

PHOTOELECTRON SPECTRA OF SOME FLUORINE SUBSTITUTED DIAZANAPHTHALENES

D. M. W. VAN DEN HAM and D. VAN DER MEER

Chemical Physics Laboratory, Twente University of Technology, Enschede (The Netherlands)

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ABSTRACT

The high resolution He 584 Å photoelectron spectra of fluorine substituted 1,2-diaza-, 1,3-diaza-, 1,4-diaza- and 2,3-diaza-naphthalene are presented. By means of fluorine substitution the analysis of the photoelectron spectra of the parent compounds can be made more definite. Unexpected shifts of the nitrogen “lone-pair” bands can be explained within the through-space and through-bond interaction model. From this explanation one can deduce that fluorine substitution can give experimental evidence about the symmetry character of the “lone-pair” molecular orbitals.

1. INTRODUCTION

Considering the host of publications that deal with the interaction between equivalent “lone-pair” orbitals, it clearly is a subject that enthrals both theorist and experimentalist (see for example refs. 1–5). The group of the diazanaphthalenes offers a splendid opportunity to study these interactions. That interaction exists in these molecules has been demonstrated both with ultraviolet spectroscopy⁵ and photoelectron spectroscopy^{6, 7}. It has been explained by Hoffmann et al.¹ by introducing the “through-space” and “through-bond” concepts. The existence of “through-bond” interaction shows that the “lone-pair” orbitals participate in the σ bonding framework. This does not imply, however, that there is no difference between “lone-pair” and σ molecular orbitals [MO's]. The “lone-pair” bands and the σ bands lie in different regions of the photoelectron spectrum. The two “lone-pair” bands that are found in every diazanaphthalene photoelectron spectrum, can be assigned to MO's in which the “lone-pair” orbitals occur as mainly symmetric and antisymmetric combinations respectively.

To study this interaction, we have to be sure about the analysis of the spectra. In those cases where “lone-pair” bands are hidden under other bands the assignment

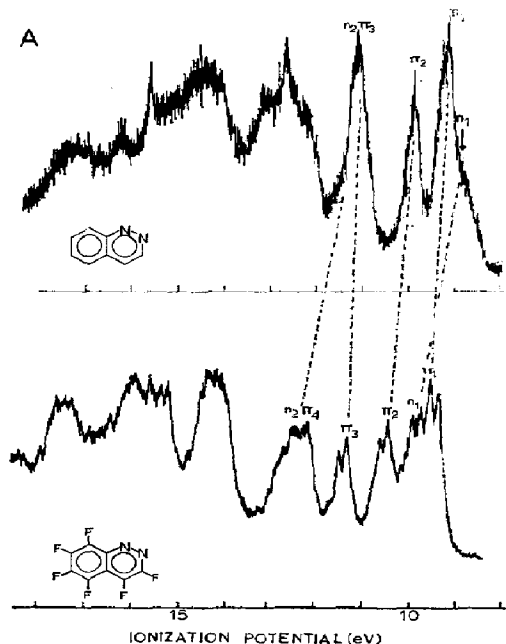
might leave some doubts. By making use of the so-called "perfluoro effect"^{8, 9}, one can try to make the analysis of the spectra more definite, as was done in the case of the spectra of quinoline and isoquinoline¹⁰.

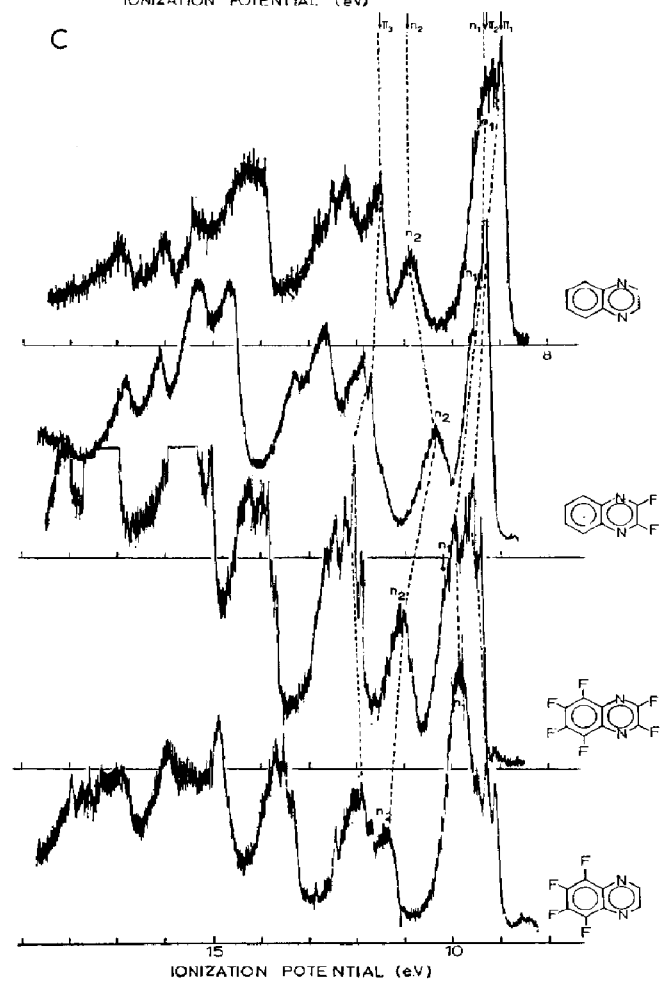
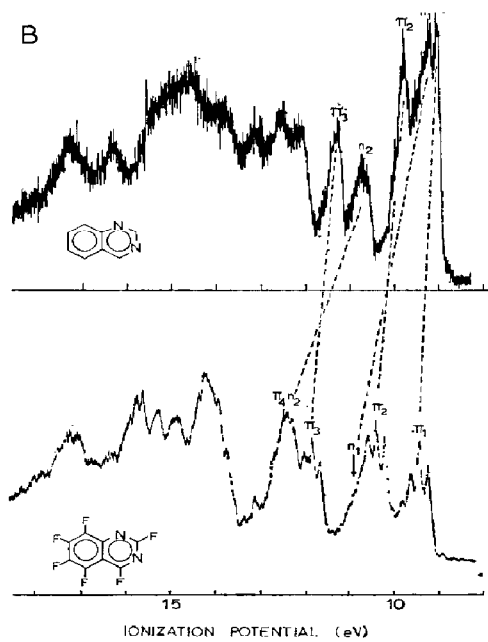
2. METHODS AND RESULTS

The spectra of the unsubstituted compounds as well as of the fluorine substituted 1,4-diazanaphthalenes, have been recorded on a Perkin-Elmer PS 15 photoelectrospectrometer; the other spectra on a Vacuum Generators spectrometer. All photoionizations have been brought about by irradiation with a He 584 Å source.

The compounds hexafluoro-1,2-diazanaphthalene (A6), hexafluoro-1,3-diazanaphthalene (B6), hexafluoro-1,4-diazanaphthalene (C6), 5,6,7,8-tetrafluoro-1,4-diazanaphthalene (C4), 2,3-difluoro-1,4-diazanaphthalene (C2) and hexafluoro-2,3-diazanaphthalene (D6) have been synthesized according to instructions in the literature¹¹⁻¹⁴. The other compounds have been obtained from commercial sources.

The spectra are presented in Figure 1 (A-D). The spectra of the unsubstituted compounds have been published before^{6, 7, 15} but have been added for reasons of comparison.





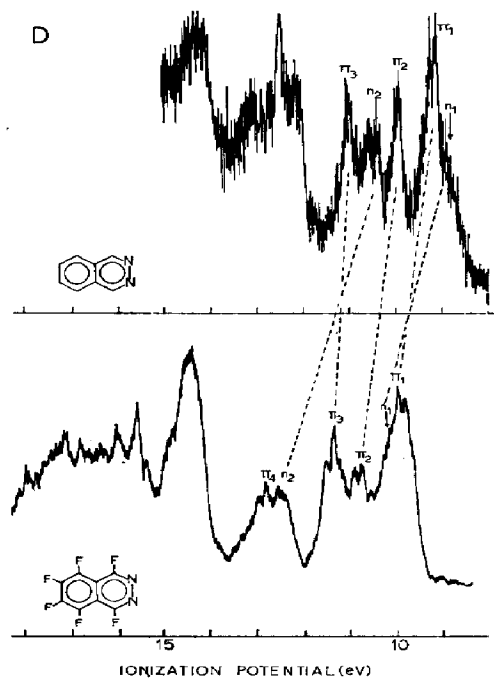


Figure 1. Photoelectron spectra of: A, 1,2-diazanaphthalene and hexafluoro-1,2-diazanaphthalene; B, 1,3-diazanaphthalene and hexafluoro-1,3-diazanaphthalene; C, 1,4-diazanaphthalene, 2,3-difluoro-1,4-diazanaphthalene, 5,6,7,8-tetrafluoro-1,4-diazanaphthalene and hexafluoro-1,4-diazanaphthalene; D, 2,3-diazanaphthalene and hexafluoro-2,3-diazanaphthalene.

3. DISCUSSION

3.1. Assignment of spectral bands to ionization from π MO's

The complexity of the studied molecules restrains us from making a complete analysis of the vibrational fine structure, so assignments of the spectral bands have to rely on comparison of the experimentally observed band shapes.

It has been observed^{6, 7} that the introduction of nitrogen atoms in the aromatic nucleus hardly changes the π band envelopes. This seems to hold also for corresponding perfluoro compounds. The only difference is that in the unsubstituted series the $0 \leftarrow 0$ vibrational component is the most intense, whereas the $1 \leftarrow 0$ transition seems to be favoured in the perfluoro series^{9, 10}.

Comparison of the spectra of the perfluoro compounds A6, B6, C6 and D6 with those of octafluoronaphthalene⁹, heptafluoroquinoline and -isoquinoline¹⁰ made it possible to select a group of bands and assign them directly to ionization from π MO's. In those cases where assignment on these grounds was disputable, we checked our assignment with Hückel calculations (see Section 3.2).

The experimental π ionization potentials have been collected in Table 1. Those potentials that have been checked with Hückel calculations appear between brackets.

TABLE 1

EXPERIMENTAL AND CALCULATED π IONIZATION POTENTIALS (eV)

<i>Spectrum</i>	<i>Compound</i>	<i>Orbital</i>	<i>IP (π) observed</i>	<i>IP (π)* Hückel</i>	<i>IP (π) EHT</i>
A	1,2-diazanaphthalene	π_1	9.10	8.80	12.43
		π_2	9.83	9.98	13.08
		π_3	(11.00)	10.95	13.61
A6	hexafluoro-1,2-diazanaphthalene	π_1	9.66	9.76	12.02
		π_2	10.57	10.50	12.83
		π_3	11.45	11.50	13.32
		π_4	(12.32)	12.62	14.15
B	1,3-diazanaphthalene	π_1	9.08	8.90	12.47
		π_2	9.80	9.96	12.99
		π_3	11.30	11.30	14.00
B6	hexafluoro-1,3-diazanaphthalene	π_1	9.43	9.76	12.10
		π_2	10.41	10.50	12.70
		π_3	11.86	11.63	13.88
		π_4	(12.45)	12.56	14.14
C	1,4-diazanaphthalene	π_1	9.00	8.99	12.55
		π_2	(9.30)	9.64	12.70
		π_3	11.56	11.66	14.14
C2	2,3-difluoro-1,4-diazanaphthalene	π_1	9.30	9.05	—
		π_2	(9.60)	9.95	—
		π_3	11.85	11.72	—
C4	5,6,7,8-tetrafluoro-1,4-diazanaphthalene	π_1	9.50	9.79	—
		π_2	9.90	9.95	—
		π_3	12.00	11.78	—
C6	hexafluoro-1,4-diazanaphthalene	π_1	9.65	9.86	12.15
		π_2	(10.10)	10.31	12.38
		π_3	12.15	11.82	13.77
		π_4	(12.57)	12.40	14.21
D	2,3-diazanaphthalene	π_1	9.07	8.80	12.52
		π_2	(9.95)	10.12	13.09
		π_3	11.00	10.82	13.54
D6	hexafluoro-2,3-diazanaphthalene	π_1	9.90	9.73	12.20
		π_2	10.85	10.60	12.80
		π_3	11.37	11.37	13.28
		π_4	(12.87)	12.75	14.26

* $\alpha = 6.42$ eV; $\beta = 3.21$ eV.

3.2. Correlation of experimental and calculated π ionization potentials

Previously¹⁰, we demonstrated that the effect of the fluorine substitution could be described with Hückel calculations. A parameter set ($\alpha_N = \alpha_C + 0.7\beta_{CC}$; $\alpha_{C(F)} = \alpha_C + 0.6\beta_{CC}$; $\alpha_F = \alpha_C + 3.0\beta_{CC}$; $\beta_{CC} = \beta_{CN}$; $\beta_{CF} = 0.7\beta_{CC}$) has been proposed, with which the π energies of the perfluoro as well as of the parent naphthalene and

monoazanaphthalenes could be predicted. It seemed reasonable to expect that the same parameter set would also work well with the diaza series.

A plot of the experimental π ionization potentials ($IP(\pi)$) versus the calculated $IP(\pi)$'s (Koopman's theorem: $IP = -\epsilon$, $\epsilon =$ orbital energy) fitted a linear relation very well (Fig. 2). We used the Hückel calculations to assign in the spectra A6, B6, C6 and D6 those π bands that we left out in first instance (see Section 3.1). One can expect that this Hückel model works equally well with partly fluorinated compounds. The π bands in the spectra C2 and C4 have been analysed mainly on the basis of these calculations.

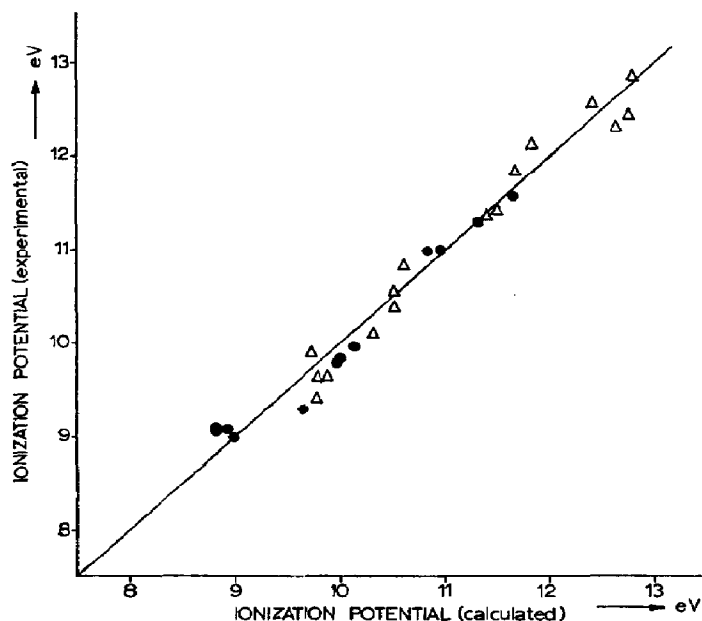


Figure 2. Correlation of experimental versus calculated π ionization potentials.

With the limitation that only isomeric molecules could be described, the results of extended Hückel theory (EHT) show a good correlation with the experimental $IP(\pi)$'s. The reason for this limitation to isomeric molecules might be that the parameters for the fluorine atom (Section 3.3) do not match the other parameters.

3.3. Perfluoro effect and assignment of bands to ionization from "lone-pair" MO's

Brundle et al.^{8, 9} pointed out that perfluorination of aromatic molecules will shift π and σ levels to a different extent. One can expect that "lone-pair" MO's, with their partly σ character will also exhibit larger shifts to lower energies than the π MO's. This phenomenon has indeed been found in the perfluoro spectra of pyridine³, quinoline and isoquinoline¹⁰ and led us to a reinvestigation of the spectra of 1,2- and 2,3-diazanaphthalene (A and D).

TABLE 2
EXPERIMENTAL AND CALCULATED "LONE-PAIR" IONIZATION POTENTIALS (eV)

Spectrum	Compound	$IP(N)_1$ <i>observed</i>	$IP(N)_2$ <i>observed</i>	$IP(N)_2 - IP(N)_1$ $= \Delta IP(N)$ <i>observed</i>	$IP(N)_1$ <i>EHT</i>	$IP(N)_2$ <i>EHT</i>	Symmetry highest "lone-pair" MO <i>EHT</i>
A	1,2-diazanaphthalene	8.90	11.05	2.15	12.14	13.85	A
A6	hexafluoro-1,2-diazanaphthalene	9.98	12.57	2.40	12.43	14.53	A
B	1,3-diazanaphthalene	9.50	10.70	1.20	12.11	12.76	A
B6	hexafluoro-1,3-diazanaphthalene	10.90	12.30	1.40	12.65	13.19	A
C	1,4-diazanaphthalene	9.30	10.90	1.60	11.85	13.79	S
C2	2,3-difluoro-1,4-diazanaphthalene	9.50	10.40	0.90	—	—	S
C4	5,6,7,8-tetrafluoro-1,4-diazanaphthalene	10.00	11.50	1.50	—	—	S
C6	hexafluoro-1,4-diazanaphthalene	10.10	11.10	1.00	12.29	13.84	S
D	2,3-diazanaphthalene	8.70	10.60	1.90	12.01	13.47	A
D6	hexafluoro-2,3-diazanaphthalene	10.12	12.29	2.17	12.13	14.13	A

The first IP in these compounds has been attributed to ionization from a "lone-pair" MO. The main argument for this assignment was the different behaviour of the first band compared to the first bands in naphthalene, the monoaza- and the other diazanaphthalenes. As the start of the first band in the perfluoro spectra A6 and D6 shows a normal π shape, this definitely settles the assignment of that part of A and D.

In all the spectra of the perfluorinated compounds we found (by comparison of band shapes and intensities) two "lone-pair" bands. Only in the case of B6 the first band was nearly totally obscured by the second π band. Scale expansion of this part of the spectrum gave some indication of the existence of an underlying "lone-pair" band.

All the "lone-pair" IP's have been marked in Figure 1A–1D and have been collected in Table 2.

Although considerable objections have been made against the use of EHT (e.g. Dewar¹⁶), we found this type of calculation useful in the prediction of the "lone-pair" splitting in the diazanaphthalene series⁶. The calculations were based on regular molecular geometry: $R(\text{CC}) = R(\text{CN}) = R(\text{NN}) = 1.397 \text{ \AA}$; $R(\text{CH}) = 1.084 \text{ \AA}$; $R(\text{CF}) = 1.360 \text{ \AA}$ and the parameters of Table 3.

TABLE 3
PARAMETERS EXTENDED HÜCKEL THEORY

Atom	Slater exponent	Alpha (2s)	Alpha (2p)
C	1.625	21.40	11.40
N	1.95	26.00	13.40
F	2.60	40.20	18.60

The results of the calculations are shown in Figure 3. The plot shows a reasonable correspondence between calculated and experimental data.

3.4. Interaction mechanisms, interaction sign

An important feature of the "through-space and through-bond" concept is that it predicts the sign of the splitting, i.e. predicts whether the symmetric (S) or the antisymmetric (A) "lone-pair" combination has the higher energy. In the case of the diazanaphthalenes these predictions are also in accordance with EHT (Table 2). To check the validity of these predictions, we investigated the effect of fluorine substitution on the magnitude of the "lone-pair" splitting in 1,2-, 2,3- and 1,4-diazanaphthalene.

If we look at the data of Table 2 there are some remarkable facts that draw the attention. First, the magnitude of the "lone-pair" splitting $\Delta\text{IP}(\text{N})$ increases in the

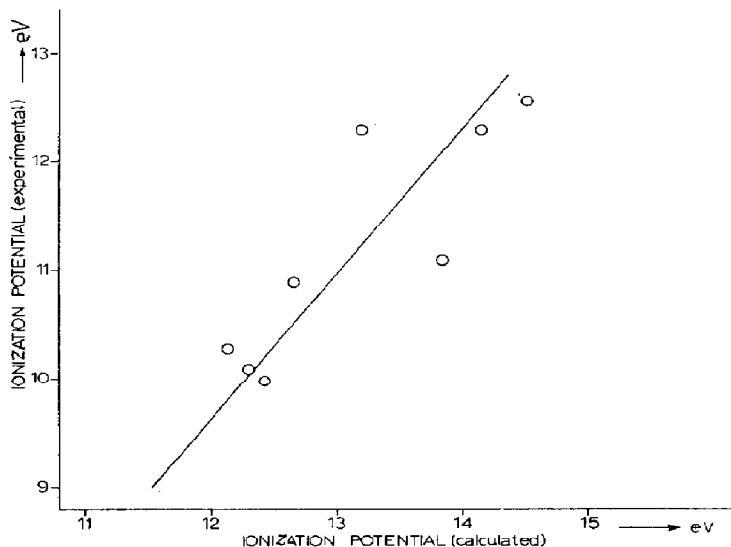


Figure 3. Correlation of experimental versus calculated "lone-pair" ionization potentials.

cases A \rightarrow A6, D \rightarrow D6, decreases in the cases C \rightarrow C6, C \rightarrow C2 and stays nearly unaltered in the case C \rightarrow C4; secondly the shifts of comparable "lone-pair" bands in the spectra of the substituted and parent compounds are in many cases much smaller than expected. We measured¹⁰ the effect of perfluoro substitution on the "lone-pairs" of quinoline and isoquinoline and found a shift of ca. 2.2 eV in both cases. One is inclined to expect slightly smaller shifts in the perfluoro series of the diazaphthalenes.

To explain these facts, we have to look more carefully at the interaction of equivalent "lone-pair" MO's. Let us assume a system with mirror plane symmetry, in which the MO's can be classified according to their transformation properties as S (symmetric) and A (antisymmetric) species. Figure 4 shows the effects of interaction and fluorine substitution.

In Figure 4, the energy gap (~ 10 eV) between the σ^* levels and the "lone-pair" levels is much larger than the one between the σ levels and the "lone-pair" levels (1 \sim 3 eV). The first energy gap (~ 10 eV) is not only in accordance with the calculations (EHT), but also with experiments concerning electron affinities of aromatic molecules¹⁷. The cases of Figure 4a-4c have been amply discussed by Hoffmann¹. Figure 4 shows that fluorine substitution causes all σ levels to shift to lower energies (inductive effect). Figure 4e shows that all the new σ MO's due to the fluorine substitution appear below the levels of the "lone-pair" MO's. Some of these new occupied σ MO's have symmetry properties that are favourable for mixing with the A combination. This means that after fluorine substitution A also has gained energy. In Figure 5 a correlation diagram of the spectra of C, C2, C6, C4, D and D6 is shown. The shifts in the levels of these molecules can be discussed in terms of Figure 4.

In 1,4-diazaphthalene (C), MO theory requires 17 occupied, 2 "lone-pair"

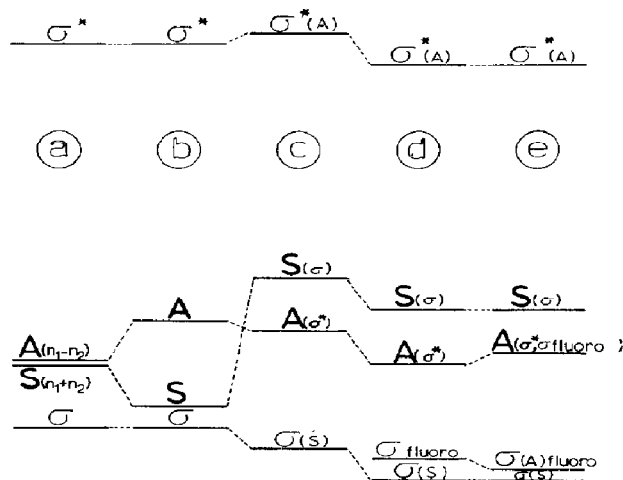


Figure 4. Effects of interaction and fluorine substitution on the "lone-pair" levels. (a) No interaction; (b) Direct interaction; (c) Interaction with σ orbitals added; (d) Inductive effect added; (e) All effects together.

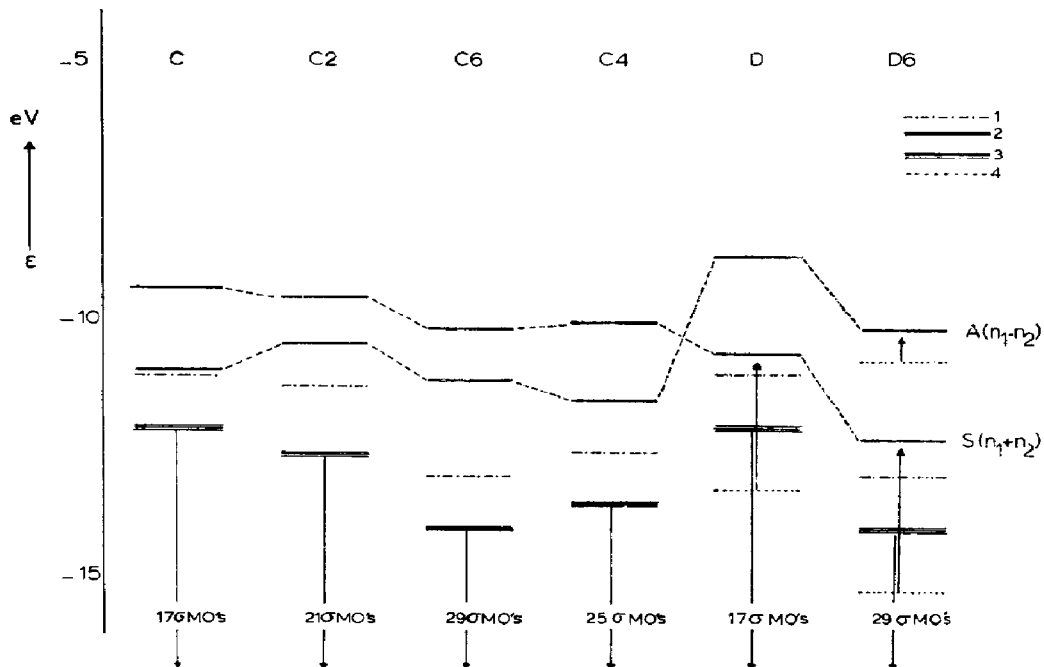


Figure 5. Orbital correlation diagram of the spectra C, C2, C6, C4, D and D6. (1) Degenerate level; (2) "lone-pair" level; (3) highest occupied σ levels; (4) hypothetical "lone-pair" level without through-bond interaction.

and 17 unoccupied σ MO's. Of the occupied σ MO's the majority will be of a symmetry type favourable for mixing with the S combination (Hoffmann et al.¹). Level A stays close to the original degenerate level, as the through-space interaction is small (or non existent).

Introduction of two fluorine atoms (case C2) will lower all σ MO's to some extent. Now MO theory generates 21 occupied σ MO's. The symmetry character of the top σ MO's becomes favourable for mixing with A. The effect will be that the energy of A will be raised by mixing with underlying σ orbitals. In the case of C6, the original degenerate level will be ~ 2 eV lower than in C. Here there are 12 extra σ MO's clustering together, with energies close to the degenerate level. Both S and A will be repelled strongly.

In C4 we see that the interaction energy of A with the new σ MO's (σ fluoro) is also influenced by the orbital shape. Here all the highest occupied σ -fluoro MO's are mainly concentrated on the aromatic nucleus. No substantial interaction due to fluorine substitution takes place and S and A will have nearly the same separation as in the parent compound. The only difference is that the inductive effect of the fluorine atoms shifts all σ and "lone-pair" MO's towards lower energy. In case D, we expect strong through-space interaction of the two "lone-pair" MO's bringing A higher up the energy scale than S. Because of the mixing of S with underlying σ MO's we shall find S closer to the degenerate level than A. In case D6 the six fluorine atoms will reduce the energy of the degenerate level by about 2 eV. The through-space interaction will be unaltered (to first order). As A mixes with the new σ -fluoro MO's in this case too, the overall effect is an increase of the splitting.

If the "lone-pair" orbitals are not equivalent, symmetry considerations are more arbitrary and it will be more appropriate to quantify the interaction by some kind of perturbation calculation. We will postpone such calculations until more experimental data, especially concerning molecules where nitrogen atoms are separated by an odd number of carbon atoms, are at hand.

4. CONCLUSIONS

1. The assignments of the first ionization potential in 1,2-diazanaphthalene and 2,3-diazanaphthalene to a "lone-pair" MO have been proven to be correct.
2. The applicability of the perfluoro effect in the separation of π and "lone-pair" bands is limited by the symmetry properties of the corresponding "lone-pair" MO's.
3. In the case of molecules with equivalently placed "lone-pairs" comparisons of the photoelectron spectra of fluorinated and parent compounds give an indication of the sign of the interaction.

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