6. The He(Iα) Photoelectron Spectra of the Perfluoroderivatives of Trisannelated Benzenes and Tetrakisannelated Cyclooctatetraenes

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Summary

The He(Iα) photoelectron (PE) spectra of tris(perfluorocyclobuta)benzene **4**(F)[1]), tris(perfluorocyclopenta)benzene **5**(F)[2]), tetrakis(perfluorocyclobuta)cyclooctatetraene **6**(F)[3]), and of tetrakis(perfluorocyclopenta)cyclooctatetraene **7**(F)[4]) are reported. A tentative assignment of the PE spectra is derived by empirical correlation with those of relevant reference compounds. The results suggest that **6**(F) retains the D_{4h}-conformation in the gas phase, *i.e.* a conformation with a planar cyclooctatetraene ring, as observed in the crystal. All four compounds exhibit a sharp increase of their first ionization energies, relative to the corresponding parent hydrocarbons, due to the perfluoro effect.

Introduction. – X-ray structure analyses have shown that the cyclooctatetraene (COT) moiety in tetrakis(perfluorocyclobuta)cyclooctatetraene[3]) **6**(F) is planar, yielding a molecular symmetry D_{4h} [1], whereas the COT-ring in tetrakis(perfluorocyclopenta)cyclooctatetraene **7**(F) of symmetry D_{2d} has practically the same structure [2] as in the parent hydrocarbon COT [3]. In particular, the dihedral angle between the planes containing the C-atoms 1,2,3,4 and 1,4,5,8 (*cf.* the formula **7**(R)) is 43.1° in COT [3] *vs.* 42° in **7** (F) [2]. Compound **6**(F) is a rather powerful organic oxidant, being reduced at +0.79 V *vs.* SCE in CH_3CN-solution [4]. Naively it might also be expected to act as a reducing agent, since a planar, central [8]annulene system should exhibit two almost degenerate, essentially non-bonding orbitals as HOMO and LUMO. However, such an argument fails to take two important factors into account: *a*) The X-ray

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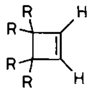
[1]) *3,3,4,4,7,7,8,8,11,11,12,12-Dodecafluorotetracyclo[8.2.0.0^{2,5}.0^{6,9}]dodeca-1,5,9-triene.*

[2]) *1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-Octadecafluoro-2,3,4,5,6,7,8,9-octahydro-*1H-*trindene.*

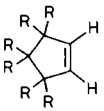
[3]) *3,3,4,4,7,7,8,8,11,11,12,12,15,15,16,16-Hexadecafluoropentacyclo[12.2.0.0^{2,5}.0^{6,9}.0^{10,13}]hexadeca-1,5,9,13-tetraene.*

[4]) *1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12-Tetracosafluoro-1,2,3,4,5,6,7,8,9,10,11,12-dodecahydrotetracyclopenta* [a,c,e,g]*cyclooctene.*

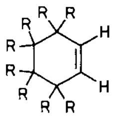
structure analysis of **6**(F) reveals [1] that the central ring exhibits a pronounced bond alternation with R(C(1)C(2)) = 143 pm and R(C(2)C(3)) = 135 pm, which leads to a split in the orbital energies of the HOMO and LUMO. *b*) The so-called 'perfluoro-effect' [5] is known to lead to a considerable lowering of the orbital energies under the conditions prevailing in the title compounds (*cf.* below). The present work was undertaken to assess the influence of the factors *a* and *b*, and, by comparison of the data of **4**(F) to **7**(F), that of the conformational difference between **6**(F) (D_{4h}) and **7**(F) (D_{2d}). A study of the reactivity and of the electronic spectrum of **6**(F) will be reported elsewhere [6].



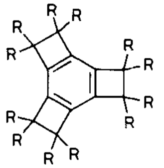
1(R)



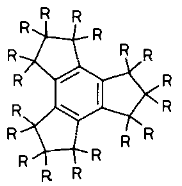
2(R)



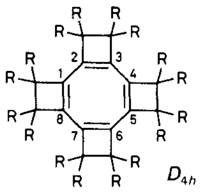
3(R)



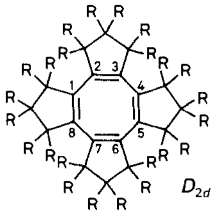
4(R)



5(R)



6(R)



7(R)

Results and Discussion. – The He(Iα) PE spectra of **4**(F) to **7**(F) are shown in the *Figure*. The positions I_j^m of the maxima of the bands ⓙ are collected in *Table 1*. For the sake of comparison, the I_j^m-values for the hydrocarbons **1**(H), **2**(H), **3**(H) [7], their fluoro derivatives **1**(F), **2**(F), **3**(F) [8], and of the trisannelated benzenes **4**(H), **5**(H) [9] are given in *Table 2*.

The analysis of the PE spectra of **4**(F) to **7**(F) is not as straightforward as one would wish, mainly for two reasons. Firstly, these molecules are too large to allow an *ab initio* and/or semiempirical calculation of useful quality because of the large number of F-atoms. In addition, the latter need extended basis sets to allow for their polarizations. Secondly, the usual empirical correlation procedure is hampered by the lack of relevant reference compounds, especially for **6**(F) and **7**(F), and by the rather special features of the perfluoro effect mentioned above [5]. Whereas the latter simpli-

Table 1. *Positions* I_j^m [eV] *of the Band Maxima in the PE Spectra of* **4**(F)–**7**(F)

Band	**4**(F)	**5**(F)	**6**(F)	**7**(F)
①	$11.5(\pi,e'')$	$11.6_5(\pi,e'')$	10.3	11.2_4
②	$12.3(\sigma,nF)$	$12.5_5(\sigma,nF)$	11.9	12.4
③	$13.3(\sigma,nF)$	$13.6_5(\sigma,nF)$	12.9	12.9
④	$\approx 14.7(\pi,a'')$[a]	$\approx 14.9(\pi,a'')$	[b]	[b]
⑤	15.2_5	16.0	15.3	15.0
⑥	15.7		15.9	

[a] Shoulder, overlapped by higher energy bands.
[b] Overlapped σ-band system.

Table 2. *The* π^{-1} *and* σ^{-1} *Ionization Energies of Some Reference Compounds*

Compound	*Ref*	I_1^m[eV]	I_2^m[eV]	I_3^m[eV]
1(H)	[7]	$9.4_5(\pi)$	$11.3(\sigma)$	
2(H)	[7]	$9.2_0(\pi)$	$11.7(\sigma)$	
3(H)	[7]	$9.1_0(\pi)$	$10.7(\sigma)$	
4(H)	[8]	$8.1_5(\pi,e'')$	$\approx 10.0(\sigma)$	
5(H)	[8]	$7.8_5(\pi,e'')$	$\approx 10.1(\sigma)$	
1(F)	[9]	$11.9_5(\pi)$	$\approx 13.4(\sigma,nF)$	$14.8(\sigma,nF)$
2(F)	[9]	$12.0_0(\pi)$	$13.8(\sigma,nF)$	$14.6(\sigma,nF)$
3(F)	[9]	$11.9_5(\pi)$	$\approx 12.8(\sigma,nF)$	$14.6(\sigma,nF)$

fies the interpretation of the PE spectra when the F-atoms of an unsaturated molecule are located on the nodal plane of the π-system (*e.g.* perfluoroethylene or perfluorobenzene [5]), it leads to congested and often poorly resolved spectra if the F-atoms are out of the nodal plane, such as in the compounds under investigation. In particular, the large separation between the π- and σ-bands observable in the PE spectra of *e.g.* perfluoroethylene and perfluorobenzene no longer exists in the PE spectra of **4**(F) to **7**(F). The overlap of the π-band and σ-band manifold in the spectra of **4**(F) and **5**(F) is even larger than in those of the parent hydrocarbons **4**(H) and **5**(H) [8]. For example the gap between the π^{-1}-band and the σ-onset in the PE spectrum of **4**(H) or **5**(H) is 1.8_5 eV or 2.2_5 eV, respectively (*cf. Table 2*), but only ≈ 0.5 eV for **4**(F) and **5**(F), so that the π^{-1}-band and the first σ-band in the PE spectra of the latter overlap to form the double maxima ① ② with a peak separation of 0.8 to 0.9 eV, as can be seen in the *Figure*.

Trisannelated Benzenes. In the PE spectrum of benzene the first three bands are located at 9.2_5 eV ($1e_{1g}$, π), ≈ 11.4 eV ($3e_{2g}$, σ) and ≈ 12.2 eV ($1a_{2u}$, π) [10]. In those of **4**(F) and **5**(F), the first π^{-1}-band has been shifted by 2.2_5 eV and 2.4_0 eV, to yield $I_1^m = 11.5$ eV and 11.6_5 eV, respectively. Assuming that the same shifts apply to the second π^{-1}-band of benzene ($1a_{2u}$), we would expect to find the corresponding ones at 14.45 eV and 14.6 eV in the PE spectra of **4**(F) and **5**(F). Indeed one observes partially overlapped bands ④ close to these values in both spectra (≈ 14.7 eV (**4**(F)), $\approx 15.2_5$ (**5**(F))), but it is by no means certain that they are due to the ejection of an electron from the a_2''-orbital (assuming D_{3h}-symmetry). However, the alternative of assigning

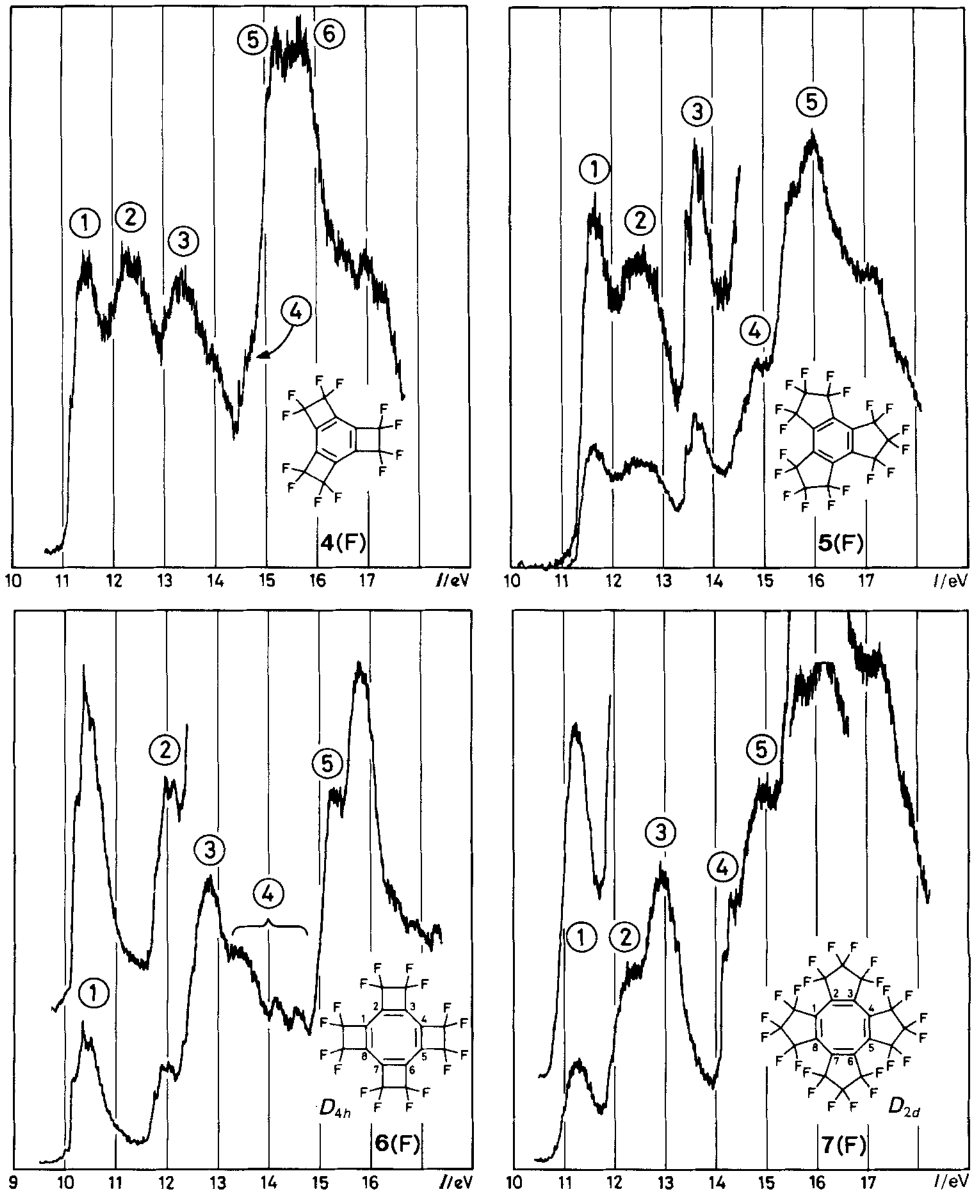


Figure. *He(Ia) PE-spectra of the perfluoroderivatives of trisannelated benzenes and tetrakisannelated cyclooctatetraenes*

band ③ to a_2'' would imply shifts of only 0.9 eV or 1.2_5 eV for **4**(F) and **5**(F), respectively, which are much too small to be reasonable. Thus, if the above assignment is tentatively accepted, we are left with the conclusion that the bands labelled ②, ③ in the PE spectra of both **4**(F) and **5**(F) are σ-bands.

Their presence is not a surprise when we compare the pairs of compounds **1**(R), **2**(R) and **3**(R) with R=H and F, of which the former two pairs can be regarded as the subunits from which **4**(R) and **5**(R) are constructed. An *ab initio* calculation of **1**(H), **2**(H) and **3**(H) [11] indicated that the two highest occupied σ-orbitals of these hydrocarbons extend rather evenly over the C–C and C–H bonds. Consequently, replacement of the H-atoms by F-atoms should shift these orbitals much more than the π-orbitals, which are lowered in energy by $\Delta\varepsilon(\pi) = -2.5_0$ eV (**1**(R)), -2.8 eV (**2**(R)) and -2.8_5 eV (**3**(R)), assuming the validity of *Koopmans'* theorem *(i.e.* $\Delta\varepsilon(\pi) = -(I_1^m$ (**1**(F)) $- I_1^m$ (**1**(H))), *etc., cf. Table 2*). Therefore bands ② and ③ of **1**(F), **2**(F), and **3**(F) must be of different origin. It is known from PE-spectroscopic studies of fluorinated alkanes and alkane derivatives [12] that electron ejection from orbitals which are essentially linear combinations of fluorine lone pair nF-orbitals give rise, among others, to σ^{-1} bands in the region of ≈ 13 eV to ≈ 15 eV of their PE spectra. For example such bands are found at 13.3 eV for CH_2F_2, 12.8 eV for CH_3CHF_2, 14.6 eV for CF_3CF_3, 12.75 eV and 15.0 eV for CF_3CF_2I, and at 12.6 eV and 14.3 eV for $CF_3CF_2CF_2I$ [12]. Thus the polydifluoromethylene chains of **1**(F), **2**(F), and **3**(F) are expected to be responsible for a pair of σ^{-1} (nF)-bands close to the above values, and this is indeed what is observed as shown in *Table 2*.

Because of the more extended σ-frame of the molecules **4**(F) and **5**(F), the corresponding bands are expected at somewhat lower ionization energies. Tentatively we have identified them with bands ② and ③, as shown in *Table 1*.

Tetrakisannelated Cyclooctatetraene (COT). In the PE spectrum of the parent hydrocarbon COT (C_8H_8), the π^{-1}-bands are located at $I_1^m = 8.4_0$ eV ($5a_1$), $I_2^m = 9.8_0$ eV (7e), $I_3^m = 11.1_5$ eV ($4b_2$) (symmetry D_{2d}) [13]. The onset of the σ-bands is found close to 11.6 eV.

As mentioned before, **6**(F) exhibits a planar COT-moiety so that the molecule belongs to D_{4h} [1], whereas in **7**(F) the COT-moiety has practically the same puckered D_{2d}-structure [2] as in COT itself [3]. Therefore a direct comparison of the PE spectra of COT, **6**(F) and **7**(F), as carried out above for benzene, **4**(F), and **5**(F), would be misleading. However, an analysis is facilitated by the fact that the position of the second π^{-1}-band in the PE spectra of **6**(F) and **7**(F) corresponds to the removal of an electron from one or the other π-orbital of the degenerate pair labelled 7e(π) in COT itself [13] [14]. This pair of degenerate orbitals has the peculiarity, that its energy is, to a large degree, independent of the twist angle φ between the double bonds, as suggested by a crude LCBO approximation. (For details *cf.* [14].) Consequently, we have to look in each of the PE spectra of **6**(F) and **7**(F) for a band in the π^{-1} ionization energy region which is close and above band ① and which occupies the same position in both spectra. Furthermore it must have double intensity, compared to band ①, because of the degeneracy of the orbitals. Obviously only the bands labelled ③ in the PE spectra of **6**(F) and **7**(F) satisfy both criteria and it is therefore reasonable to assume that they do indeed correspond to the π-orbitals of symmetry e. If so, the shift induced by the perfluoro-polymethylene chains amounts to 3.1 eV, *i.e.* half an eV more than the shift of the benzene e_{1g} π-orbital in **4**(F) and **5**(F) (see above).

There is no doubt that band ① in the PE spectra of **6**(F) and **7**(F) belongs to the HOMO, *i.e.* the highest occupied π-orbital derived from $5a_1$ of COT. Assuming *Koopmans'* theorem its orbital energy is $\varepsilon(a_1) = -10.3$ eV in **6**(F) and $\varepsilon(a_1) = -11.2_5$ eV in

7(F) which corresponds to an orbital gap $\varepsilon(a_1) - \varepsilon(e) = 2.6$ eV in **6**(F) and $\varepsilon(a_1) - \varepsilon(e) = 1.6_5$ eV in **7**(F). The former agrees perfectly with the value expected for a planar π-system. The interaction parameter $B = \langle \pi_a | H | \pi_b \rangle$ for two coplanar, linked two-centre π-orbitals as *e.g.* in butadiene or hexatriene [14] [15] is found to have the value $B = -1.2_5$ eV. For four cyclically conjugated π-orbitals the HOMO is expected to lie at $\varepsilon_{HOMO} = A_\pi\text{-}2B\cos\varphi$. Here, A_π is the energy of the basis π-orbitals and φ the twist angle. The gap measured above is $\varepsilon_{HOMO} - A_\pi = -2B\cos\varphi = 2.5$ eV $\cos\varphi$. Obviously the observed value 2.6 eV demands $\varphi = 0$, *i.e.* a planar π-system. On the other hand the reduced gap of 1.6_5 eV found for **7**(F) leads, according to 1.65 eV = (2.5 to 2.6 eV) $\cos\varphi$ to a twist angle of $\varphi \approx 50°$, as compared to the experimental value of $\varphi \approx 60°$ [2]. This is as good an agreement as can be expected from such an extremely crude argument.

In view of the above, the lowest π-orbitals of **6**(F) and **7**(F) would be expected at -15.5_5 eV and -14.5_5 eV, respectively. The corresponding bands in the PE spectra should therefore be part of the extended band systems observed in the intervals of ≈ 15 eV to 18 eV for **6**(F) and 14 eV to 18 eV for **7**(F). It is suggested as a working hypothesis that the peaks labelled ⑤ correspond to this $\pi(a_1)^{-1}$ ionization process.

Having identified the bands ①, ③ and (perhaps) ⑤ as π^{-1}-bands in the PE spectra of **6**(F) and **7**(F), we are left with the bands ② and the unresolved band systems ④. As before in the case of **4**(F) and **5**(F), these bands are associated with electron ejection from σ-orbitals which are linear combinations of F lone-pair orbitals nF. Note that the lower energy bands ② are observed at practically the same locations in the case of **4**(F) and **5**(F) (12.3 eV and 12.5_5 eV, respectively).

Conclusions. – The conformational change of the COT-moiety from flat in **6**(F) to puckered (twist angle *ca.* 60°) in **7**(F) is clearly reflected by the splitting of the π^{-1} ionization energies in the PE spectra of these compounds; the corresponding LCBO interaction parameter B changes from 1.3 eV for **6**(F) to 0.8 eV for **7**(F). The basis energies A_π are strongly shifted by the perfluoro effect, *e.g.* by 3.4 and 3.8 eV, respectively, in the pairs **4**(H)/**4**(F) and **5**(H)/**5**(F). Qualitative arguments [6] and MINDO/3 calculations [16] suggest that the structures of the unknown hydrocarbons **6**(H) and **7**(H) should be similar to those of **6**(F) and **7**(F), respectively. If the shifts of compounds **4**(R) and **5**(R) are assumed to hold for **6**(R) and **7**(R), the first ionization potentials for **6**(H) and **7**(H) are predicted as 6.9 and 7.5 eV, respectively. Thus, **6**(H) is expected to be sensitive to (air) oxidation.

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