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PLANAR AND NON-PLANAR UNSATURATION—II[1]
TWISTING-DISTORTIONS IN FULVALENIC STRUCTURES

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Abstract—A π-electronic method, adapted to the study of non-planar unsaturated molecules, is used to examine the consequences of twisting about the exocyclic bond in derivatives of fulvene and fulvalene. The geometry, electronic spectrum, ionization and reduction potentials of fulvene, 6,6-disubstituted fulvenes, fulvalene, octachlorofulvalene, tetrabenzofulvalene and (9-fluorenylidene)cyclopentadiene are considered. The last-mentioned molecule and its dimer have been prepared and their properties are reported. Incidental comments on the applicability of the Hückel rule ("4n + 2") to annelated odd-membered rings and on charge-distribution in fused non-alternants are also made.

INTRODUCTION

THE DEVIATIONS of penta-, hepta- and sesquifulvalenes from coplanarity have been considered in terms of three distortional modes:

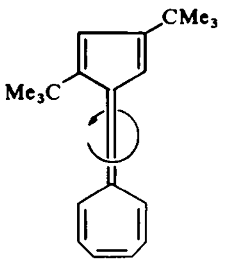
a. Twisting about the exocyclic bond has been proposed[2,3] in I and II and observed in solid 7-(tetrachlorocyclopentadienylidene)-7H-benzocycloheptene[4] (III) and octachlorofulvalene[5] (IVa). It is one of the deformations that characterize bisfluorenylidene[6] (Va) and some of its derivatives,[7] e.g. Vb, and may account[8] for the facile $[\pi^{14}a + \pi^{2}s]$-cycloaddition of heptafulvalene (VI).

b. Folding about the exocyclic bond is revealed, by NMR[9] and crystallography,[7] in derivatives of bisfluorenylidene, itself probably *syn*-folded in solution.[10] The non-vanishing dipole moment of IVa in cyclohexane[11] suggests here also the lack of central symmetry. Folding accounts for the two isomeric compounds[12] of formula VII, and reaches its extreme in norcaradienic structures such as VIII.[13]

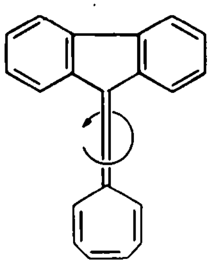
c. Tilting about endocyclic axes, investigated[14,15] mainly in dibenzotropone (IX), is probably less significant in pentafulvalenes,[7] but still accounts[16] for some data[17] concerning bifluorenylidene.

Chemical shifts apart,[7,9,10,12] the effect of geometrical distortion upon other molecular properties has almost never been studied. Some propositions as to the relation with bond-alternation and spectral quantities have been recorded,[2,3] and it has been remarked[18,19] that the properties of Va are suggestive of a nonplanar structure. Twisting-energy curves have been computed for fulvalene[20] (IVb) but, on the whole, MO treatments (Hükel-type,[18,21] σ-superposed-SCF,[22] SCF-CI[23–26] and CNDO[27]) have concentrated upon planar structures.

Here we consider the consequences, upon ground-state and excited-state properties, of twisting pentafulvalenic structures about their exocyclic bond; fulvene itself is also examined. The method used is the LCAO-SCF-CI technique that was developed to meet non-planar unsaturation,[1,28] and which includes all non-neighbouring interaction terms, bi- and mono-electronic. Interatomic distances (R), ionization (IP)



I



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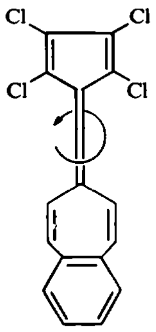
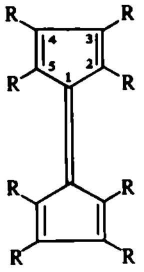
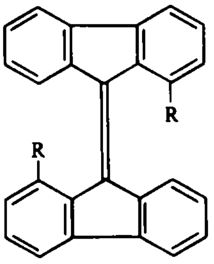


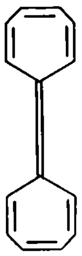
III



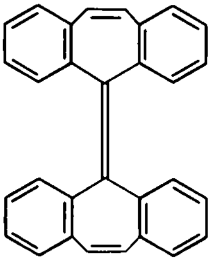
IVa R = Cl
IVb R = H



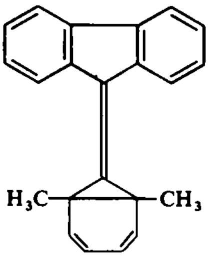
Va R = H
Vb R = Me$_2$CH.OCO



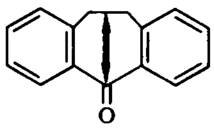
VI



VII



VIII



IX

and half-wave ($E_{\frac{1}{2}}$) reduction potentials* are evaluated from SCF bond-orders (P) and from the eigenvalues (ε) of the highest-occupied (HOMO) and lowest-vacant (LVMO) molecular orbitals,

$$R_{pq}\,(\text{Å}) = 1{\cdot}534\text{–}0{\cdot}211P_{pq}$$

$$-\text{IP} = 0{\cdot}921\,\varepsilon_{\text{HOMO}}\text{–}0{\cdot}620$$

$$E_{\frac{1}{2}} = -0{\cdot}733\,\varepsilon_{\text{LVMO}}\text{–}1{\cdot}726$$

Spectral quantities are based on monoexcitation CI-treatments.

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* These quantities are discussed, with extensive tabulation, in Ref.[29–31]

In certain cases (see later) input geometries were based on experimental data, but for most structures a preliminary estimation was required. For this, we carried out ωβ-calculations,[32] with[33, 34]

$$\omega = 1{\cdot}4, \quad \beta_{pq}(n+1) = \beta_0 \exp\left[0{\cdot}55P_{pq}(n) - 0{\cdot}3668\right],$$

and derived bond lengths, at self consistence, from[34]

$$R_{pq}\,(\text{Å}) = 1{\cdot}524 - 0{\cdot}194P_{pq}.$$

Noticing that internal angles in carbocyclic structures are usually within 5° of the regular value, θ_n,* the length R of one of the sides was next expressed in terms of the ωβ-lengths of the other sides and of the unknown angles, and all angles let vary from $\theta_n - 5°$ to $\theta_n + 5°$. Sets of angles for which R is close to its ωβ-value could thus be identified. A final choice between these sets was based on the least-squares proximity to θ_n (*cf*[38, 39]).

RESULTS AND DISCUSSION

1. *Fulvene*

We start with fulvene (X) where fulvalenic features are already apparent. The initial geometry was based on that of 6,6-dimethylfulvene,[36] and all (i.e. 3 × 3) monoexcited configurations were taken into account.

The computed distances, indicative of bond-alternation, are very close to those of the 6,6-dimethyl derivative: $R_{15} = 1{\cdot}477$ Å (vs 1·476), $R_{12} = 1{\cdot}340$ (1·340), $R_{23} = 1{\cdot}473$ (1·462), $R_{56} = 1{\cdot}339$ Å (*vs* 1·347). Atoms 5, 2(3) and 6 are predicted to be positive, 1(4) negative, with the ring, on the whole, negative. IP is evaluated as 8·77 eV, thus *lower* than the benzene value[29] by about 0·5 eV; for $E_{\frac{1}{2}}$ we calculate −2·22 v (reported[40] −1·65, −1·85 v). The theoretical spectrum (Table 1), with assignments coinciding with those of previous authors,[41] agrees well with experiment,[42] except that oscillator-strengths are somewhat exaggerated.[43] The first transition, allowed but weak, is followed by two strong absorptions, and the next band—which extends in practice[42] from 178 to 168 nm—is analyzed as consisting of two transitions, distinguishable by symmetry.

To simulate fulvalenic twisting, we now let the exocyclic p(π)-AO rotate about the molecular axis. The predicted outcome is that single bonds contract, double bonds stretch, charge-separation becomes more pronounced, IP and $E_{\frac{1}{2}}$ diminish. Of much interest is the spectral behaviour: as indicated in Table 1 and shown graphically in Fig 1, the first two bands weaken and move bathochromically. Put differently: if some internal steric strain brings exocyclic twisting about, the strong 240-band would be displaced to the red and its intensity diminish. It may be recalled that conjugative interaction also leads to bathochromic shifting which, however, is hyperchromic.[41] It is therefore interesting to note that the intensity of the first strong absorption in 6,6-diphenylfulvene[44] [XI, 328 nm (lg ε 4·36) in dioxan], in which twisting is expected about 5–6 (as well as about 6–7 and 6–7′) is not significantly higher than the corresponding value[45] in 6,6-dimethylfulvene [269 (4·30) in cyclohexane].

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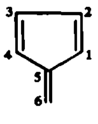
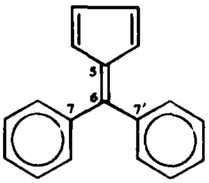
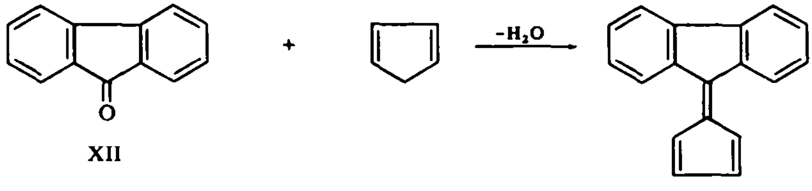
* For example, they are 93° and 87° in dimethylenecyclobutene[35] ($\theta_4 = 90°$), 106°, 108°, 109° in dimethylfulvene[36] ($\theta = 108°$), close to 120° ($\equiv \theta_6$) is fused benzenoids,[37] 122°, 132°, 130°, 126°, 125°, 132°, 130° in the 7-membered ring[4] of compound III ($\theta_7 = 128{\cdot}6$).



X



XI



XII

XIII

TABLE 1. ABSORPTION SPECTRUM OF PLANAR FULVENE[a]

	Source	Destiny	λ	f	Pol.[b]	Exp.[c,d]	Fate on distortion[e]
1	HOMO	LVMO	346	0·064	⊥	400–300, max at 360 f = 0·008, ε(max) 200	↑(↓)
2	HOMO-1	LVMO	241	0·818	∥	267–205, max at 235 f = 0·34, ε(max) 14000	↑(↓)
3	HOMO	LVMO + 1	194	0·372	∥	202–191, max at 202	↑(↓)
4	HOMO	LVMO + 2	185	0·088	⊥	178 }	
5	HOMO-1	LVMO + 2	167	0·136	∥	168 }	
6	HOMO-1	LVMO + 1	158	0·042	⊥		

[a] Wavelengths (λ) in nm, oscillator-strengths (f). [b] With respect to the molecular axis. [c] Ref. 38. d Solution values[40] (in EtOH): 373 (lgε 2·45), 242 nm (4·16). [e] ↑ denotes bathochromic, ↓ hypsochromic displacement; in parenthesis—hyperchromic (↑) or hypochromic (↓) change.

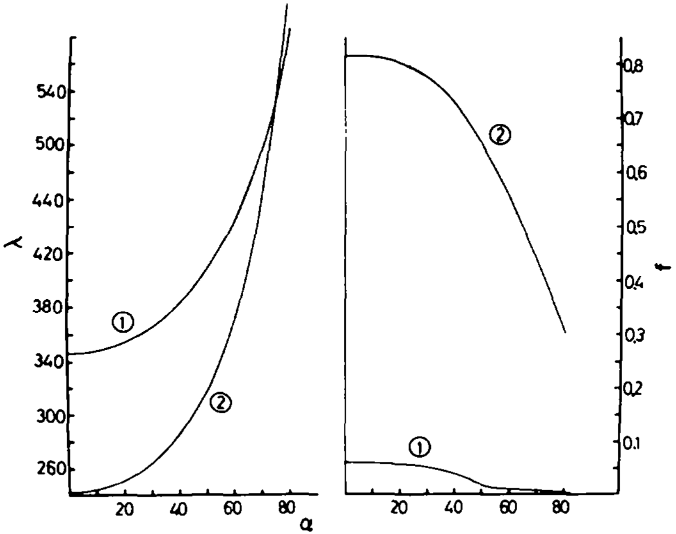


FIG. 1. Fulvene. Calculated wavelength (λ, nm) and oscillator-strength (f) for the two first absorptions, as function of the twisting (α) of the exocyclic p(π) atomic orbital

2. *Fulvalene*

Fulvalene (IVb) is known only in dilute solution,[46, 47] but there are grounds[20] to believe that it is planar. Input distances and angles were estimated through the ωβ-approach. Calculations were also performed for a hypothetical structure having the skeleton of the octachloro derivative[5] (IVa). Monoexcitation-CI was complete (i.e. 5 × 5).

Interatomic distances, as computed for the planar structure (R_{12} = 1·470, R_{23} = 1·344, R_{34} = 1·468 Å), are close to the fulvene values, excepting bond 1–1′ which is longer (1·361 *vs* 1·339 Å). They resemble the values[22] (1·467, 1·351, 1·460, 1·364, respectively) derived by total-energy minimization, which indicates again[1] that our procedure is equivalent, in a certain sense, to optimization techniques. The predicted charge distribution (q_1 = +0·072, q_2 = −0·052, q_3 = +0·016) differs with other calculations,[21, 48] but recalls our results for alternant hydrocarbons:[1] junction atoms (1,1′) are positive, charge-alternation prevailing otherwise. The computed ionization potential is 8·70 eV, thus *higher* by about 0·6 eV than the value measured[29] or computed[1] for naphthalene. The very low value of −1·33 v is calculated for $E_{\frac{1}{2}}$, in line with the known properties[49] of fulvalenic structures.

The agreement of the theoretical (Table 2) with the experimental spectrum[46] is better than in previous calculations.[21, 23, 25–27] The first excitation is forbidden, but expected to acquire some intensity in distorted structures. The next absorptions, one weak and one strong, are equivalent—by source, destiny, intensity and polarization—to the first two transitions in fulvene; likewise, they are predicted to undergo a bathochromic-hypochromic change upon twisting.

TABLE 2. ABSORPTION SPECTRUM OF PLANAR FULVALENE[a]

	Source	Density	λ	*f*	Pol.[b]	Exp.[c]	Fate on distortion
1	HOMO − 2	LVMO	448	—	B_{1g}	tailing	↑(↓)
2	HOMO	LVMO	435	0·047	⊥	416, weak	↑(↓)
3	HOMO − 1	LVMO	291	1·604	‖	sharp maxima with decreasing intensity at 314 (ε 47000), 300, 289, 278, 266	↑(↓)
4	HOMO	LVMO + 1	216	—	B_{1g}		
5	HOMO − 1	LVMO + 1	211	—	Ag		
6	HOMO − 2	LVMO + 1	207	0·124	⊥		

[a] *cf* footnotes a, d to Table 1. [b] Perpendicular (B_{3u}) or parallel (B_{2u}) to the axis through 1-1′. [c] Solution values from Ref. 46.

As in fulvene, rotation about the exocyclic bond is accompanied by contraction of single bonds, stretching of double bonds, accentuation of charges and decrease in IP and $|E_{\frac{1}{2}}|$.

Octachlorofulvalene (IVa) absorbs above 600 nm,[49, 50] octafluorofulvalene[51]—at 578. In an attempt to identify the source of this extraordinary shifting of the fulvalenic absorptions, we also considered a hypothetical fulvalene, shaped like the carbocyclic system[5] in octachlorofulvalene. Only steric (not mesomeric) factors distinguish this structure from ordinary fulvalene: it has a long exocyclic linkage (1·49 Å) and a relatively short 3–4 bond (1·39 Å). It was found indeed that these particularities alone could account for the properties of the octachloro compound: in the hypothetical carbocyclic structure, absorptions are red-shifted with respect to those of ordinary fulvalene, and twisting is predicted to shift them even more. This is shown, for the three longest-wave absorptions, in Fig 2. The measured spectrum coincides with the theoretical at a twist-angle of 30°, (which might be compared with 41°, measured[5] in the *solid* state). Assignments are given in Table 3.

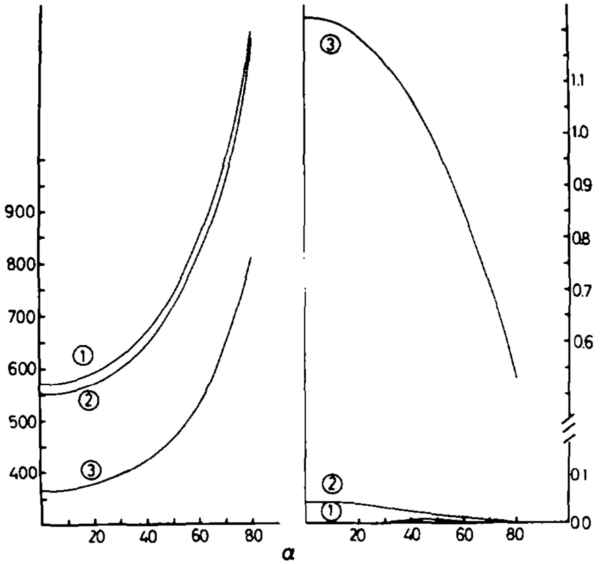


FIG 2. Fulvalene, exocyclic bond 1·49 Å. Calculated wavelength (λ, nm) and oscillator-strength (f) for the first three absorptions, as function of twisting (α) about the exocyclic bond

TABLE 3. ABSORPTION SPECTRUM OF AN EXOCYCLICALLY-STRETCHED FULVALENE, TWISTED THROUGH 30°[a]

	Source	Destiny	λ	f	Pol.[b]	Exp.[c]
1	HOMO − 2	LVMO	622	0·003	B_1	
2	HOMO − 1	LVMO	601	0·030	B_3	CH_2Cl_2: 604 (2·40) CH: 610 (2·40)
3	HOMO	LVMO	395	1·140	B_2	CH_2Cl_2: 390 (4·60) CH: 390 (4·61)
4	HOMO	LVMO + 1	244	—	A	
5	HOMO − 1	LVMO + 1	232	0·015	B_1	CH: 208 (4·45)
6	HOMO − 2	LVMO + 1	222	0·186	B_3	
7			220	0·121		
8			193	0·008		
9			190	0·472		

[a] *cf.* footnote a to Table 1. [b] D_2-symmetry, 1-1′ is B_2. [c] λ_{max} (and lg ε) for dissolved octachlorofulvalene (IVa), taken from Ref. 49 and 50; CH – cyclohexane.

The shift may thus be interpreted as an indirect outcome of halogen–halogen repulsions, which keep the two halves of the molecule apart and twisted; conjugative effects probably play a minor role.[49] The phenomenon has counterparts in benzocyclic chemistry:[49a] it is known, for example, that 4,5-disubstitution of phenanthrene by the bulky halogens (Cl, Br, I) leads to bathochromic shifting, while 4,5-difluorophenanthene absorbs lower than the parent compound.

Let us add that the input interatomic distances (i.e. those of the carbocyclic skeleton in IVa) differ markedly from the computed (output) values: computed $R_{11'}$ is 1·370 Å (*vs* 1·49 in IVa), R_{12} = 1·464 (1·47), R_{23} = 1·350 (1·36), R_{34} = 1·456 (1·39). This may be taken to mean that the exocyclically-stretched structure "strives" to revert to ordinary fulvalene geometry. Also, $E_{\frac{1}{2}}$, computed for the stretched and twisted structure, is −0·83 v as against −1·17, calculated for a normal fulvalene twisted through the same angle. Hence a ready explanation for the tendency of IVa to form charge-transfer complexes.[49]

3. *Dibenzofulvalene*

Dibenzofulvalene (fluorenylidenecyclopentadiene, XIII) has been prepared[52] from fluorenone (XII) and cyclopentadiene; a later attempt to repeat the synthesis is reported[53] to have led directly to a dimer. Input geometries were calculated, as described above, by the ωβ and angle-optimization techniques. Sixteen monoexcited configurations (i.e. 4 × 4) were included in the CI-treatment; in two cases (20°, 30°) a more extensive calculation (5 × 5) was also performed. The material was prepared and some of its properties will be described here.

In Fig 3, the input geometry serves as background for the computed bond-lengths and charge densities. The non-annelated 5-membered ring is predicted to be negative,

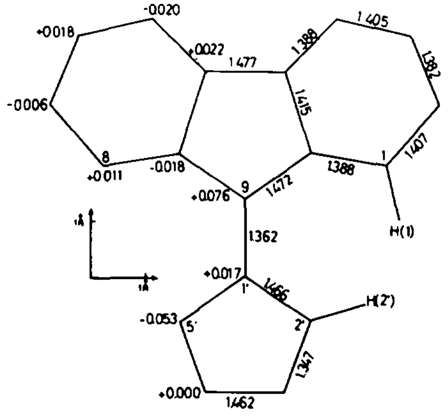


FIG 3. Fluorenylidenecyclopentadiene. Input geometry (drawn to scale), calculated distances (Å) and charges (marked) in a hypothetical planar structure

the fluorenylidene moiety-positive.* Again, junction atoms (9, 1′) are positive, charge-alternation prevailing otherwise. IP and $E_{\frac{1}{2}}$ are 7·27 eV and −1·55 v, both values lower than those obtained for unfused fulvalene.

As might be seen in Fig 3, the distance H(1)-H(2′) is *ca* 1·6 Å. Would this suffice to twist the molecule out of a plane?

Guided by previous studies of biphenyl[59] and fulvalene,[20] we have sought the total-energy minimum by combining, at various conformations, the electronic energy with the non-bonded interaction potentials. We considered only the repulsive-attractive potentials among the hydrogens at 1, 8, 5′, 2′ (Fig 3) and used [20, 59] Bartell's formulation,[60]

$$V(\mathrm{eV}) = [6590 \exp(-R/0{\cdot}245)-49{\cdot}2R^{-6}]/23{\cdot}055$$

to obtain the necessary quantities. Equally, the π-electronic energy, E(π), derived[61] from the SCF-results, was not implemented by core–core repulsion terms (*cf*[59]).

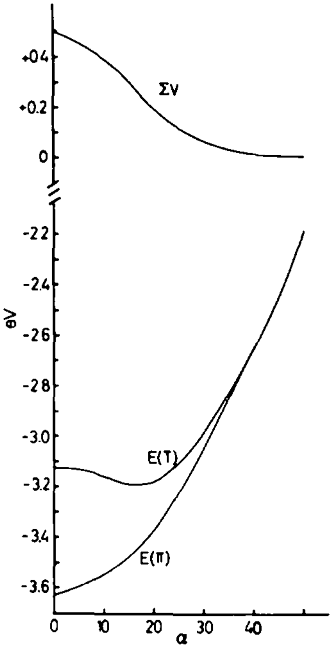


FIG 4. Fluorenylidenecyclopentadiene. Calculated non-bonded interactions (ΣV), π-electronic energy [E(π)] and their sum [E(T)], as function of twist (α) about the exocyclic bond (arbitrary zero points)

* This should come as no surprise even to believers in the Hückel rule ("4n + 2", *cf*[32]), for fluorene forms a stable cation[53a] and fluorenone (XII) has a positively-charged carbocyclic component: the dipole moment[54] of XII (3·3–3·4 D) is certainly not lower than that of other ketones[55] (*ca* 3 D). The distribution, certainly, has its particularities, and this is reflected in the relatively high energy[56] (1720 cm^{-1}) required for C=O stretching.

The positivity of the fluorenylidene moiety in XIII is already discernible at the stage of Hückel-type and ωβ-calculations, and is not limited to our version[1, 28] of SCF: the same result was obtained with a conventional SCF-program.[23, 57] In fact, other calculations (unpublished) suggest that dibenzo [*a*, *c*] annelation to odd-membered rings reduces the pertinence of the Hückel rule, in the sense that delocalization energies, in cation and anion, tend to become alike. A more formalistic view would be that the rule loses its force when topological-symmetry D_{nh}, with its implications of degeneracy,[58] is replaced by C_{2v}.

The energy components, $E(\pi)$ and ΣV, as well as their sum, $E(T)$, are traced in Fig 4 against the angle of twist. The minimum occurs at around 20°, which predicts ground-state twisting.

Encouraged by the previous success in correlating spectra, we now proceed to an alternative estimation of the twisting angle in XIII. As before, we trace the calculated absorptions against the angle of twist (Fig 5), and compare the predicted position of band 2, which is the first strong absorption, with the experimental curve (Fig. 6): agreement is obtained at 30–40°. Bearing in mind, however, that CI was here rather limited (4 × 4), and that more extensive CI lowers the predicted energies,* we expect theory and experiment to coincide below 30–40°, which brings us back to *ca* 20° as the angle of twist.

The preparation of fluorenylidenecyclopentadiene proceeded as described,[59] except that elementary analysis and IR spectroscopy revealed some contamination by fluorenone.† The IR spectrum (1670, 1590, 1482, 1458, 1368 cm^{-1}) resembles closely the one published[3] for dibenzosesquifulvalene (II), and the NMR has a typical[62] A_2X_2 pattern, bounded by 662 and 805 H_z (downfield from TMS), superposed on an aromatic massif. The mass spectrum contains a series of weak peaks at *m/e* 230–226, one at 180, very intense absorptions at 166 and 165, then signals at 152 and lower *m/e*-ratios. The main fragmentation process may thus be envisaged as starting at the twisted, zwitterionic form (XIV); upon impact, it loses an electron to produce C_5H_4–$C_{13}H_8^+$ (XV, *m/e* 228), which immediately collapses to $C_5H_3^\circ + C_{13}H_9^+$ (*m/e* 165) $C_5H_2^\circ + C_{13}H_{10}^+$ (*m/e* 166). The signal at 180 reveals again the contaminating fluorenone, and the one at 152 is due to ionized biphenyl.[63]

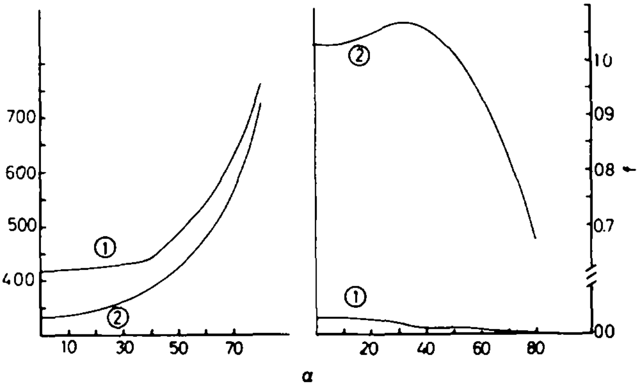


FIG 5. Fluorenylidencyclopentadiene. Calculated wavelength (λ, nm) and oscillator-strength (f) for the first two absorptions (16 excited configurations), as function of twisting (α) about the exocyclic bond

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* This was re-verified for the present case by 5 × 5—calculations for structures twisted through 20° and 30°.

† Recrystallization is not feasible because of dimerization. IR spectra were taken in CCl_4 on a Perkin-Elmer model 457. UV spectra were recorded on a Unicam SP.800, NMR (at −1·26°)—on a Varian HA-100. Mass spectra were registered on a Varian MAT CH4, ion source TO4, with gas cartridge (not direct introduction); ionizing energy 70 eV, high-temperature inlet at 300°.

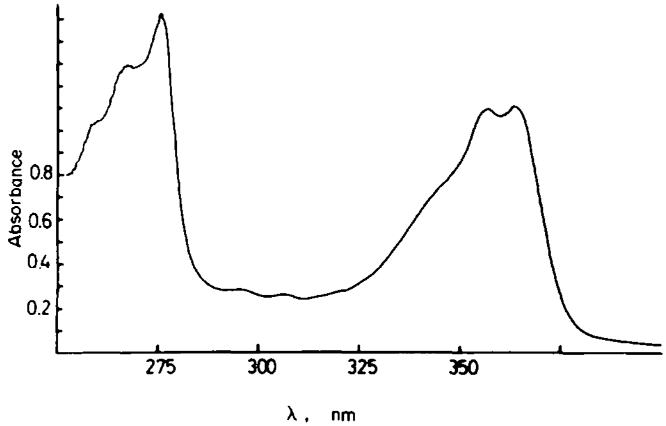
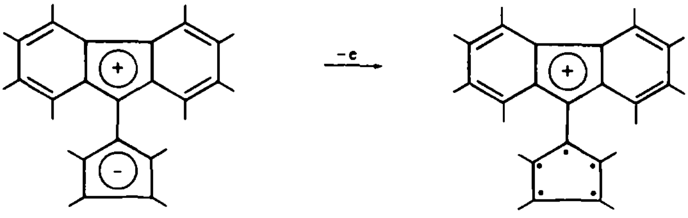


FIG 6. Fluorenylidenecyclopentadiene. Absorption spectrum, 5 × 10^{-5} mol l^{-1} in dioxan



XIV XV

In dioxan, our material absorbs at 377 (lg ε 4·35), 363 (4·34), 340s (4·10), 306 (3·72), 295 (3·75) and 276 nm (4·48) (Fig 6).* As mentioned above, this corresponds to twisting through *ca* 20°, in line with the minimum-range of the E(T)-curve (Fig 4).

When heated in a solvent (hexane), fluorenylidenecyclopentadiene (XIII) transforms into a highly-insoluble yellow dimer, dec. 270–280°. Its mass spectrum (sample recrystallized from xylene) contains a weak absorption at *m/e* 456 [M^+(dimer)], no signals down to a prominent, satellited peak at 228 [M^+ (monomer)], then peaks at 202 (monomer minus CHCH), 179, 165, 164 and lower *m/e*-ratios. The peak at 202 shows that the dimer was not produced by a [2 + 2]-reaction (which could have led, e.g., to XVI), but contains CH=CH linkages, as in the [4 + 2] structures, XVII and XVIII.

4. *Tetrabenzofulvalene*

There are indications[16] that the benzo-rings in bisfluorenylidene (tetrabenzofulvalene, Va) are tilted from the mean molecular plane, and that folding[10] and twisting[6] obtain, at least in solution. Here we examine the suitability of a model with twisting alone.

Fig 7 contains the input (ωβ) and output (SCF) bond-lengths and angles, as well as the electronic charges computed for a hypothetical coplanar structure; it is clear that

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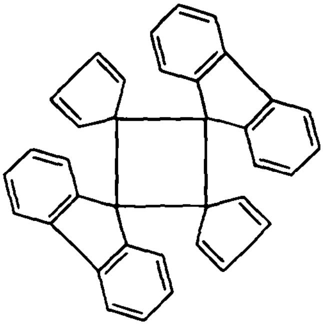
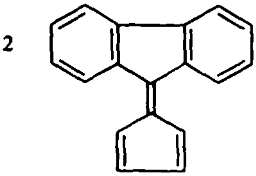
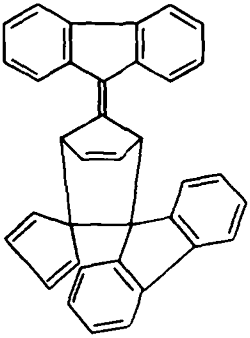
* In the same solvent, fluorenone absorbs at[64] 378 nm (lgε 2·43), 328 (2·89), 308 (3·24), 294 (3·62) and 258 nm (4·90).



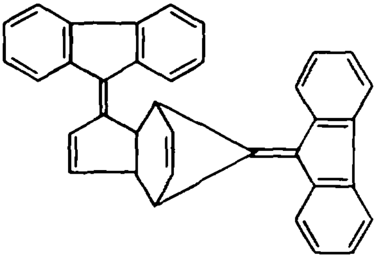
XVI



XIII



XVII



XVIII

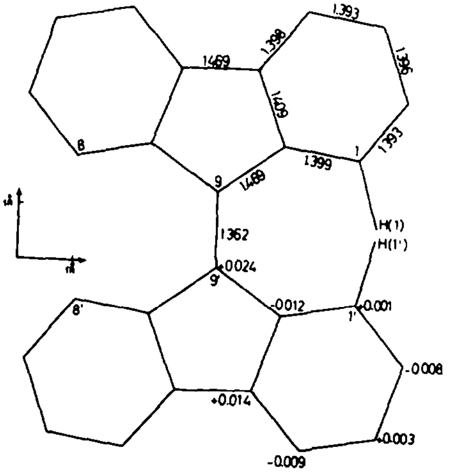


FIG 7. Bisfluorenylidene. Input geometry (drawn to scale), calculated distances (Å) and charges (marked) in a hypothetical planar structure

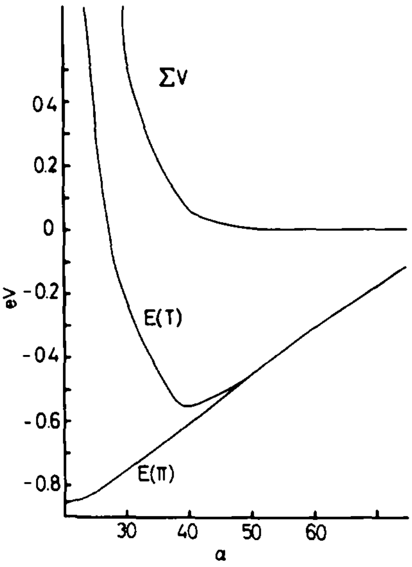


FIG 8. Bisfluorenylidene. Calculated non-bonded interactions (ΣV), π-electronic energy [E(π)] and their sum [E(T)], as function of twist (α) about the exocyclic bond (arbitrary zero points)

the molecule must distort in order to alleviate the interference at 1–1′ and 8–8′. Fig 8 now indicates that, if twisting constituted the only mechanism of relief, one part of the molecule would rotate, with respect to the other, through 40°. This value, which is close to the one encountered in solid octachlorofulvalene[5] and gaseous biphenyl,[65] cannot be representative in bisfluorenylidene, where other distortions are feasible. Also, the ionization potential of Va,[66] 8·5 ± 0·2 eV, exceeds the value calculated for twisted bisfluorenylidene (7·23 at 40°). These results rationalize the experimental finding that, in this compound, twisting is accompanied by other distortions.

CONCLUSION

In the preceding pages we have employed a π-electronic technique to study planar and non-planar dispositions in fulvenes and fulvalenes. The results for the unsubstituted, non-annelated molecules were in good agreement with the available experimental data. The charge-transfer complexing and spectral properties of octachlorofulvalene were interpreted as deriving mainly from stretching and twisting about the central bond. Twisting was also proposed to account for the measured spectrum of fluorenylidenecyclopentadiene, but it could be inferred that other types of distortion prevail in tetrabenzofulvalene.

We are aware[67] that a π-electronic approach,[68] where a sole AO is considered at an apex, is not strictly justifiable in studies of non-planar unsaturation: σ and π-levels are intermixed even in planar conjugated molecules.[69] It is to be expected that all-valence and all-electron methods, when they become economical,[70] will achieve more. For the moment, we share with others[71] the belief that π-electronic methods are useful[59] in elucidating some consequences of deformation in large unsaturated organic molecules. We hope to have shown that, in spite of conceptual limitations, our approach contributes to the understanding of some particularities of nonplanar structures.

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