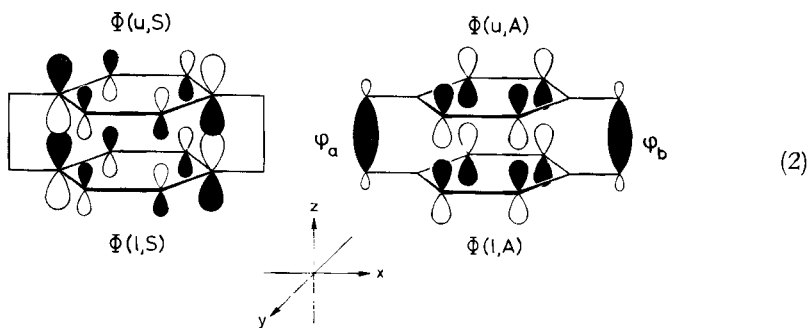
Finally we include two C,C-$\sigma$-orbitals $\varphi_a$ and $\varphi_b$ of the C(1), C(2) and C(9), C(10) carbon-carbon-bonds in the linear combination

$$\Psi = c_1 \, \Phi \, (u, S) + c_2 \, \Phi \, (l, S) + c_3 \, \Phi \, (u, A) + c_4 \, \Phi \, (l, A) + c_5 \, \varphi_a + c_6 \, \varphi_b$$

(3)

In a first approximation we postulate that

$$\langle \Phi \, (i, X) \,|\, \mathcal{H} \,|\, \Phi \, (i, X) \rangle = A; \quad \langle \Phi \, (u, X) \,|\, \mathcal{H} \,|\, \Phi \, (l, X) \rangle = \tau$$

(4)

for $i = u, l$ and $X = S, A$ and that

$$\langle \varphi_j | \mathcal{H} | \varphi_j \rangle = \alpha; \quad \langle \varphi_j | \mathcal{H} | \Phi (i, S) \rangle = \pm \beta / \sqrt{3} \qquad (5)$$

the sign of the right side in the latter expression depending on the relative phases of $\varphi_j$ $(j = a, b)$ and $\Phi (i, S)$ $(i = u, l)$ $(cf. (2))$.

For reasons of symmetry the molecular orbitals $\Psi_i$ derivable from the basis functions (2) are

$$\mathbf{b}_{2g}(\pi) = \frac{1}{\sqrt{2}} (\Phi (u, S) + \Phi (l, S))$$

$$\mathbf{b}_{3u}(\pi) = \frac{\lambda}{\sqrt{2}} (\Phi (u, S) - \Phi (l, S)) - \frac{\xi}{\sqrt{2}} (\varphi_a - \varphi_b)$$

$$\mathbf{b}_{3g}(\pi) = \frac{1}{\sqrt{2}} (\Phi (u, A) + \Phi (l, A))$$

$$\mathbf{b}_{2u}(\pi) = \frac{1}{\sqrt{2}} (\Phi (u, A) - \Phi (l, A)) \qquad (6)$$

$$\mathbf{b}_{3u}(\sigma) = \frac{\xi}{\sqrt{2}} (\Phi (u, S) - \Phi (l, S)) + \frac{\lambda}{\sqrt{2}} (\varphi_a - \varphi_b)$$

$$\mathbf{a}_{g}(\sigma) = \frac{1}{\sqrt{2}} (\varphi_a + \varphi_b)$$

where $\xi \approx 2 \langle \varphi_a | \mathcal{H} | \Phi (u, S) \rangle / (A-\alpha) = -2\beta / \sqrt{3}(A-\alpha)$ and $\xi^2 + \lambda^2 = 1$. The corresponding $\pi$-orbital energies $\varepsilon(\Psi_j)$ are then

$$\varepsilon(\mathbf{b}_{2g}(\pi)) = \varepsilon(\mathbf{b}_{3g}(\pi)) = A + \tau$$

$$\varepsilon(\mathbf{b}_{3u}(\pi)) \qquad \approx A - \tau + \frac{4}{3} \beta^2 / (A - \alpha) \qquad (7)$$

$$\varepsilon(\mathbf{b}_{2u}(\pi)) \qquad = A - \tau$$

The expressions on the right side of formulae (7) are nothing but a much simplified rationalization of the results obtained by *Gleiter* [3]. In agreement with his calculation they suggest that the first feature in the PE. spectrum of **1** *i.e.* the composite band at 9.5 eV is due to the superposition of three bands (labelled 1, 2, 3 in Fig. 1) arising from the ejection of the photoelectron from $\mathbf{b}_{2g}(\pi)$, $\mathbf{b}_{3g}(\pi)$ and $\mathbf{b}_{3u}(\pi)$ respectively. This is supported by the integrated intensity of this multiple band, which is slightly larger than three times the intensity of the single band 4 (ejection from $\mathbf{b}_{2u}(\pi)$). This ratio does not differ too much when He II radiation is used.

Little evidence can be advanced at this stage for the relative sequence of the three orbitals $\mathbf{b}_{2g}(\pi)$, $\mathbf{b}_{3g}(\pi)$, $\mathbf{b}_{3u}(\pi)$. The half-width of the composite band is $\sim 0.9$ eV, as compared to $\sim 0.6$ eV for the double band of *p*-ditrifluoro-methyl-benzene, trifluoro-methyl-benzene [8] or similar derivatives of benzene which do not possess a 'lose-bolt' substituent. Consequently the spread of the three individual, overlapping bands 1, 2
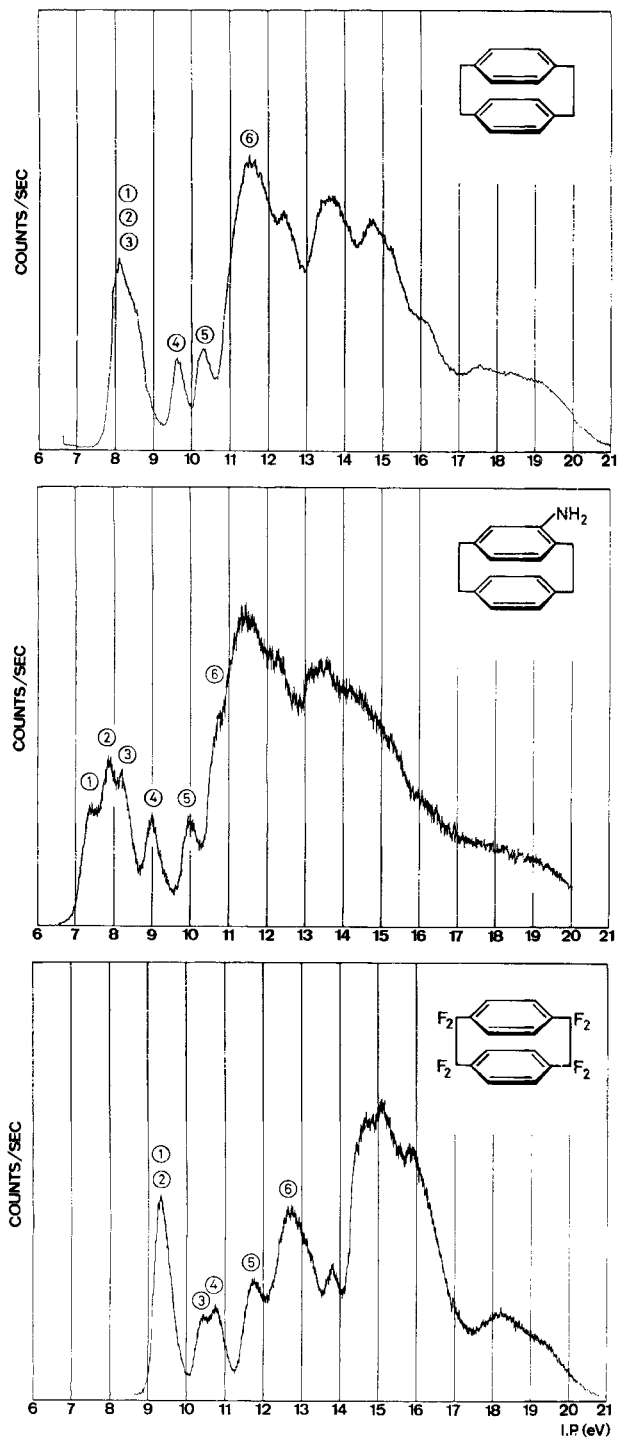
Fig. 1. *PE. spectra of [2,2]para-cyclophane* (**1**), *4-amino[2,2]pa-racyclophane* (**2**) *and 1,1,2,2,9, 9,10,10-octafluoro[2,2]paracyclo-phane* (**3**)

and 3 cannot be significantly larger than 0.3 eV. However, we note that the triple band exhibits a rather sharp onset which strongly suggests that the component at lowest ionization potential (*i.e.* band 1) is presumably not the one due to ejection from $\mathbf{b}_{3u}(\pi)$. The reason is that the band associated with this process should be rather broad as a consequence of the large through bond interaction *i.e.* the mixing of $(\boldsymbol{\Phi}\,(\mathrm{u, S}) - \boldsymbol{\Phi}\,(1, \mathrm{S}))/\sqrt{2}$ with $(\boldsymbol{\varphi}_{a} - \boldsymbol{\varphi}_{b})/\sqrt{2}$ as shown in (6). In the following discussion we shall make the conservative assumption that bands 1, 2 and 3 are accidentally degenerate *i.e.* that they possess orbital energies $\varepsilon(\mathbf{b}_{2g}(\pi)) \approx \varepsilon(\mathbf{b}_{3u}(\pi)) \approx \varepsilon(\mathbf{b}_{3g}(\pi)) \approx -8.3$ eV. (Note that the calculations reported in [3] suggest the sequence $\mathbf{b}_{2g}(\pi)$ above $\mathbf{b}_{3u}(\pi)$ above $\mathbf{b}_{3g}(\pi)$).

Table 1. *Vertical* $(I_{v, j})$ *and adiabatic* $(I_{v, a})$ *ionization potentials of [2,2]paracyclophane* (**1**) *and its derivatives* **2** *and* **3**. All values in eV. Adiabatic ionization potentials are in parentheses

| | **1** This work | [2] | [1] | **3** | | **2** | |
|---|---|---|---|---|---|---|---|
| 1 | $^2\mathrm{B}_{2\,g}$ $8.1_0$ $(7.6_0)$ | 8.1 | ⎫ | $^2\mathrm{B}_{2\,g}$ ⎫ | | $\tilde{\mathrm{X}}$ | $7.5_0$ $(6.9_0)$ |
| | | | ⎬ 8.4 | ⎬ $9.3_0$ $(8.9_0)$ | | | |
| 2 | $^2\mathrm{B}_{3\,u}$ $8.4_0$ | 8.6 | ⎪ | $^2\mathrm{B}_{3\,g}$ ⎭ | | $\tilde{\mathrm{A}}$ | $7.9_0$ |
| 3 | $^2\mathrm{B}_{3\,g}$ | | ⎭ | $^2\mathrm{B}_{3\,u}$ $10.5_0$ $(10.1_0)$ | | $\tilde{\mathrm{B}}$ | $8.2_0$ |
| 4 | $^2\mathrm{B}_{2\,u}$ $9.6_5$ $(9.3_0)$ | 9.5 | 9.7 | $^2\mathrm{B}_{2\,u}$ $10.7_5$ | | $\tilde{\mathrm{C}}$ | $9.0_0$ $(8.7_0)$ |
| 5 | $^2\mathrm{B}_{1\,u}$ $10.3_0$ $(10.0_0)$ | | 10.3 | $^2\mathrm{B}_{1\,u}$ $11.7_5$ $(11.3_0)$ | | $\tilde{\mathrm{D}}$ | $10.0_0$ $(9.7_0)$ |
| 6 | 11.3 | | 11.7 | 12.7 | | $\tilde{\mathrm{E}}$ | 10.7 |

To calibrate our model we use the observed vertical ionization potentials $I_{v,j}$ (Tab. 1) assuming the validity of *Koopmans'* theorem [9]

$$I_{v,j} = -\varepsilon(\boldsymbol{\Psi}^\circ_j) \tag{8}$$

where $\boldsymbol{\Psi}^\circ_j$ is the molecular orbital vacated in the process corresponding to the band j. Apart from the assumption that the three highest occupied $\pi$-orbitals $\mathbf{b}_{2g}(\pi)$, $\mathbf{b}_{3u}(\pi)$ and $\mathbf{b}_{3g}(\pi)$ are accidentally degenerate $(\varepsilon(\mathbf{b}_{2g}(\pi)) \approx \varepsilon(\mathbf{b}_{3u}(\pi)) \approx \varepsilon(\mathbf{b}_{3g}(\pi)) = -8.3$ eV$)$ and that $\varepsilon(\mathbf{b}_{2u}(\pi)) = -9.7$ eV, we need an estimate for $\alpha$ (see (5)) to solve (7) in terms of A, $\tau$ and $\beta$. Parametrized LCBO-treatments [10] or the application of localization procedures [11] to SCF-procedures used for the interpretation of PE. spectra [12] suggest a value of $\sim -16$ eV for the C,C-bond self-energy. However, in our model we have to take the interaction with the C,H-orbitals into consideration which tends to destabilize $\boldsymbol{\varphi}_a$ and $\boldsymbol{\varphi}_b$. Consequently the value $\alpha = -14$ eV was chosen, as suggested by *Gleiter* [3]. Solving (7) yields:

$$\mathrm{A} = -9.0 \text{ eV}; \quad \tau = 0.7 \text{ eV}; \quad |\beta/\sqrt{3}| = 1.4 \text{ eV} \tag{9}$$

**The PE. spectrum of [2, 2]paracyclophane (1).** – According to the model discussed above, the triple band at 8.5 eV corresponds to the transition of **1** to **1**$^+$ in the $\pi$-states $^2B_{2g}$, $^2B_{3u}$ and $^2B_{3g}$ with $^2B_{3u}$ being either the second or third state. Because of the bend in the two phenylene units ($R_{3,14} = 2.78$ Å, $R_{4,13} = 3.09$ Å [13]) we may assume that through-space interaction between $\boldsymbol{\Phi}$ (u, S) and $\boldsymbol{\Phi}$ (l, S) (which have large atomic orbital coefficients in positions 3,6,11 and 14) is larger than between $\boldsymbol{\Phi}$ (u, A) and $\boldsymbol{\Phi}$ (l, A) (which have a node going through these centres). Accordingly we may assume that the ground state of **1**$^+$ is $^2B_{2g}$, as proposed in ref. [2] and [3]. There is little doubt that the isolated single band 4 at 9.7 eV corresponds to the $^2B_{2u}$ state of **1**$^+$.

In benzene the lowest $\pi$-orbital $\mathbf{a_{1u}}(\pi)$ has an energy $\varepsilon(\mathbf{a_{1u}}(\pi)) = -12.2$ eV [4]. Methylsubstitution in *para*-position, to yield *p*-xylene, shifts this orbital to roughly – 11 eV [14]. If we assume that through-space interaction between the corresponding orbitals of the upper and lower phenylene moieties in **1** is again described by $\tau = 0.7$ eV (see (9)) then the combination antisymmetric with respect to the x, y-plane should lie at $-11 + 0.7 = -10.3$ eV. Ejection of an electron from this orbital will therefore lead to band 5 at 10.3 eV which corresponds to the $^2B_{1u}$ state of **1**$^+$. Note that this orbital $\mathbf{b_{1u}}(\pi)$ has the wrong symmetry for through bond interaction.
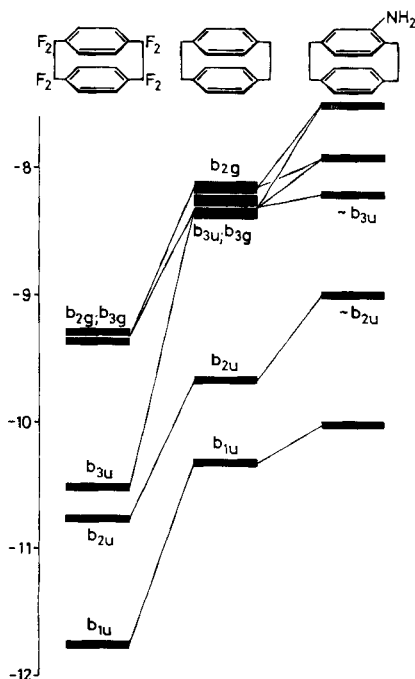
This assignment is the one given in Tab. 1 and Fig. 2.



Fig. 2. *Orbital-correlation diagram.* The orbital energies are those derived from the PE. spectra according to (8).

**The PE. Spectrum of 1,1,2,2,9,9,10,10-octafluoro[2,2]paracyclophane (3).** – Replacement of the four methylene groups **1** by four difluoromethylene units to yield **3** will affect primarily the *Coulomb* integrals A and $\alpha$ (see (4) and (5)). Assuming that

no dramatic change in geometry occurs as a consequence of this substitution, the resonance integrals $\tau$ and $\beta$ defined in (4) and (5) will remain unchanged.

From the PE. spectra of trifluoromethyl-benzene, $p$-ditrifluoromethyl-benzene and of related trifluoromethyl substituted benzene derivatives [8] [15] it is known that both $e_{1g}(\pi)$ orbitals are equally stabilized by roughly $-0.5$ eV per trifluoromethyl substituent so that no split occurs between the symmetric and antisymmetric orbital, presumably because of an accidental cancellation of inductive and conjugative effects [16]. Consequently we expect that A for the four $\pi$-orbitals $\boldsymbol{\Phi}$ (i, X) is lowered to A' = A – 1 eV = –10 eV approximately.

On the other hand it has been shown that $\sigma$-orbitals such as $\varphi_a$ and $\varphi_b$ are depressed considerably if the hydrogen atoms are replaced by fluorine [4]. Depending on the type of C, C-bond this depression can easily exceed –5 eV, so that $\alpha$, as defined in (5) will be shifted to $\alpha' \approx -20$ eV, or lower, in 3.

This depression of $\alpha$ has a rather amusing consequence for the orbital sequence in 3 as compared to that of 1. As indicated in (7) through bond interaction shifts the $b_{3u}(\pi)$ orbital in 1 by $\dfrac{4}{3}\,\beta^2/(A-\alpha)$ towards higher energies. Therefore, an increase in the difference $A - \alpha = 5$ eV (in 1) to $A' - \alpha' \approx 10$ eV or more (in 3) will lead to a sizeable reduction of through bond interaction in the latter molecule. In other words, we can effectively 'turn off' through bond interaction by lowering the orbital energy of the $\sigma$-orbitals 'out of reach' of the interacting $\pi$-orbitals.

This special type of fluoro-effect is nicely demonstrated by the PE. spectrum of 3, as shown in the correlation diagram of Fig. 2. The fluorine induced shifts are –1.0 to –1.3 eV for the orbitals $b_{2g}(\pi)$, $b_{3g}(\pi)$, $b_{2u}(\pi)$ and $b_{1u}(\pi)$ but –2.1 eV for $b_{3u}(\pi)$. This result indicates that the interpretation given for the PE. spectrum of 1 is essentially correct.

**The PE. spectrum of 4-amino[2, 2]paracyclophane (2).** – To conclude we discuss the PE. spectrum of 2. The influence of an amino substituent in position $\varrho$ on the orbital energy $\varepsilon(\boldsymbol{\Psi}_j)$ can be described as an inductive perturbation $\delta\alpha$ of the *Coulomb* term associated with the atomic orbital $\boldsymbol{\phi}_\varrho$ and/or a conjugative interaction between $\boldsymbol{\phi}_\varrho$ and $\boldsymbol{\phi}_N$, the doubly occupied atomic orbital of the amino group. In the framework of our simple model both mechanisms lead to the same predictions because a first order inductive effect will shift $\boldsymbol{\Psi}_j$ by $\delta\varepsilon_{ind}(\boldsymbol{\Psi}_j) = c_{j\varrho}^2\delta\alpha$ whereas the second order conjugative effect leads to $\delta\varepsilon_{conj}(\boldsymbol{\Psi}_j) = c_{j\varrho}^2\,\beta_{CN}^2/(\varepsilon(\boldsymbol{\Psi}_j) - \alpha_N)$ *i.e.* both effects are essentially proportional to $c_{j\varrho}^2$, as long as the difference $\varepsilon(\boldsymbol{\Psi}_j) - \alpha_N$ stays roughly constant. The coefficient $c_{j\varrho}$ is usually taken from the unperturbed molecular orbitals $\boldsymbol{\Psi}_j$, *i.e.* under the implicit assumption that the perturbed orbital $\boldsymbol{\Psi}_j'$ does not differ significantly from $\boldsymbol{\Psi}_j$. We shall now show that in systems such as 1 and 2 the problem is slightly more complex, because a substituent (*e.g.* an amino group in position 4) will compete with the C, C-$\sigma$-orbitals $\varphi_a$ and $\varphi_b$ for the nodes or the largest atomic orbital coefficients of the molecular orbitals $\boldsymbol{\Phi}$ (u, S) and $\boldsymbol{\Phi}$ (u, A), thus causing a rotation of these orbitals.

Perturbing the substituted centre 4 by $\delta\alpha = \langle\boldsymbol{\phi}_4|\mathbf{h}|\boldsymbol{\phi}_4\rangle$ (where $\mathbf{h}$ stands for the perturbation operator) introduces, in addition to the matrix elements given in (4) and (5), the following ones into the secular determinant based on (3):

$$\langle \boldsymbol{\Phi}\,(u,S)\,|\mathbf{h}|\boldsymbol{\Phi}\,(u,S)\rangle = \delta\alpha/12$$
$$\langle \boldsymbol{\Phi}\,(u,A)|\mathbf{h}|\boldsymbol{\Phi}\,(u,A)\rangle = \delta\alpha/4 \qquad (10)$$
$$\langle \boldsymbol{\Phi}\,(u,S)\,|\mathbf{h}|\boldsymbol{\Phi}\,(u,A)\rangle = \delta\alpha/4\,\sqrt{3}$$

Chosing arbitrarily $\delta\alpha = 3$ eV and using the parameters (10), we obtain the following results for the model of **2**, which are compared to those of the unperturbed system **1**:

| **1** (Sym. $D_{2h}$) Unperturbed: $\delta\alpha = 0$ | | **2** (Sym. $C_1$) Perturbed: $\delta\alpha = 3$ eV | |
|---|---|---|---|
| Orbital | Energy eV | Orbital | Energy eV |
| $\boldsymbol{\Psi}_1 \equiv b_{2g}(\pi)$ | $-8.3$ | $\boldsymbol{\Psi}_1'$ | $-7.6$ |
| $\boldsymbol{\Psi}_2 \equiv b_{3g}(\pi)$ | $-8.3$ | $\boldsymbol{\Psi}_2'$ | $-8.3$ |
| $\boldsymbol{\Psi}_3 \equiv b_{3u}(\pi)$ | $-8.3$ | $\boldsymbol{\Psi}_3'$ | $-8.3$ |
| $\boldsymbol{\Psi}_4 \equiv b_{2u}(\pi)$ | $-9.7$ | $\boldsymbol{\Psi}_4'$ | $-9.5$ |
| $\boldsymbol{\Psi}_5 \equiv a_g(\sigma)$ | $-14.0$ | $\boldsymbol{\Psi}_5'$ | $-14.0$ |
| $\boldsymbol{\Psi}_6 \equiv b_{3u}(\sigma)$ | $-15.4$ | $\boldsymbol{\Psi}_6'$ | $-15.4$ |

(11)

We note that according to our model for **2**, two of the first four bands, *i.e.* 1 and 4, are shifted towards lower ionization potentials by 0.7 and 0.2 eV respectively relative to the corresponding bands in the PE. spectrum of **1**, whereas the positions of bands 2 and 3 remain unchanged. As can be seen from Fig. 1 and 2 this is a fairly good description of the observed spectra.

However, for a more precise comparison we need to know how the orbitals $\boldsymbol{\Psi}_1'$ to $\boldsymbol{\Psi}_4'$ of **2** relate to the orbitals of the unperturbed system **1**. To this end we form the overlap matrix $\mathbf{S}$ between the two sets of molecular orbitals $\boldsymbol{\Psi}_j'$ and $\boldsymbol{\Psi}_k$

$$\mathbf{S} = (S_{jk}) = (\langle \boldsymbol{\Psi}_j' | \boldsymbol{\Psi}_k\rangle) \qquad (12)$$

which yields:

| | $\boldsymbol{\Psi}_1$ $b_{2g}(\pi)$ | $\boldsymbol{\Psi}_2$ $b_{3g}(\pi)$ | $\boldsymbol{\Psi}_3$ $b_{3u}(\pi)$ | $\boldsymbol{\Psi}_4$ $b_{2u}(\pi)$ | $\boldsymbol{\Psi}_5$ $a_g(\sigma)$ | $\boldsymbol{\Psi}_6$ $b_{3u}(\sigma)$ | |
|---|---|---|---|---|---|---|---|
| $\boldsymbol{\Psi}_1'$ | .442 | .766 | $-.386$ | $-.262$ | 0 | .019 | |
| $\boldsymbol{\Psi}_2'$ | $-.865$ | .501 | 0 | 0 | 0 | 0 | |
| $\boldsymbol{\Psi}_3'$ | $-.201$ | $-.348$ | $-.916$ | $-.004$ | 0 | .001 | (13) |
| $\boldsymbol{\Psi}_4'$ | $-.119$ | $-.206$ | .109 | $-.964$ | 0 | .011 | |
| $\boldsymbol{\Psi}_5'$ | 0 | 0 | 0 | 0 | 1 | 0 | |
| $\boldsymbol{\Psi}_6'$ | $-.006$ | $-.012$ | .007 | .015 | 0 | 1.000 | |

This matrix (13) shows that $\boldsymbol{\Psi}_3' \approx \boldsymbol{\Psi}_3 = b_{3u}(\pi)$ and $\boldsymbol{\Psi}_4' \approx \boldsymbol{\Psi}_4 = b_{2u}(\pi)$, which means that these two orbitals resemble closely those of the parent molecule. In contrast $\boldsymbol{\Psi}_1'$ and $\boldsymbol{\Psi}_2'$ differ from $\boldsymbol{\Psi}_1$ and $\boldsymbol{\Psi}_2$. The ratio of the overlaps of $\boldsymbol{\Psi}_2'$ with $\boldsymbol{\Psi}_1 \equiv b_{2g}(\pi)$ and $\boldsymbol{\Psi}_2 \equiv b_{3g}(\pi)$ is $S_{21}/S_{22} = -\sqrt{3}$, which means that $\boldsymbol{\Psi}_2'$ is simply the antisymmetric orbital $\boldsymbol{\Psi}_2 \equiv b_{3g}(\pi)$ of **1** switched by 60° as shown in the diagram b of Fig.3. The reason for this switch is obvious: the orbital $\boldsymbol{\Psi}_2$ of **1** is antisymmetric with respect to the x,y-plane, so that the interaction with $\varphi_a$ und $\varphi_b$ is zero. The perturbed centre 4

in **2** choses the node of the orbital with the result that no asymmetry and no inter-action with $\varphi_a$ and $\varphi_b$ is induced. The case of $\Psi_1'$ is slightly more complex. In a first
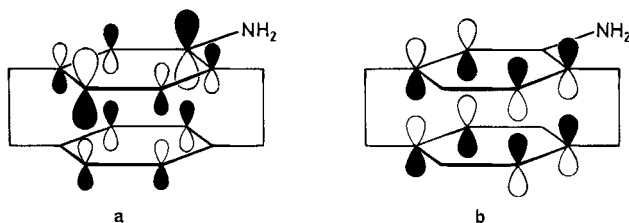


Fig. 3. *Schematic representation of the 'switched' orbitals* $\Psi_1'$, (a) *and* $\Psi_2'$, (b) *of 4-amino[2,2]para-cyclophane*

approximation the orbital may be represented as shown in the diagram of Fig. 3. Here the centre 4 choses the largest atomic orbital coefficient of $\Phi$ (u, S) so that this orbital is switched again by 60°. However, the lower orbital corresponds more closely to $\Phi$ (1, A). Thus it becomes rather difficult to correlate $\Psi_1'$ in a simple way to one of the $\pi$-orbitals $\Psi_j$ of **1**.

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