Powerful Oxidizing Properties of a Planar [8]Annulene: Tetrakis(perfluorocyclobuta)cyclooctatetraene[1]) and Its Radical Anion

by **Fabian Gerson***, **Walter Huber**, **Pascal Merstetter**, **Gaby Persy**, **Robert L. Soulen**, **Christoph Spöndlin**, and **Jakob Wirz***

Institut für Physikalische Chemie der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel

The central eight-membered ring of tetrakis(perfluorocyclobuta)cyclooctatetraene (**1**) is flat both in the crystal and in solution, but tetrakis(perfluorocyclopenta)cyclooctatetraene (**2**) assumes a tub shape similar to that of parent cyclooctatetraene. This sterically induced structural difference strongly affects the physical properties of compounds **1** and **2**. The first and second reduction potentials of **1** in solution, +0.79 and +0.14 V *vs.* SCE, are considerably more positive than the corresponding values, +0.20 and −0.21 V, of **2**. Accordingly, mere contact with Hg metal in *N,N*-dimethylformamide converts **1** to an unusually stable radical anion $\mathbf{1}^{\bullet -}$ that is persistent in air. The temperature-independent coupling constant, $a_F = +0.320$ mT, of the sixteen equivalent β-^{19}F-nuclei in $\mathbf{1}^{\bullet -}$ is much smaller than the expected value, and the *g* factor of $\mathbf{1}^{\bullet -}$ is markedly lower than those generally found for structurally related radical anions. In contrast, the characteristic data for $\mathbf{2}^{\bullet -}$, generated from **2** with K metal in 1,2-dimethoxyethane, comply with the expected data. The coupling constants $a_F = +0.976$ and +0.935 mT, each of eight β-^{19}F-nuclei in $\mathbf{2}^{\bullet -}$, average +0.951 mT upon raising the temperature from 220 to 260 K. The gas-phase electron affinity of **1**, $A = 3.4 \pm 0.2$ eV, which was estimated from the reduction potential in solution and from charge-transfer absorption spectra obtained from a series of methylated benzenes and naphthalenes, is among the highest known for neutral organic molecules.

Introduction. – When *Richard Willstätter* first presented his synthesis of cycloocta-1,3,5,7-tetraene (COT) in a lecture given at the *Chemische Gesellschaft Zürich* [1], *Alfred Werner* immediately pointed out that this molecule might have a nonplanar structure. Its unexpected reactivity would, therefore, not disprove *Thiele*'s contemporary theory that all cyclic π-systems should be 'aromatic' [2]. In fact, COT is by no means a flat molecule; the dihedral twist angle between adjacent −HC=CH− segments is *ca.* 60° [3]. Nevertheless, even for hypothetically planar COT, one would nowadays expect an even higher reactivity, comparable to that of 'antiaromatic' cyclobutadiene [4]. The enigmatic special properties of 'aromatic' benzene have since been explained by *Hückel*'s rule of $(4n+2)$ [5], but debate on more subtle issues still continues [6].

The puckered structure of COT should not be attributed to a destabilization energy of the π-system ('antiaromaticity'), but to the unfavorable C−C−C bond angles of 135° and to the nonbonded interactions between the H-atoms in a flat octagonal structure [7]. Several strategies to force planarity on COT have been explored, including *i*) replacement of one or two C=C bonds by a triple linkage [8], *ii*) fusion to a

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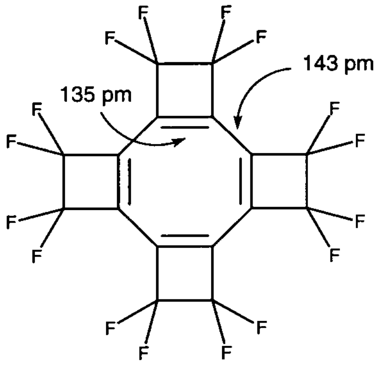
[1]) Systematic names according to the *IUPAC* nomenclature. **1**: *1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-hexadecafluoro-1,2,3,4,5,6,7,8-octahydrotetracyclobuta[*a,c,e,g*]cyclooctene*; **2**: *1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12-tetracosafluoro-1,2,3,4,5,6,7,8,9,10,11,12-dodecahydrotetracyclopenta[*a,c,e,g*]cyclooctene.*

planar ring system [9], and *iii*) photoionization of the flat dianion of COT in a rigid matrix [10]. Work along the lines *i* and *ii* has led to the isolation of some novel extended π-systems incorporating an (essentially) planar eight-membered ring [9], but their relation to COT is rather remote. Unfortunately, the elegant approach *iii* was not successful.

X-Ray crystal-structure analyses [11] showed that the COT core of tetrakis(perfluorocyclobuta)cyclooctatetraene 1) (**1**) is flat, whereas that of tetrakis(perfluorocyclopenta)cyclooctatetraene 1) (**2**) assumes a boat conformation closely similar to parent COT. Hence, the pair of molecules **1** and **2** provides a unique chance to study the effect of planarization on the physical properties of a cyclic 8π-system.



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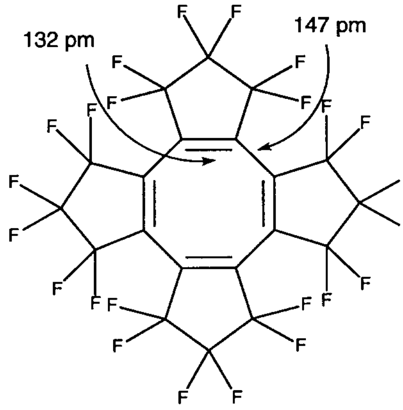

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The structural difference between **1** and **2** is clearly reflected by the first two π^{-1}-ionization bands in the photoelectron (PE) spectra of these compounds [12]: the energy gap increases by 1 eV, and the lowest ionization energy decreases by the same amount on going from **2** to **1**. In contrast, the position of the third π^{-1} band is insensitive to the dihedral angle between the π-bonds. Compared to the π^{-1} band of similar origin in COT, these ionizations are shifted by *ca.* 3 eV to higher energies, due to annelation by the electron-attracting perfluorocycloalkane substituents.

Compound **1** is among the most powerful neutral organic oxidants known. The cyclic voltammogram of **1** exhibits two reversible reduction waves at $E^{(1)}_{1/2} = +0.79$ and $E^{(2)}_{1/2} = +0.14$ V *vs.* SCE [13]. The first of them is by 2.4 V more positive than the corresponding potential of COT at -1.61 V. This finding can be rationalized by the cooperative inductive and conformational effects of perfluorocyclobutane annelation: because neutral **1** already has a planar geometry, little reorganization energy is required for electron transfer.

The first electronic transition of [4*n*]annulenes is particularly sensitive to bond-length alternation and conformational changes [14]. Crystals of **1** are deep red, those of **2** are colorless. By comparing the electronic absorption spectra of **1** in the solid state and in solution, it is established that the planar structure of **1**, as determined by X-ray crystal-structure analysis, is not due to crystal-packing forces and, thus, persists in solution. Charge-transfer absorption spectra of **1** in the presence of aromatic donors are reported and used to estimate the electron affinity of **1**. Finally, the electronic structure of the radical anions $\mathbf{1}^{\bullet -}$ and $\mathbf{2}^{\bullet -}$ is probed by ESR spectroscopy.

Results. – *The Electronic Spectrum of* **1**. Determination of the absorption spectrum of **1** was not trivial, because its very weak authentic bands ($\varepsilon \leq 100$ M^{-1} cm^{-1} in the visible region and $\varepsilon \leq 1000$ M^{-1} cm^{-1} down to 300 nm) are easily swamped by strong absorptions arising from decomposition products. Decay of **1** occurs within seconds in protic solvents, and more slowly in other solvents such as MeCN or CH_2Cl_2, presumably caused by the presence of acid or H_2O traces. On the other hand, dilute solutions of **1** in spectrograde air-saturated hexane (up to 10^{-3} M) proved to be stable for years. Solutions prepared from different crystals of **1** gave somewhat variable results: weak absorption bands in the near UV region (250–400 nm, apparent extinction coefficients of *ca.* 10^2 M^{-1} cm^{-1}) were present in some solutions, but not in others. These variable bands must be attributed to an impurity or a decay product of **1**. Attempts to purify **1** by chromatography on silica gel or Alox failed because of decomposition; that on cellulose, with benzene as eluent, separated small amounts of a yellow-colored impurity. An absorption spectrum of **1** in hexane solution, where the 'impurity bands' are absent, is shown in *Fig. 1*. Also presented in *Fig. 1* is the visible-absorption spectrum of a thin crystal of **1**. The apparent distortion of absorbances exceeding 2 in the spectrum of the crystal (420–500 nm) is most likely an artifact due to stray light or uneven thickness of the crystal. Thus, apart from an obvious difference in the resolution of the vibrational fine structure, the two spectra are closely similar. The frequency shifts, observed by changing the solvent or the temperature, were the same for all of the vibrational maxima in the visible region, indicating that the entire absorption band in the range of 360–650 nm arises from a single electronic transition.

Charge-Transfer Absorption Spectra of **1**. Addition of aromatic hydrocarbons (*ca.* 10^{-2} M) to dilute solutions of **1** (*ca.* 2×10^{-4} M) in hexane led to the appearance of one or two broad (width at half-height *ca.* 6000 cm^{-1}), *Gaussian*-shaped absorption bands in

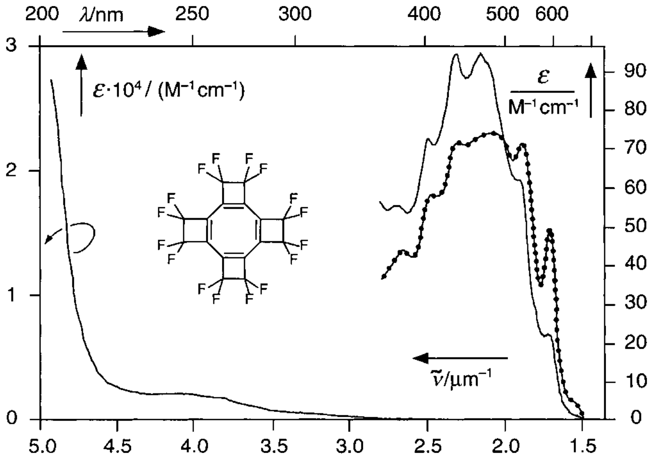

Fig. 1. *Electronic absorption spectrum of* **1** *in hexane solution* (—) *and in a crystal* (-•-)

the visible region are attributed to the formation of charge-transfer (CT) complexes between the acceptor **1** and the aromatic donors. Thereby, *p*-xylene, which has a narrow energy gap between the first two ionization potentials, gave two partially overlapping CT bands. The absorption maxima of the CT bands of **1** with various donors in hexane solution and the vertical gas-phase ionization energies of the donors, I_v [15][16], are given in the *Table.*

Table. *Position of the Charge-Transfer Absorption Bands of* **1** *in Hexane in the Presence of Aromatic Donors*

Aromatic donor molecule	λ_{max}/nm	$h\nu_{max}$/eV	I_v/eV	Ref.
Benzene	480	2.58	9.23	[15]
p-Xylene (first band)	620	2.00	8.44	[15]
p-Xylene (second band)	525	2.36	9.05	[15]
1,3,5-Trimethylbenzene	622	1.99	8.42	[15]
Hexamethylbenzene	850	1.46	7.85	[15]
Naphthalene	690	1.80	8.18	[16]
1-Methylnaphthalene	768	1.61	8.01	[16]
2-Methylnaphthalene	728	1.70	8.01	[16]
Cyclobuta[*b*]naphthalene	744	1.67	7.96	[16]
1,4-Dimethylnaphthalene	880	1.41	7.82	[16]
1,5-Dimethylnaphthalene	881	1.41	7.85	[16]
1,8-Dimethylnaphthalene	895	1.39	7.64	[16]
2,3-Dimethylnaphthalene	758	1.64	7.89	[16]
2,7-Dimethylnaphthalene	756	1.64	7.89	[16]
2,3,6,7-Tetramethylnaphthalene	835	1.48	7.60	[16]
Acenaphthene	898	1.38	7.76	[16]

The intensities of the CT bands with naphthalene as a donor were determined as a function of the donor concentration, $[\mathrm{D}]_0 = 2 \times 10^{-3}$ to 5×10^{-2} M, $[\mathbf{1}] = 2 \times 10^{-4}$ M. Due to the large excess of naphthalene, its concentration is only marginally reduced by complex formation, $[\mathrm{D}] = [\mathrm{D}]_0 - [\mathrm{complex}] \approx [\mathrm{D}]_0$ (*Benesi-Hildebrand* conditions [17]). The absorbance of the CT complex, A_{CT}, is then given by *Eqn. 1*, where $\varepsilon_{\mathrm{CT}}$ is the molar extinction coefficient at the absorption maximum of the CT band, d ist the cell length, and K is the association constant of the complex, $K \equiv [\mathrm{complex}]/([\mathrm{D}]\,[\mathbf{1}]) \approx [\mathrm{complex}]/\{[\mathrm{D}]_0\,([\mathbf{1}] - [\mathrm{complex}])\}$. *Eqn. 1* was not inverted to obtain a linear relation in $[\mathrm{D}]_0$, because that procedure would give excessive weight to small values of A_{CT} in a linear regression. Nonlinear fitting of *Eqn. 1* to the absorbance data given in *Experimental* provided the following values for the fitting parameters: $\varepsilon_{\mathrm{CT}} = (5.4 \pm 0.3) \times 10^3$ M^{-1} cm^{-1} and $K = 27 \pm 2$ M^{-1} ($d = 1$ cm, fixed).

$$A_{\mathrm{CT}} = \varepsilon_{\mathrm{CT}}\, d\, \frac{K[\mathrm{D}]_0[\mathbf{1}]_0}{1 + K[\mathrm{D}]_0} \tag{1}$$

In *Fig. 2* the positions of the CT-band maxima, E_{CT}, are plotted *vs.* the vertical ionization potentials of the donors. The data are reasonably well represented by a linear relationship $E_{\mathrm{CT}} = aI_v + b$. The following values of the parameters a and b were determined by a linear regression: $a = 0.74 \pm 0.04$ and $b = -4.26 \pm 0.34$ eV.

Cyclic Voltammetry. The reduction potentials of **2** were measured by cyclic voltammetry at room temperature. Like **1** [13], compound **2** displays two reversible

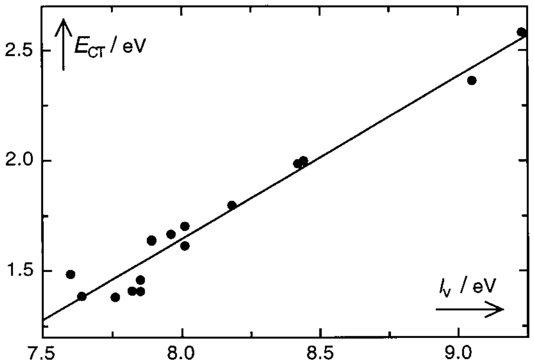

Fig. 2. *Correlation of charge-transfer transition energies of* **1** *with various aromatic donors in hexane*, E_{CT}, *with the vertical ionization energies*, I_v, *of the corresponding donors*

reduction waves in MeCN, albeit at considerably less positive potentials, $E^{(1)}_{1/2} = + 0.20 \pm 0.01$ and $E^{(2)}_{1/2} = - 0.21 \pm 0.01$ V *vs.* SCE.

Radical Anions. Reduction of compounds **1** and **2** to their radical anions was carried out with K in 1,2-dimethoxyethane (DME), either by a direct contact with the metallic mirror or indirectly by the method of solvated electrons[18]. For **1**, however, mere shaking of the DME solution of the compound with Hg metal was sufficient to produce the highly persistent radical anion $\mathbf{1}^{\bullet-}$ which survived even in the presence of air. Its largely temperature-independent ESR spectrum ($g = 2.0010 \pm 0.0001$), shown in *Fig. 3*, exhibits 17 equidistant lines, of which the outermost ones could be detected only by high amplification. Their binomial distribution of intensity and their spacing by the coupling constant, $|a_F| = 0.320 \pm 0.001$ mT, point to sixteen equivalent β-^{19}F-nuclei in the eight CF_2 groups²). This $|a_F|$ value was confirmed by the corresponding ^{19}F-ENDOR spectrum. Flanking each hyperfine line, two pairs of satellites with a relative intensity of *ca.* 4% indicated an interaction with two sets of eight equivalent ^{13}C-isotopes. The pertinent coupling constants $|a_C|$ were 0.191 ± 0.001 mT and 0.135 ± 0.001 mT, whereby the lines associated with the smaller $|a_C|$ value were markedly broadened upon lowering the temperature. Based on the arguments presented in the *Discussion*, this coupling constant was assigned to the ^{13}C-isotopes in the π-centers of the cyclooctatetraene ring, leaving the larger $|a_C|$ value for those in the CF_2 groups.

The temperature-dependent ESR spectra ($g = 2.0021 \pm 0.0001$) of the persistent radical anion $\mathbf{2}^{\bullet-}$ obtained at 205 and 235 K are partly reproduced in *Fig. 4*. At the lower temperature, their analysis, corroborated by the corresponding ^{19}F-ENDOR spectra, yielded coupling constants $|a_F|$ of 0.976 ± 0.005 and 0.935 ± 0.005 mT, each for a set of eight nuclei, along with $|a_F| = 0.090 \pm 0.001$ and 0.059 ± 0.001 mT, each for a set of four. The two large $|a_F|$ values were assigned to the β-^{19}F-nuclei in the eight CF_2 groups bound to the π-centers of the cyclooctatetraene ring and the two small ones to their γ-counterparts in the four remaining groups²). According to a TRIPLE-resonance experiment carried out on the ENDOR signals [19], the signs of the β- and γ-^{19}F-coupling constants are opposite. On raising the temperature, the two large β values

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²) In ESR spectroscopy, nuclei separated by 0, 1, 2, ... sp^3-hybridized C-atoms from a π-center are denoted α, β, γ, ...

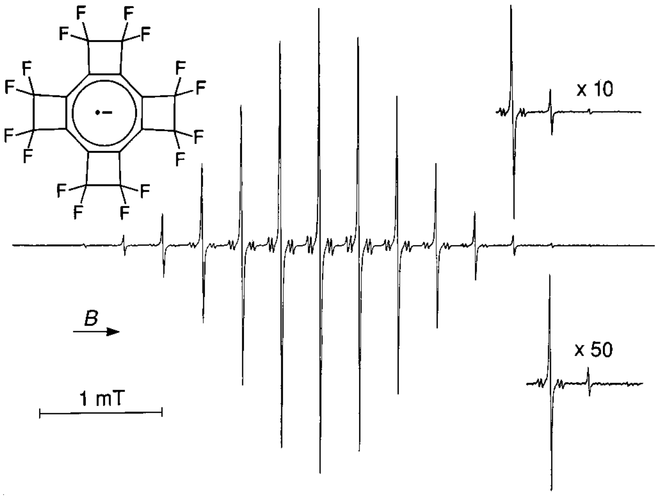

Fig. 3. *ESR Spectrum of the radical anion* $\mathbf{1}^{\bullet -}$. Solvent: DME, counterion: K^+, temperature: 243 K.

gradually collapsed into one (0.951 ± 0.005 mT for sixteen ^{19}F-nuclei, at 260 K), while the two small γ values did not significantly change.

Discussion. – For a qualitative discussion of the absorption spectrum, the presence of the perfluorocyclobutane rings will be ignored, *i.e.*, we assume that the spectrum of **1** should correspond to that of hypothetically planar COT with the same amount of C−C bond-length alternation [14]. This assumption is justified by the following arguments. The influence of perfluoroalkyl substituents on the electronic absorption spectra of conjugated π-systems is generally well described as an inductive effect [20]. In the present case, all unsaturated C-atoms of **1** are symmetry-equivalent. Thus, there will be no charge reorganization within the π-system upon electronic excitation, and the inductive effect on the π-orbital energies will cancel in the transition energies. The same arguments apply to the absorption spectra of benzene and tris(perfluorocyclobuta)benzene, and indeed their spectra are quite similar (benzene, λ_{max}/nm (log(ε/[M^{-1} cm^{-1}]), ^1L_b: 254 (2.40), ^1L_a: 204 (3.94); tris(perfluorocyclobuta)benzene, ^1L_b: 253 and 259 (2.38), ^1L_a: ≤ 200 (≥ 4.0). In contrast, the first absorption band of **1** (*Fig. 1*) lies at much longer wavelengths than that of parent COT, which exhibits only an end absorption in the visible region. This large shift may be attributed to the structural difference between planar **1** and puckered COT.

The electronic absorption bands of **1** follow the general pattern exhibited by planar [4*n*]hydrocarbons [14], and the assignment of the main bands is straightforward. A *Hückel*-orbital scheme for COT is shown in *Fig. 5*. The degeneracy of the open-shell orbitals has been removed by assuming some bond-length alternation ($\beta = \beta_0 \pm \delta\beta$) which reduces the molecular symmetry from D_{8h} to D_{4h}. The dipole-forbidden HOMO-LUMO transition ($b_{2u} \leftarrow b_{1u}$) gives rise to the lowest excited $^1A_{2g}$ configuration, the energy of which is equal to $4\,\delta\beta$ in the *Hückel* approximation. It is obvious from the nodal properties of the HOMO and LUMO that the first absorption band of the COT chromophore will be extremely sensitive to changes in bond lengths and to deviations

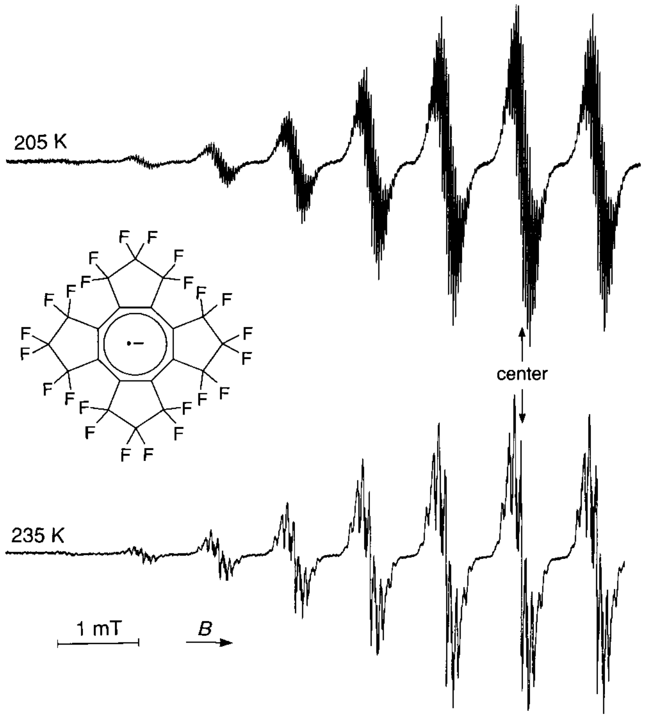

Fig. 4. *Low-field parts of the ESR spectra of the radical anion* $\mathbf{2}^{\bullet-}$. Solvent: DME, counterion: K^+, temperature as indicated.

from planarity. The next four configurations ($e_g \leftarrow b_{1u}$ and $b_{2u} \leftarrow e_g$) give rise to two excited states of E_u symmetry which are accidentally degenerate in the absence of electronic correlation. They are split by first-order Configuration Interaction (CI).

The results of a standard PPP SCF CI calculation [21] for planar COT, which included all singly excited configurations and allowed the resonance integrals to reach self-consistency with the bond orders, $\beta_{\mu\nu} = -2.318 \exp(0.335[p_{\mu\nu} - 2/3])$ eV [22], are in satisfactory agreement with experiment. The very weak absorption band of **1** observed in the visible region is predicted to occur at 667 nm (${}^1A_{2g}^{+} \leftarrow {}^1A_{1g}^{-}$, oscillator strength $f = 0$), while the strong end absorption rising below 210 nm corresponds to the allowed transition that is calculated to appear at 197 nm (${}^1E_u^{+} \leftarrow {}^1A_{1g}^{-}, f = 2.8$). The transition to the lower ${}^1E_u^{-}$ state is predicted to lie at 258 nm ($f = 0$, forbidden by the parity rule [21]) and is tentatively associated with the weak shoulder observed at *ca.* 250 nm in the spectrum of **1**. A further forbidden excited state, namely the lowest doubly excited state (${}^1A_{1g}^{-}$, not included in the CI calculation), may be expected in that region.

Comparison of the first reduction potentials, $E_{1/2}$, of **1** (+0.79 V [13]) and **2** (+0.20 V) with the corresponding value for COT (−1.61 V [13]) indicates that the shift by +1.8 V on going from COT to **2** is due to the annelation by the electron-attracting perfluoroalkane ring. A further change of +0.6 V, on passing from **2** to **1**, is attributed to the structural change, as **1** needs not be flattened on conversion to its radical anion $\mathbf{1}^{\bullet-}$. *Chen* and *Wentworth* [23] have shown that gas-phase electron

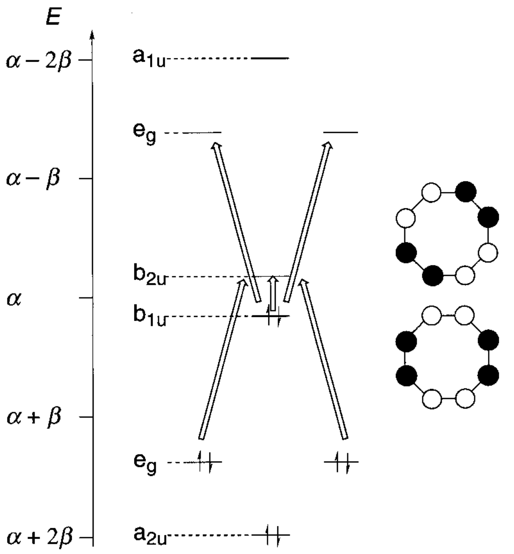

Fig. 5. Hückel-*orbital energy scheme of a planar cyclooctatetraene with alternating bond lengths*

affinities, A, and half-wave reduction potentials, $E_{1/2}$, obey a direct linear relationship. Electron affinities of 23 compounds, for which the reduction potentials were determined in aprotic solvents *vs.* SCE, were best reproduced by *Eqn. 2*. Application of this relation to **1** gives $A(\mathbf{1}) = 3.28 \pm 0.26$ eV.

$$A = eE_{1/2} + (2.49 \pm 0.26)\ \text{eV} \qquad (2)$$

Another estimate of $A(\mathbf{1})$ may be obtained from the position of the CT absorption maxima with various donors. Unfortunately, the parameters of the empirical linear relationship, $E_{\mathrm{CT}} = aI_{\mathrm{v}} + b$ (*Fig. 2*) do not have a simple physical meaning [24]. Therefore, we follow the procedure of *Chen* and *Wentworth* [23], who have *assumed* the validity of *Eqn. 3* and have determined the constant C characteristic of various 'benzenoid' donor molecules using a series of acceptor molecules of known electron affinity. They also showed that electron affinities, A, derived from reduction potentials on the basis of *Eqn. 2* and from CT spectra on the basis of *Eqn. 3*, are in good agreement. The values for benzene, methylated benzenes, and naphthalene determined by *Chen* and *Wentworth* were in the range of $C = -2.8$ to -3.2 eV. Based on an average value of $C = -3.0$ eV, the data given in the *Table* provide an electron affinity $A(\mathbf{1}) = (3.38 \pm 0.14)$ eV, in accord with the value estimated above (*Eqn. 2*). The weighted average is $A(\mathbf{1}) = (3.4 \pm 0.2)$ eV, which is among the highest of any neutral organic compound [25].

$$I_{\mathrm{v}} + C = E_{\mathrm{CT}} + A \qquad (3)$$

The powerful oxidizing properties of **1** are further manifested by the result that its radical anion can be generated by mere contact with Hg metal. Both the g factor, 2.0010, and the ^{19}F-coupling constant, $|a_{\mathrm{F}}| = 0.320$ mT, for $\mathbf{1}^{\bullet -}$, which are strikingly lower than the corresponding values, 2.0021 and 0.951 mT, for $\mathbf{2}^{\bullet -}$, must be considered unusual (by chance, $|a_F| = 0.320$ mT is very close to $|a_H| = 0.323$ mT [26] for the eight protons in COT$^{\bullet-}$). It is not easy to find examples of radical anions that could serve for predicting the β-^{19}F-coupling constants for $\mathbf{1}^{\bullet-}$ and $\mathbf{2}^{\bullet-}$. The few pertinent π-radicals dealt with in the literature are those substituted by CF_3 groups [27]. Comparison with structurally related hydrocarbon radicals suggests that, on replacement of a CH_3 by a CF_3 substituent, the $|a_F|$ value should be larger than $|a_H|$ by a factor of *ca.* 2, provided that the spin distribution is not markedly altered. For π-radical anions annelated with one cyclobutane or cyclopentane moiety, hyperfine data of several derivatives of benzene [28–30], naphthalene [30][31], and COT [30] are reported. In all cases, the coupling constants of the β-protons in the CH_2 groups lie in the range $|a_H| = 0.4-0.6$ mT, with the values for the cyclobutane being 20–40% larger than those for the cyclopentane rings. We are not aware of data for related radical anions containing annelated perfluoroalkane rings. According to the findings for CH_3 and CF_3 substituents, the β-^{19}F-coupling constant for $\mathbf{1}^{\bullet-}$ and $\mathbf{2}^{\bullet-}$ should amount to $|a_F| \approx 1$ mT. This expectation is borne out by $|a_F| = 0.951$ mT for $\mathbf{2}^{\bullet-}$, whereas the corresponding value, 0.320 mT, for $\mathbf{1}^{\bullet-}$ is clearly much smaller. Because of the scarcity of suitable reference data in the literature and the difficulty of carrying out reliable theoretical calculations on ^{19}F-coupling constants, one must suppose that a 1,3-interaction [30] is highly effective in the perfluorocyclobutane rings of $\mathbf{1}^{\bullet-}$, in addition to the hyperconjugative 1,2-interaction. Whereas hyperconjugation requires, in general, a positive sign for the coupling constants [32a], the 1,3-interaction could make a negative contribution to a_F, thus decreasing its absolute value. On the whole, β-^{19}F-coupling constants should be positive, *i.e.*, $a_F = +0.320$ mT for $\mathbf{1}^{\bullet-}$ and $+0.951$ mT (to which $+0.976$ and $+0.935$ mT average out) for $\mathbf{2}^{\bullet-}$. In the latter radical anion, an opposite sign is indicated experimentally for the γ-^{19}F-coupling constants, resulting in $a_F = -0.90$ and -0.59 mT.

Of the two ^{13}C-coupling constants observed for $\mathbf{1}^{\bullet-}$, the one with the smaller absolute value, $|a_C| = 0.135$ mT, is almost identical to that reported for COT$^{\bullet-}$ (0.130 mT) [26], a finding which strongly suggests that this coupling constant should be assigned to the ^{13}C-isotopes in the C-atoms of the eight-membered ring. Such an assignment, with a positive sign of the coupling constant, $a_C = +0.135$ mT, is supported by the broadening of the pertinent satellite lines at high field, diagnostic of a substantial local π-spin population at the C-center [32b]. The ^{13}C-coupling constant for $\mathbf{1}^{\bullet-}$ with the larger $|a_C|$ values must, therefore, belong to the isotopes in the C-atoms of the eight CF_2 groups and, according to theory [32a], have a negative sign, leading to $a_C = -0.191$ mT.

It is rather unexpected that the sixteen β-^{19}F nuclei in $\mathbf{2}^{\bullet-}$ with the large coupling constants ($|a_F| = 0.976$ and 0.935 mT) become equivalent at higher temperatures, whereas their eight γ-counterparts with the smaller $|a_F|$ values (0.090 and 0.059 mT) do not. This finding is, however, not unprecedented, as an analogous observation was made for the coupling constants of β- and γ-protons in the radical anion of indane [29].

Experimental. – Tetrakis(perfluorocyclobuta)cyclooctatetraene[1]) (**1**) and tris(perfluorocyclobuta)benzene were synthesized by a copper-induced coupling of 1,2-diiodo-3,3,4,4-tetrafluorocyclobutene, and tetrakis(perfluorocyclopenta)cyclooctatetraene[1]) (**2**) was formed by the corresponding treatment of 1,2-diiodo-3,3,4,4,5,5-hexafluorocyclopentene [33].

Synthesis of **1** (improved version of the procedure reported previously in [33]). Dry and freshly prepared active Cu powder (2.54 g, 0.04 mol [34]; the precipitate was immediately washed with acetone and Et_2O, allowing minimum exposure to air) and 1,2-diiodo-3,3,4,4-tetrafluorocyclobutene (1.85 g, 0.0049 mol [35]) were added to a sublimation apparatus under dry N_2. The mixture was left overnight, then heated to 90–93° in an oil bath for 24 h, and finally to 135° for another 24 h. The dark red solid (0.65 g) collected from the cold finger was triturated in 5 ml of hot hexane, and filtered leaving 0.40 g of red crystals. Evaporation of the filtrate left 0.22 g of a mixture of tris(perfluorocyclobuta)benzene and 2,2′-diiodobis[tetrafluorocyclobutene]. The red crystals were placed in a glass tube, sealed under vacuum, and heated to 100° in a thermal gradient sublimation apparatus. Large, clear-red crystals of **1** (0.38 g, 62.6%, m.p. 201–201.5°) were obtained after 48 h. The product gave a single spot by TLC on cellulose; decomposition occurred on Alox, silica gel, or Fluorisil. ^{19}F-NMR (C_6D_6): -119.6 (br. *s*, *fwhh* = 27). ^{13}C-NMR (C_6D_6, F-decoupled): 142.50 ($=\mathrm{C}\langle$); 115.06 ppm ($-CF_2$). MS: 496 (100, M^+), 477 (48, $[M-\mathrm{F}]^+$), 446 (30, $[M-\mathrm{CF}_2]^+$), 427 (61, $[M-\mathrm{CF}_3]^+$). The electronic absorption spectrum is displayed in *Fig. 1*.

Absorption Spectra. The absorption spectrum of solid **1** was determined by placing a large, thin crystal of **1** on the entrance slit of a polychromator that was equipped with a diode-array detector. Charge-transfer absorption spectra were measured with dilute solns. of **1** and a large excess (*ca.* 10^{-2} M) of various aromatic donors (*Table*) in hexane. The following absorbances were determined at $\lambda_{\max} = 690$ nm ($\varepsilon_{\mathrm{CT}}/[\mathrm{M}^{-1}\,\mathrm{cm}^{-1}]$) of the CT band with naphthalene as a donor in 2.15×10^{-4} M solns. of **1** in hexane at r.t., A_{CT}([naphthalene]/10^{-2} M): 0.062 (0.203), 0.158 (0.555), 0.216 (0.766), 0.264 (1.063), 0.310 (1.422), 0.423 (2.227), 0.685 (5.18).

Cyclic Voltammetry. For the measurement of **2** in MeCN, a Pt disk, Pt wire, and Bu_4NPF_6 were used as working electrode, counter-electrode, and conducting salt, resp. The ferrocene/ferrocene$^+$ wave served for calibration. The scan was 300 mV s^{-1} on a *Metrohm Polarecord E506* equipped with a VA-stand *663* and a VA-scanner *E612*.

ESR Spectra were recorded on a *Varian-E9* instrument, while a *Bruker-ESP-300* system served for the ENDOR and TRIPLE-resonance studies.

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