

THE INFLUENCE OF FLUORO SUBSTITUENTS ON CYCLOPROPA- -BENZENE, -NAPHTHALENE, AND -ANTHRACENE

Jacques LECOULTRE^a, Edgar HEILBRONNER^{a*},
Paul MÜLLER^b and Domingo RODRIGUEZ^b

^a *Institut für Physikalische Chemie, Universität Basel, CH-4056 Basel, Schweiz*

^b *Département de Chimie Organique, Université de Genève, CH-1211 Genève 4, Suisse*

Received November 13th, 1987

Accepted December 16th, 1987

Dedicated to Dr R. Zahradnik on the occasion of his 60th birthday.

The He(I α) PE spectra of cyclopropabenzene, cyclopropa[*b*]naphthalene, cyclopropa[*b*]anthracene, their 1,1-difluoro derivatives and of some of their substituted derivatives have been recorded, analyzed and assigned by correlation with the PE spectra of the parent molecules benzene, naphthalene and anthracene. It is shown that the PE spectroscopic data yield no information about the presence or absence of a Mills–Nixon effect in the molecules investigated. The inductive effect of the bridging CH₂ group of the cyclopropeno ring is close to zero, whereas that of the CF₂ group leads to positive ionization energy shifts in good agreement with previous experience. The hyperconjugative interaction of the local pseudo- π orbital of the CH₂ group yields a significant destabilisation of the π -orbitals of B₁ symmetry.

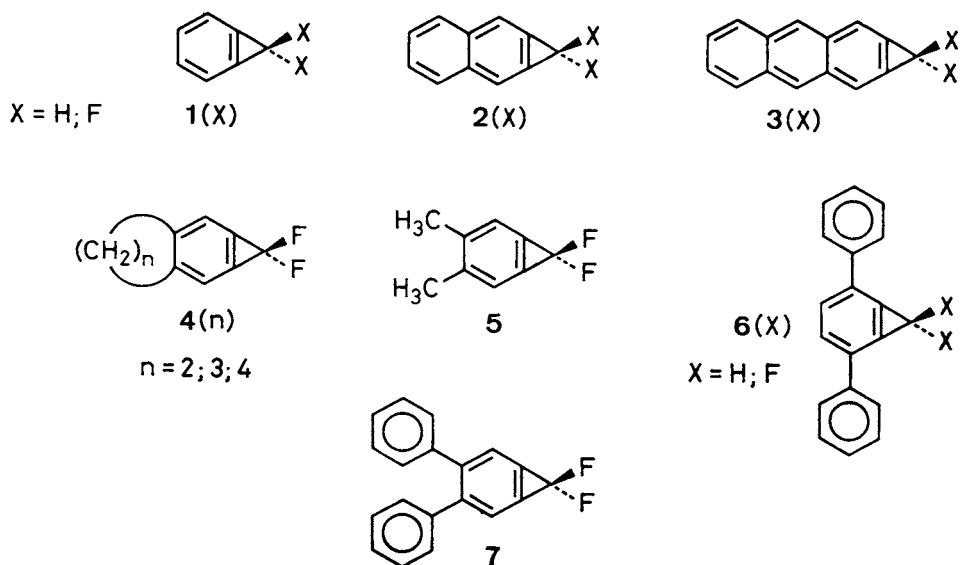
Substituting some or all H-atoms of a hydrocarbon C_nH_m by F-atoms leads to ionization energy shifts ΔI_j^m , which – unfortunately – do not fall into a simple pattern. For example, perfluorination of planar unsaturated or aromatic π -systems will leave the positions of the π^{-1} -bands in the PE-spectra unchanged (e.g. for the pair ethene, tetrafluoroethene, $\Delta I_1^m = 0.002$ eV, see ref.¹) or will shift them by less than ~ 1 eV (e.g. benzene, hexafluorobenzene, $\Delta I_1^m = 0.88$ eV, see refs^{2–4}, cf. ref.⁵), whereas the σ^{-1} -bands are shifted by $\Delta I_j^m \approx 2.5$ to 4 eV towards higher ionization energies. This effect, which allows one to discriminate between π^{-1} - and σ^{-1} -bands in the PE-spectra of planar π -systems has been termed “perfluoro effect” by Brundle, Robin and their coworkers^{1–4}. If the F atoms do not lie in the nodal plane of the π -system, e.g. if the methyl group of toluene is replaced by a trifluoromethyl group, then all bands, π^{-1} and σ^{-1} , are shifted towards higher ionization energies by substantial amounts^{6,7}.

The rationalization of the lack of dependence of π^{-1} ionization energies on “in-plane” F-substitution, i.e. the compensation of the ionization energy increasing

* Author for correspondence.

effect due to the high electronegativity of the F-atom, by the ionization energy decreasing F-lone-pair/ π -electron repulsion, was originally proposed by Clark, Murrell and Tedder⁸. This compensation breaks down if the F-atoms occupy out-of-plane positions. In this case the electronegativity effect dominates, as shown by the large positive ΔI_j^m observed for *all* PE bands. However, these shifts are not easy to parametrize in a transparent fashion. From this point of view a comparison of the ionization energies I_j^m of the F-substituted molecules discussed below with the I_j^m of the corresponding parent hydrocarbons is of special interest, because of the fact that the F-atoms lie on a symmetry plane of the molecule which is not the plane of its π -system. In this respect the situation is reminiscent of that encountered in F-substituted cumulenes e.g. tetrafluoroallene⁹ or tetrafluorobutatriene¹⁰.

The molecules investigated in this work are cyclopropabenzene **1**(H), ref.¹¹, the PE spectrum of which has been discussed previously¹², 1,1-difluorocyclopropabenzene **1**(F), ref.¹³, cyclopropa[*b*]naphthalene **2**(H), ref.¹⁴, and its 1,1-difluoro derivative **2**(F), ref.¹⁵, cyclopropa[*b*]anthracene **3**(H) and its 1,1-difluoro derivative **3**(F), refs^{16,17}, the 3,4-disubstituted derivatives **4**(n) and **5** of **1**(F), ref.¹⁸, 2,5-diphenylcyclopropabenzene **6**(H), ref.¹³, and its 1,1-difluoro derivative **6**(F), refs^{19,20}, and finally 1,1-difluoro-2,5-diphenylcyclopropabenzene **7**, ref.¹⁸.



RESULTS

The He(I α) PE spectra of the molecules **1**(X), **2**(X), **4**(n), and **5** have been recorded at temperatures below $\sim 50^\circ\text{C}$, whereas temperatures around 120°C were necessary

for **3(X)**, **6(X)**, and **7**. The observed ionization energies I_j^m are collected in Tables I and II, and for the molecules **6(H)** and **6(F)** in Table III. As can be seen from the examples shown in Fig. 1 the PE spectra are reasonably well resolved. In Fig. 2 the PE band positions I_j^m observed for the molecules **1(X)**, **2(X)**, and **3(X)**, with X = H

TABLE I

Ionization energies I_j^m (in eV) and orbital labels for the low energy bands in the He(I α) PE spectra of the molecules **1(X)**, **2(X)**, **3(X)** with X = H or F, and of the parent hydrocarbons benzene, naphthalene and anthracene. Estimated errors: ± 0.02 eV if two decimals given, ± 0.05 eV if second decimal as subscript, ± 0.1 eV if only one decimal given. The orbital labels refer to the axes defined in Scheme 1

Compound	Band				
	1	2	3	4	5
Benzene	9.25 $1e_{1g}$	9.25 $1e_{1g}$	~ 11.5		
	9.24	9.24			
1(H)	8.82 b_1	9.48 a_2	10.17		
1(F)	10.1 b_1	10.1 a_2			
Naphthalene	8.15 a_u	8.88 b_{1u}	10.01 b_{2g}	~ 11	
	8.15	8.88	9.98		
2(H)	8.12 a_2	8.68 b_1	10.1 ₅ a_2		
2(F)	8.58 a_2	9.5 ₀ b_1	10.6 ₅ a_2		
Anthracene	7.40 b_{2g}	8.52 b_{3g}	9.16 a_u	10.13 b_{2g}	10.21 b_{1u}
	7.41	8.54	9.19	10.18	10.28
3(H)	7.39 a_2	8.3 ₅ b_1	9.1 ₅ a_2	~ 10.2 a_2	~ 10.2 b_1
3(F)	7.79 a_2	9.04 b_1	9.62 a_2	~ 10.5	10.6

TABLE II

Shifts of PE band positions (in eV) of benzene, naphthalene and anthracene due to cyclo-CH₂ annelation

Compound	Band		
	1	2	3
1(H)	-0.4 ₅	+0.2 ₅	
2(H)	-0.0 ₅	-0.2 ₀	+0.1 ₅
3(H)	0.0 ₀	-0.2 ₀	-0.0 ₅

TABLE III
Shifts of PE band positions (in eV) of benzene, naphthalene and anthracene due to cyclo-CF₂ annelation

Compound	Band			
	1	2	3	mean
1(F)	0.85	0.85		0.85
2(F)	0.43	0.62	0.66	0.57
3(F)	0.39	0.51	0.44	0.45

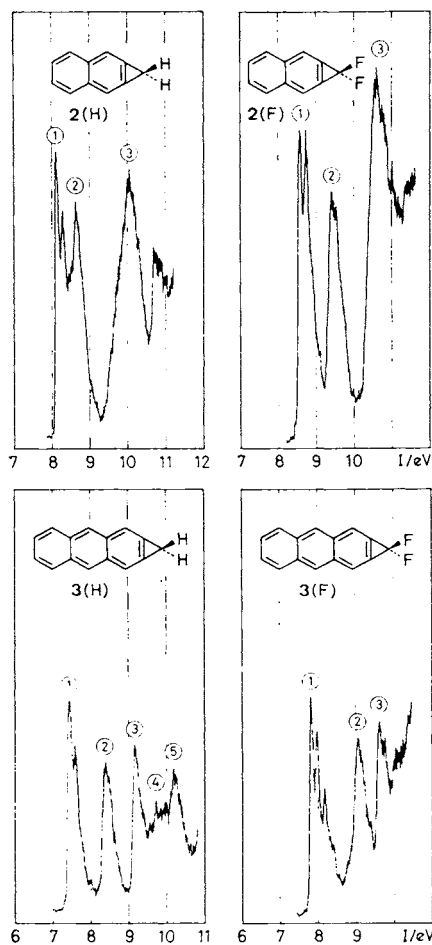


FIG. 1
He(I α) PE spectra of cyclopropa[*b*]naphthalene **2(H)**, cyclopropa[*b*]anthracene **3(H)** and their 1,1-difluoro derivatives **2(F)** and **3(F)**

or F, are correlated with those of the parent hydrocarbons benzene, naphthalene and anthracene²¹⁻²³ (cf. Table I). The change in symmetry labels associated with the descent in symmetry from D_{6h} or D_{2h} to C_{2v} is based on the convention for the coordinate axes as depicted in Scheme 1 (using naphthalene and **2(H)** as examples). Note that the e_{1g} π -orbitals of benzene give rise to a b_1 and an a_2 orbital in **1(X)**.

The shifts of the bands *j* in the PE spectra of the molecules **1(X)**, **2(X)**, and **3(X)**, due to the presence of the CH_2 or the CF_2 moiety (i.e. $X = \text{H}$ or $X = \text{F}$), are defined

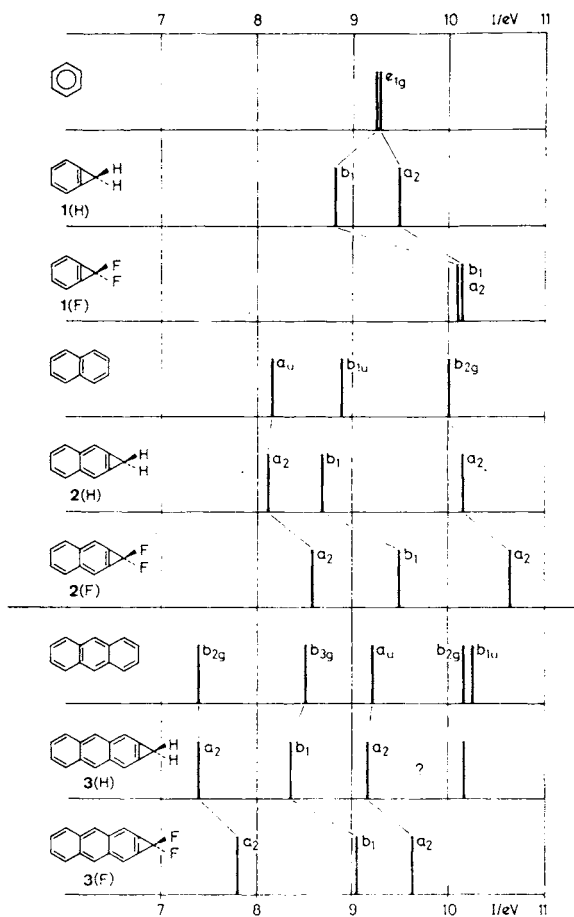


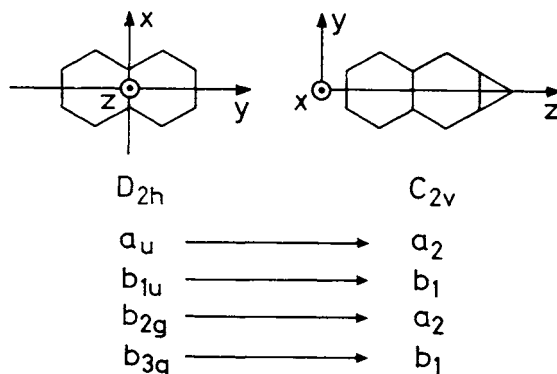
FIG. 2

π -Band correlation diagram for benzene \rightarrow **1(H)** \rightarrow **1(F)**, naphthalene \rightarrow **2(H)** \rightarrow **2(F)** and for anthracene \rightarrow **3(H)** \rightarrow **3(F)**

according to

$$\Delta I_j^m(\mathbf{N}(X)) = I_j^m(\mathbf{N}(X)) - I_j^m(\text{parent}) \quad (1)$$

for $\mathbf{N} = 1, 2$, and 3 , relative to the band positions in the PE spectra of the parent hydrocarbons benzene, naphthalene and anthracene. The values shown in Tables II and III are observed (cf. Table I and Fig. 2). Whereas the unexpected pattern of the $\Delta I_j^m(\mathbf{N}(H))$ -shifts needs some comments (cf. below), the $\Delta I_j^m(\mathbf{N}(F))$ values are, more or less, as expected. In particular, the mean shift decreases with increasing size of the parent system.



SCHEME 1

The assignment of the double band 1 2 in the PE spectra of $4(n)$ and 5 (cf. Table IV) is of course the same as for $1(F)$. The individual band positions I_1^m and I_2^m have

TABLE IV

Ionization energies I_j^m (in eV) of the first two bands ($j = 1$ or 2) in the PE spectra of the molecules $1(F)$, $4(n)$ with $n = 2, 3$ or 4 , and of 5 . $\langle I_{1,2}^m \rangle = (I_1^m + I_2^m)/2$. $\Delta I_{1,2}^m = I_2^m - I_1^m$. $W_{1/2}$ is the full width at half height of the peak consisting of the two overlapping bands 1 and 2. Estimated error: ± 0.05 eV if second decimal given as subscript, otherwise ± 0.1 eV. Values in parenthesis refer to the maximum of the unresolved double band 1 2

Compound	I_1^m	I_2^m	$I_{1,2}^m$	$\Delta I_{1,2}^m$	$W_{1/2}$
1(F)	(10.1)	(10.1)	10.1 ₀	~ 0	0.6 ₀
4(2)	9.3 ₅	9.7 ₀	9.5 ₀	0.3 ₅	0.8 ₀
4(3)	9.2 ₀	9.7 ₀	9.4 ₅	0.5 ₀	0.9 ₅
4(4)	(9.4 ₅)	(9.4 ₅)	9.4 ₅	~ 0.2 ₅	0.7 ₅
5	(9.6 ₀)	(9.6 ₀)	9.6 ₀	~ 0.2	0.7 ₅

been assessed as follows (cf. Fig. 3). In the PE spectrum of **1(F)**, bands 1 and 2 fall practically on top of each other, leading to a double band of full width at half height $W_{1/2} = 0.60$ eV, from which we deduce that $W_{1/2}$ for each of the two components must be slightly smaller, say $W_{1/2}^o \approx 0.5$ eV. In the PE-spectra of **4(2)** and **4(3)** the two components 1, 2 are nicely split, so that their individual positions I_1^m and I_2^m can be determined (see Table IV). Assuming that $W_{1/2}^o$ of each band remains unaffected by substitution in positions 4 and 5, one expects that $W_{1/2}$ and $\Delta I_{1,2}^m = I_2^m - I_1^m$ satisfy the condition $\Delta I_{1,2}^m = W_{1/2} - W_{1/2}^o$, with $W_{1/2}^o \approx 0.5$ eV. As can be seen from Table IV, this is indeed the case. The double band 1 2 in the PE spectra of **4(4)** and **5** is beyond deconvolution. However, applying the above approximation, we can derive plausible $\Delta I_{1,2}^m$ estimates from the observed $W_{1/2}$ values, as shown in the last two columns of Table IV. Obviously nothing can be deduced from the PE spectra of Fig. 3, concerning the orbital sequence (assuming Koopmans theorem). However, by comparison with *o*-substituted benzenes^{1,2} the assignment 1, b_1 ; 2, a_2 seems plausible.

The assignment of the bands in the PE spectra of **6(H)** and **6(F)** is straightforward (cf. Fig. 4 and Table V). The PE spectrum of *p*-terphenyl has been recorded by Schmidt^{2,3}. The intensity ratios of the first three bands at $I_1^m = 8.04$ eV, $I_2^m = 9.03$ eV, $I_3^m = 9.95$ eV are 1 : 4 : 1 approximately, which suggests that these bands should be correlated with the following π -orbitals (assuming D_{2h} symmetry): 1 $3b_{2g}$; 2 ($1a_g, 3b_{1u}, 2b_{3g}, 1b_{3g}$); 3 $2b_{2g}$. Within a standard HMO treatment (cf. top of Fig. 4) the four orbitals associated with the composite band 2 are accidentally degenerate. From these orbital diagrams it is obvious that orbital $2b_{3g}$ will be the one suffering by far the greatest destabilization, if the central benzene ring is bridged in positions 2

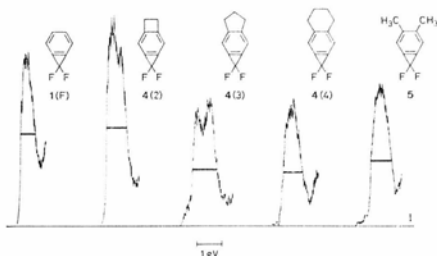


FIG. 3

Double-band 1 2 in the He(I α) PE spectra of **1(F)**, **4(n)** with $n = 2, 3, 4$ and of **5**. Band positions and characteristic data are given in Table IV. The horizontal bars indicate the width at half height $W_{1/2}$, also given in Table IV

and 3 by a methylene group to yield **6(H)**, whereas the energy of the three other orbitals $1a_u$, $1b_{3g}$, and $3b_{1u}$ (degenerate with $2b_{3g}$ in *p*-terphenyl) should remain unaffected. The two orbitals $3b_{2g}$ and $2b_{2g}$, associated with bands 1 and 3, respectively, are expected to shift by only small amounts (cf. the results in the series **1(H)**, **2(H)**, **3(H)**). All these expectations are nicely borne out by the experimental results

TABLE V
Ionization energies I_j^m (in eV) of terphenyl and its derivatives

Compound	Band			
	1	2	3	4
<i>p</i> -Terphenyl ²³	8.04	9.03–9.20	9.95	
6(H)	7.8 ₅	8.6 ₅	9.0	~9.8
6(F)	8.2 ₀	9.2 ₅	10.5 ₅	

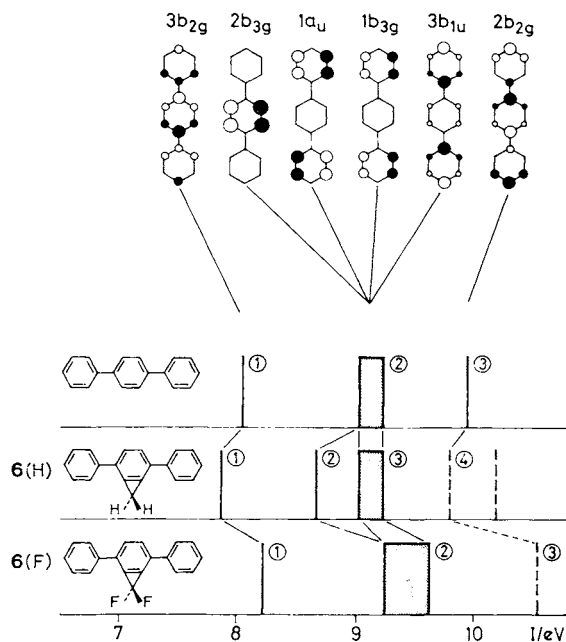
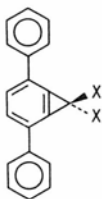


FIG. 4
 π -Band correlation diagram for *p*-terphenyl \rightarrow **6(H)** \rightarrow **6(F)** (see Table V)

summarized in Fig. 4. In fact, the observed band shifts and, in particular, the splitting of band 2 of *p*-terphenyl into two bands, 2 and 3, in the spectrum of **6**(H) with an intensity ratio of 1 : 3 is convincing proof for the essential correctness of the assignment of the *p*-terphenyl PE spectrum. As in the previous examples, replacement of the methylene hydrogen atoms by fluorine atoms, moves all PE bands towards higher ionization energies. In particular, band 2 of **6**(H) is shifted so much that it merges with the remaining three partial bands ($1a_u^{-1}$, $1b_{3g}^{-1}$, $3b_{1u}^{-1}$) to form again a single, broad peak at ~ 9.5 eV.

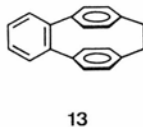
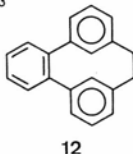
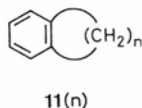
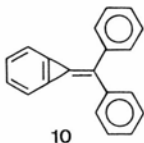
DISCUSSION

In the following we shall use only qualitative arguments, couched in HMO language, to discuss the implications of our PE spectroscopic results for the electronic structure of the molecules under discussion. Such a restriction is indicated, because it has been shown by Apeloig and Arad^{24,25} that semi-empirical MO calculations lead to the wrong equilibrium structure of **1**(H), **1**(F) and of related molecules. Thus MINDO/3 (refs^{26,27}) and MNDO (ref.²⁸) calculations predict a lengthening of the methylene-bridged C—C bond in **1**(H) and **1**(F) relative to the standard length 139 pm in benzene (MINDO/3: **1**(H), 145 pm; MNDO: **1**(H), 143 pm; **1**(F), 142 pm (refs^{24,25})) in sharp contrast to experimental evidence which shows that this bond is shortened, e.g. for the cyclopropenobenzene derivatives **8**, **9**, and **10**: $R_{12}(\mathbf{8}) = 133$ pm (ref.²⁹), $R_{12}(\mathbf{9}) = 135$ pm (ref.³⁰), $R_{12}(\mathbf{10}) = 136$ pm (ref.³¹). The rotational constants of **1**(F) derived from the microwave spectrum of this molecule³², are compatible with



8 : X = COOCH₃

9 : X = Cl



the above results. Finally, the X-ray structure analysis of **2**(H) yielded $R_{23} = 137$ pm (ref.³³). On the other hand *ab initio* calculations on a STO-3G (ref.³⁴), 3-21G (ref.³⁵) or 3-21G* (ref.³⁶) level did yield a shortened C—C-bond in positions 1, 2 of **1**(H) (134.3 pm, 133.7 pm, and 133.3 pm, respectively), refs^{24,25}, but these methods are unfortunately prohibitive for molecules of the size discussed here, especially if they carry two additional F-atoms.

Qualitatively speaking the shifts ΔI_j^m listed in Tables II and III could be rationalized in terms of mainly three effects:

a) Annulation of the parent hydrocarbons with a cyclopropeno ring leads to first order changes $\Delta R_{\mu\nu}$ of the C—C bond lengths $R_{\mu\nu}$ and thus to shifts $\Delta \varepsilon_j$ in the orbital energies ε_j , and, within Koopmans approximation, to ionization energy shifts $\Delta I_j^m = -\Delta \varepsilon_j$, if the $\Delta R_{\mu\nu}$ are significant.

b) The bridged positions μ and ν (e.g. 1a and 7a in **2**(X)) and those *ortho* to them, say μ' and ν' (e.g. 2 and 7 in **2**(X)) will suffer inductive perturbations $\delta\alpha_\mu = \delta\alpha_\nu = \delta\alpha$ and $\delta\alpha_{\mu'} = \delta\alpha_{\nu'} = m\delta\alpha$ (m is transmission factor, $m < 1$), leading to first-order shifts of the orbital energies ε_j : $\Delta \varepsilon_j = [c_{\mu j}^2 + c_{\nu j}^2 + m(c_{\mu' j}^2 + c_{\nu' j}^2)] \delta\alpha$. The value of $\Delta \varepsilon_j$ (and thus of ΔI_j^m) depends on the sign and size of $\delta\alpha$.

c) Finally, the out-of-phase linear combination of the CH or CF σ -bond-orbitals of the methylene or difluoromethylene group, and the linear combination of the CF₂ group lone-pair orbitals of local B_1 symmetry (cf. Table II) will lead to "through-space" interactions^{37,38} with the b_{1u} and b_{3g} orbitals of the parent hydrocarbon moieties, and thus to positive shifts $\Delta \varepsilon_j$ of the orbital energies ε_j of the occupied molecular orbitals with ε_j above ~ -14 eV.

Of the three effects, effect a), the influence of bond length changes $\Delta R_{\mu\nu}$ on the orbital energies ε_j , seems to be the most interesting one, in view of the recent resurgence of interest³⁹ in the "Mills–Nixon-effect"⁴⁰, i.e. the first order (partial) double bond fixation induced in the aromatic π -system by an orthocondensed cyclopropeno ring. Unfortunately, at the level of precision used in the present work, PE spectroscopy is not a good tool for obtaining significant information about first- or second-order double-bond fixation (i.e. effect a)) except under particular circumstances, e.g. in the case of cyclobutadiene derivatives⁴¹. The reason for this failure is easy to demonstrate, using benzene and the hypothetical molecule cyclohexatriene as an example. If the latter molecule is assumed to exhibit strictly localized double bonds, $R(\text{C}=\text{C}) \approx 133$ pm, $R(\text{C}-\text{C}) \approx 145$ pm and D_{3h} symmetry, its π -orbital energies can be calculated using the self energies $A_\pi \approx -10.2$ eV and the cross-terms $B_{\pi\pi} \approx -1.2$ eV derived from an analysis of polyene PE-spectra⁴². The result is $I_{1,2}^v \approx 9.0$ eV for the double band associated with the $e''(\pi)$ orbital (HOMO) and $I_3^v \approx 12.6$ eV for the $a_2''(\pi)$ band, values which differ little from the benzene π^{-1} -ionization energies $I_{1,2}^v(e_{1g}) = 9.25$ eV and $I_3^v(a_{2u}) = 12.38$ eV (refs^{21,22}), notwithstanding the extreme localization assumed in our cyclohexatriene model. Need-

less to say that from the data reported in this work, nothing can be deduced concerning the presence, let alone the extent of a "Mills-Nixon-effect", because the extent of double bond fixation is much smaller than the one postulated above^{24,25,39}. In this respect PE spectroscopy fails as a diagnostic in the same way as it did for revealing ionization energy changes associated with the twisting and bending of C=C or C≡C bonds⁴⁴.

Remain the effects *b*) and *c*), to explain the ΔI_j^m values presented in Tables II and III as the resultant of inductive and (hyper)conjugative perturbations in the molecules **N**(H) and **6**(H), and of the perfluoro effect in **N**(F), **4**(n), **5**, **6**(F), and **7**, which is expected to be the main cause for the shifts of the individual bands in the PE spectra of the latter molecules with respect to the parent hydrocarbons. We deal first with the hydrocarbons.

In a previous communication¹² concerning the PE spectra of cycloalkenobenzenes **11**(n), it had been concluded that the CH₂ group in **11**(1) ≡ **1**(H) exerts a negative inductive effect, $\delta\alpha < 0$, in positions 1 and 2 of the benzene ring, leading to $I_2^m(a_2) = 9.48$ eV relative to $I_{1,2}^m(e_{1g}) = 9.25$ eV of benzene. The destabilization of the HOMO of **1**(H) is then attributed to the out-of-phase interaction of the b_1 component (within C_{2v}) of the degenerate benzene HOMO's e_{1g} with the methylene pseudo- π -orbital, which overcompensates the inductive lowering, to yield $I_1^m(b_1) = 8.82$ eV for **1**(H). In view of the present results this rationalization should be taken with a grain of salt. They suggest that in the case of **1**(H) the situation may not be as simple as assumed formerly⁶, because of the Jahn-Teller distortion of ground-state benzene radical cation C₆H₆⁺ and of the possible importance of vibronic mixing in C₆H₆⁺, two effects which had not been taken into consideration. In particular the Jahn-Teller stabilization in C₆H₆⁺ is of the order of 0.1 eV (ref.⁴⁷) which means that the first vertical transition of benzene to undistorted C₆H₆⁺ of D_{6h} symmetry could well be situated close to 9.4 to 9.5 eV, if we refer to the centre of gravity of the corresponding band. If this were true, then the second band of **1**(H) (9.48 eV) would exhibit zero shift, meaning that the inductive effect of the CH₂ group in this molecule is close to zero, i.e. $\delta\alpha \approx 0$ eV.

A conservative analysis of the shifts ΔI_j^m of **2**(H) and **3**(H), cf. Table II, which takes into account the experimental uncertainties, leads also to the conclusion that the inductive effect of the cyclopropeno methylene group is practically zero and that its hyperconjugative interaction with the b_1 orbitals of the naphthalene or anthracene moieties in **2**(H) and **3**(H) is the cause for the larger negative shifts ΔI_2^m of the corresponding ionization energies. However, the differences between the shifts listed in Table II do not correlate in a straightforward manner with the atomic orbital coefficients of the corresponding linear combinations of the parent hydrocarbons.

Replacement of the methylene hydrogen atoms in **N**(H) by fluorine atoms, to yield **N**(F), leads — as expected — to larger, positive shifts of all ionization energies, cf. Table III. However, the observed shift sizes are rather erratic and do not correlate

in a simple fashion with atomic orbital coefficients calculated by semi-empirical methods for the parent hydrocarbons (benzene, naphthalene, anthracene) or for the cyclopropeno derivatives **N(H)**. In particular it is not possible to derive a reasonable combination of inductive and conjugative first-order perturbation parameters which mimic the observed relative shifts sizes even qualitatively. Again this is hardly surprising in view of the complex behaviour of the PE spectra of non-planar, unsaturated hydrocarbons under the influence of F-substitution^{6,7,48}. The only safe conclusion that can be drawn is that the mean size of the shifts (Table III) is in keeping with previous observation^{1-7,48}, and that no additional, abnormal electronic effects have to be invoked to rationalize the present results.

In the PE spectra of the cycloalkenobenzenes **11(n)** (ref.¹²), the mean ionization energy $\langle I_{1,2}^m \rangle$ of the first two bands are shifted, relative to the $1e_{1g}^{-1}$ band of benzene by -0.32 eV for **11(2)**, -0.50 eV for **11(3)** and -0.55 eV for **11(4)**. The band splittings $\Delta I_{1,2}^m$ are 0.54 eV, 0.58 eV and 0.52 eV respectively. For *o*-xylene one observes an $\langle I_{1,2}^m \rangle$ shift of -0.42 eV and $\Delta I_{1,2}^m = 0.52$ eV (refs^{12,49}). These values should be compared to those listed in Table IV for **4(n)** and **5**, relative to **1(F)**. The mean shifts are -0.6_0 eV for **4(2)**, -0.6_5 for **4(3)** and **4(4)**, -0.5 eV for **5**, i.e. practically the same as for the **11(n)** series and for *o*-xylene. On the other hand the $\Delta I_{1,2}^m$ are now slightly smaller, in particular for **4(4)** and **5**. The assignment of the bands 1 and 2 to the b_1^{-1} and a_2^{-1} ionization processes, respectively, is presumably correct.

The relative shifts of the bands in the PE spectra of *p*-terphenyl, **6(H)** and **6(F)**, cf. Fig. 4, follow the same pattern. It is obvious from the *p*-terphenyl orbitals presented on top of Fig. 4, that only the b_1 orbital of **6(H)**, which is of $2b_{3g}$ parentage, will be significantly destabilized by the methylene group, leading to the well-detached band 2 in the PE spectrum of **6(H)**. The remaining three bands, derived from $1a_u$, $1b_{3g}$, and $3b_{1u}$ of *p*-terphenyl, form a single maximum that cannot be deconvoluted. Replacement of CH_2 by CF_2 leads once more to a positive ionization energy shift and to a coalescence of the four bands into a single, broad feature in the region of 9.2 to 9.6 eV. It is remarkable that the influence of the CF_2 group seems to extend into the phenyl substituents, because even those bands are shifted, which are associated with orbitals mainly localized on these phenyl groups.

The PE-spectrum of **7** (not reproduced in this work) is rather poor and badly reproducible. The only significant results are the ionization energies $I_1^m = 8.6_5$ eV of the first, single band and $I_{2,\dots}^m = 9.2_5$ eV of a composite band, which is broad, extends up to ~ 10 eV, and cannot be deconvoluted. Reference hydrocarbons for which reliable PE-spectra are available are the cyclophanes **12** and **13** (ref.⁵⁰). These exhibit a pair of overlapping bands 1 2 at 7.8_5 to 8.4_5 eV for **12** and 8.0 to 8.3 eV for **13**. Therefore ~ 8.0 eV is a safe estimate for the position I_1^m of band 1. Relative to this value, the first band of **7** is shifted by $\Delta I_1^m \approx 0.6_5$ eV towards higher values, in keeping with the previously observed shifts under the influence of the CF_2 group.

CONCLUSIONS

As has been shown, the PE spectroscopic investigation of molecules such as **1(H)** to **7** cannot yield information about the presence or absence of a Mills–Nixon effect^{24,25,39}, because its influence on the ionization energies I_j^m of these molecules would be too small to be detectable within the limits of error of our measurements. Assuming that this effect can be safely neglected, an analysis of the PE spectra of **1(H)**, **2(H)**, **3(H)**, and **7** leads to the conclusion that the inductive effect of the bridging CH_2 group is close to zero, because it leads to marginal shifts of the orbital energies of the π -orbitals of A_2 symmetry, for which a hyperconjugative interaction with the pseudo- π orbital of the CH_2 group is symmetry-forbidden. On the other hand, such a destabilizing interaction with the π -orbitals of B_1 -symmetry is allowed, which explains the significant negative shifts ΔI_1^m of **1(H)** and ΔI_2^m of **2(H)** or **3(H)** (cf. Table II). In accordance with expectation¹⁻⁷, the presence of a bridging CF_2 group leads to sizeable positive shifts ΔI_j^m of all bands in the PE spectra of the molecules exhibiting a difluorocyclopropeno-moiety. An unexpected feature is that this orbital energy stabilizing effect spreads into the phenyl groups of **6(F)**, i.e. into parts of the molecule three or more bonds removed from the CF_2 group.

We thank Mrs H. C. Nguyen-Thi and Mr J. P. Schaller for their help in preparing the samples used in this investigation. This work is part of the projects 2-805-0-85 and 2-429-0-84, part 173 (part 172, cf. ref.⁵¹) of the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung. Support by Ciba-Geigy SA, Sandoz SA and F. Hoffmann-La Roche & Cie SA, Basel, is gratefully acknowledged.

REFERENCES

1. Brundle C. R., Robin M. B., Kuebler N. A., Basch H.: *J. Am. Chem. Soc.* **94**, 1451 (1972).
2. Brundle C. R., Robin M. B., Kuebler N. A.: *J. Am. Chem. Soc.* **94**, 1466 (1972).
3. Streets D. G., Ceasar G. P.: *Mol. Phys.* **26**, 1037 (1973).
4. Bieri G., Åsbrink L., von Niessen W.: *J. Electron Spectrosc. Relat. Phenom.* **23**, 281 (1981).
5. Bastide J., Hall D., Heilbronner E., Maier J. P., Plevey R. G.: *J. Electrom Spectrosc. Relat. Phenom.* **16**, 205 (1979).
6. Åsbrink L., Svensson A., von Niessen W., Bieri G.: *J. Electron Spectrosc. Relat. Phenom.* **24**, 293 (1981).
7. Heilbronner E. in: *Molecular Spectroscopy* (A. R. West, Ed.). Heyden, London 1977; and references therein.
8. Clark D. T., Murrell J. N., Tedder J. M.: *J. Chem. Soc.* **1963**, 1250.
9. Thomas R. K., Thompson H.: *Proc. R. Soc., A* **339**, 29 (1974).
10. Basch H., Bieri G., Heilbronner E., Jones T. B.: *Helv. Chim. Acta* **61**, 46 (1978).
11. Vogel E., Grimme W., Korte S.: *Tetrahedron Lett.* **41**, 3625 (1965).
12. Brogli F., Giovannini E., Heilbronner E., Schurter R.: *Chem. Ber.* **106**, 961 (1973).
13. Müller P.: *Helv. Chim. Acta* **57**, 704 (1974).
14. Billups W. E., Chow W. Y.: *J. Am. Chem. Soc.* **95**, 4099 (1973).
15. Müller P., Nguyen-Thi H. C.: *Israel J. Chem.* **21**, 135 (1981).
16. Müller P., Rodriguez D.: *Helv. Chim. Acta* **66**, 2540 (1983).

17. Müller P., Rey M.: *Helv. Chim. Acta* 65, 1157 (1982).
18. Müller P., Rodríguez D.: *Helv. Chim. Acta* 69, 1546 (1986).
19. Müller P., Etienne R., Pfyffer J., Pineda N., Schipoff M.: *Helv. Chim. Acta* 61, 2482 (1978).
20. Müller P.: *J. Chem. Soc., Chem. Commun.* 1974, 274.
21. Turner D. W., Baker C., Baker A. D., Brundle C. R.: *Molecular Photoelectron Spectroscopy*. Wiley-Interscience, London 1970.
22. Boschi R., Clar E., Schmidt W.: *J. Chem. Phys.* 60, 4406 (1974).
23. Schmidt W.: Private communication.
24. Apeloig Y., Arad D.: *J. Am. Chem. Soc.* 108, 3241 (1986).
25. Clary D. C., Lewis A. A., Morland D., Murrell J. N., Heilbronner E.: *J. Chem. Soc., Faraday Trans.*, 1974, 1889.
26. Bingham R. C., Dewar M. J. S., Lo D. H.: *J. Am. Chem. Soc.* 97, 1285 (1975).
27. Lewis F. V.: *Chem. Rev.* 86, 1111 (1986).
28. Dewar M. J. S., Thiel W.: *J. Am. Chem. Soc.* 99, 4899, 4907 (1977).
29. Carstensen-Oeser E., Müller B., Dürr H.: *Angew. Chem., Int. Ed.* 11, 422 (1972).
30. Halton B., McLennan J. T., Robinson W. T.: *Acta Crystallogr.*, B 29, 154 (1973).
31. Halton B., Randall C. H., Gainsford G. J., Stang P. J.: *J. Am. Chem. Soc.* 108, 5949 (1986).
32. Pozzi R., Ramaprasad K. R., Lucken E. A. C.: *J. Mol. Struct.* 28, 111 (1975).
33. Billups W. E., Chow W. Y., Leavell K. H., Lewis E. S., Margrave J. L., Sass R. L., Shieh J. J., Werness P. G., Wood J. L.: *J. Am. Chem. Soc.* 95, 7878 (1973).
34. Hehre W. J., Pople J. A.: *J. Am. Chem. Soc.* 92, 2191 (1970).
35. Binkley J. S., Pople J. A., Hehre W. J.: *J. Am. Chem. Soc.* 102, 939 (1980).
36. Pietro W. J., Franci M. M., Hehre W. J., DeFrees D. J., Pople J. A., Binkley J. S.: *J. Am. Chem. Soc.* 104, 5039 (1982).
37. Hoffmann R.: *Acc. Chem. Res.* 4, 1 (1971).
38. Gleiter R.: *Angew. Chem.* 86, 770 (1974); *Angew. Chem., Int. Ed.* 13, 696 (1974).
39. Hiberty P. C., Ohanessian G., Delbecq F.: *J. Am. Chem. Soc.* 107, 3095 (1985).
40. Mills W., Nixon I. G.: *J. Chem. Soc.* 1930, 2510.
41. Lauer G., Müller C., Schulte K.-W., Schweig A., Maier G., Alzérreca A.: *Angew. Chem.* 87, 194 (1975); *Angew. Chem., Int. Ed.* 14, 172 (1975).
42. Ermer O., Heilbronner E.: *Angew. Chem.* 95, 414 (1983); *Angew. Chem., Int. Ed.* 22, 402 (1983); and references therein.
43. Beez M., Bieri G., Böck H., Heilbronner E.: *Helv. Chim. Acta* 56, 1028 (1973); Honegger E., Yang Z.-z., Heilbronner E., Döring W. v. E., Schmidhauser J. C.: *Helv. Chim. Acta* 67, 640 (1984).
44. Honegger E., Schmelzer A., Heilbronner E.: *J. Electron Spectrosc. Relat. Phenom.* 28, 79 (1982).
45. Schmidt H., Schweig A., Krebs A.: *Tetrahedron Lett.* 1974, 1471.
46. Bieri G., Heilbronner E., Kloster-Jensen E., Schmelzer A., Wirz J.: *Helv. Chim. Acta* 57, 1265 (1974).
47. Miller T. A., Bondybey V. E. (Eds) in: *Molecular Ions: Spectroscopy, Structure and Chemistry*, p. 201. North Holland, Amsterdam 1983.
48. Heilbronner E., Jefford C. W.: Unpublished results.
49. Klessinger M.: *Angew. Chem.* 84, 544 (1972); *Angew. Chem., Int. Ed.* 11, 525 (1972).
50. Yang Z.-z., Kováč B., Heilbronner E., Lecoultre J., Chan C. W., Wong H. N. C., Hopf H., Vögtle F.: *Helv. Chim. Acta* 70, 299 (1987).
51. Lecoultre J., Heilbronner E., Eichenberger Th., Balli H.: *Helv. Chim. Acta*, in press.