

THE INFLUENCE OF BOND FIXATION ON THE ELECTRONIC SPECTRA OF SUBSTITUTED FULVENES

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Abstract—It is shown that the position of the first strong band in the spectra of the 6-substituted fulvenes can be understood by Hückel theory only if account is taken of the strong double bond fixation in these compounds. The measure of bond fixation which fits the experimental data (β single/ β double \approx 0.54) is in good agreement with that deduced by Nakajima to give a balance between π - and σ -bond energies. The substituted shifts for the 6-substituted fulvenes are mainly determined by the mesomeric effect, and the situation is therefore in strong contrast with azulene, the other common non-alternant that has been studied and for which the shifts of the visible band are dominated by the inductive effect.

THE spectra of the substituted fulvenes have been little analysed although extensive data is now available in the literature. The parent compound, one of the simplest non-alternant hydrocarbons, is of considerable theoretical interest on account of its strong double bond fixation.¹

Non alternants have non-uniform charge distributions in their ground and excited states and the influence of substituents on their spectra may be expected to be predominantly determined by the inductive effect. Azulene is the archetype of that situation.² However, if there is strong bond fixation, this non-uniform charge distribution will be smoothed out and the molecule will tend to behave as a conjugated polyene for which the mesomeric effect of the substituent is more important.

Straub *et al.*³ showed that the simple Hückel model in which all bonds are taken to have equal length failed to explain the direction of the spectral shifts induced by alkyl substituents in the exocyclic position. Although they did not try a Hückel model with bond length variation, they did show that a "molecules-in-molecules" calculation based on weakly coupled double bonds was successful. We shall show that a Hückel model which allows for bond-length variation provides just as good a framework for understanding these spectral shifts and may be used successfully for a wide range of substituents. We shall also show that the substituents exert their influence mainly through their mesomeric effects.

The spectrum of fulvene consists of a weak band at 362 nm ($\log \epsilon = 2.4$) and a much stronger one at 242 nm ($\log \epsilon = 4.1$).³ In the HMO model the first transition is $a_2 \rightarrow b_1^*$ giving an excited state of B_2 symmetry and a band which is polarized perpendicular to the two-fold symmetry axis. The strong band, polarized along the two-fold axis, arises from $a b_1 \rightarrow b_1^*$ transition and has an excited state of A_1 symmetry.

When substituents are introduced at the exocyclic position the strong band moves to lower energies more appreciably than the weak band and for most compounds

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the weak band is not detectable. For this reason we concentrate our attention in this paper on the shift of the strong band alone.

Calculations within the Pariser–Parr–Pople approximations for fulvene and some symmetrically disubstituted fulvenes show⁴ that this band is closely associated with a one electron transition of $b_1 \rightarrow b_1^*$ type, configuration interaction being negligible. There is therefore some justification for using the Hückel model which has been shown to be quite successful under these circumstances for alternant hydrocarbons.

We have allowed for the effect of bond length variation in our calculations by making the resonance-integral for the formal double and single bonds conform to the relationship:

$$\frac{\beta \text{ single}}{\beta \text{ double}} = \frac{1 - a}{1 + a}$$

Calculations were made with $a = 0, 0.1, 0.2$ etc, and standard Hückel parameters^{5a, b, *} were used for the substituents. The compounds examined cover the majority of known fulvenes with substituents in the exocyclic position. However, those for which serious steric interaction of the substituents might obscure the results (e.g. disubst. Phenyl-fulvenes etc) have been omitted.

RESULTS

6-Mono-substituted compounds. When the Hückel energies of the compounds 1–9 given in Table 1 were calculated as a function of the bond alternation parameter, it was found that some measure of bond fixation led to a distinct improvement in the overall correlation. The best fitting was found with $a = 0.3$. This value was chosen from a qualitative examination of the graphs. We do not consider that a detailed least squares fitting would be significant, because of the uncertainties connected with hetero-atom parameters. With $a > 0.3$ the results appeared to be distinctly worse. Figs. 1 and 1a show the results for the two cases $a = 0$ and $a = 0.3$. The improvement is best seen by considering some of the individual effects of substituents which are given in the wrong order in Fig. 1 (e.g. compare fulvene with compounds 1 and 2 or the pairs of compounds 3 and 4, 5 and 9). Most of the relative effects of pairs of substituents are correctly accounted for in Fig. 1a.

6,6-Disubstituted compounds. Similarly, data are given in Table 2 for the A_1 -band of some 6,6-disubstituted fulvenes. Again an optimum correlation is found for $a = 0.3$ as shown in Figs. 2 and 2a. For compound 7 model (c) was used for the Me group (discussion). The improvement seems to be even more striking than for the mono-substituted fulvenes.

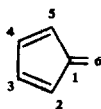
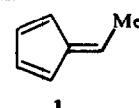
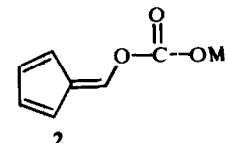
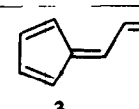
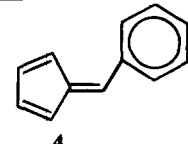
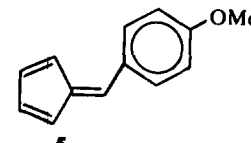
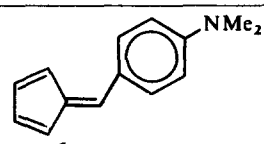
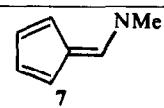
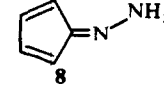
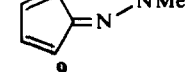
For reasons which shall be discussed later heptafulvene and sesquifulvalene have been added to Table 2 and Figs. 2 and 2a.

DISCUSSION

The following discussion of the material presented is focused upon (a) an interpretation of the correlations 1a and 2a in terms of substituent effects and (b) the

* All $h\bar{x}$ were reduced by 0.3 β per substituting alkyl group.

TABLE 1. EXPERIMENTAL* AND CALCULATED ENERGIES FOR THE A₁-BAND† OF 6-MONOSUBSTITUTED FULVENES

Compound	$\Delta x [\beta]$ $a = 0$	$\Delta x [\beta]$ $a = 0.3$	ΔE exp. nm (cm ⁻¹)	$\log \epsilon$	Ref.
	1.25	1.81	242 (41,300)	4.10	3
	1.36 (a) 1.27 (b) 1.28 (c)	1.81 (a) 1.76 (b) 1.72 (c)	255 (39,200)	4.24	7
	1.27	1.70	266 (37,600)	4.36	6
	0.93	1.55	295 (33,900)	4.50	3
	0.99	1.33	300 (33,300)	—	8
	0.96	1.27	337 (29,600)	4.39	9
	0.80	1.08	390 (25,600)	4.52	9
	1.23	1.43	319 (31,300)	4.48	6
	1.09	1.58	307 (32,500)	4.16	6
	0.96	1.31	327 (30,800)	4.41	6

* Hydrocarbons were used as solvents throughout, except for 1 (EtOH).

† This designation is correct only for fulvene and symmetrically disubstituted fulvenes (C_{2v}-Symmetry). But for the sake of convenience it is used for the corresponding band in 6-monosubstituted fulvenes (pseudo-C_{2v}-symmetry in the HMO-method) as well as for the unsymmetrically disubstituted fulvenes in Table 2.

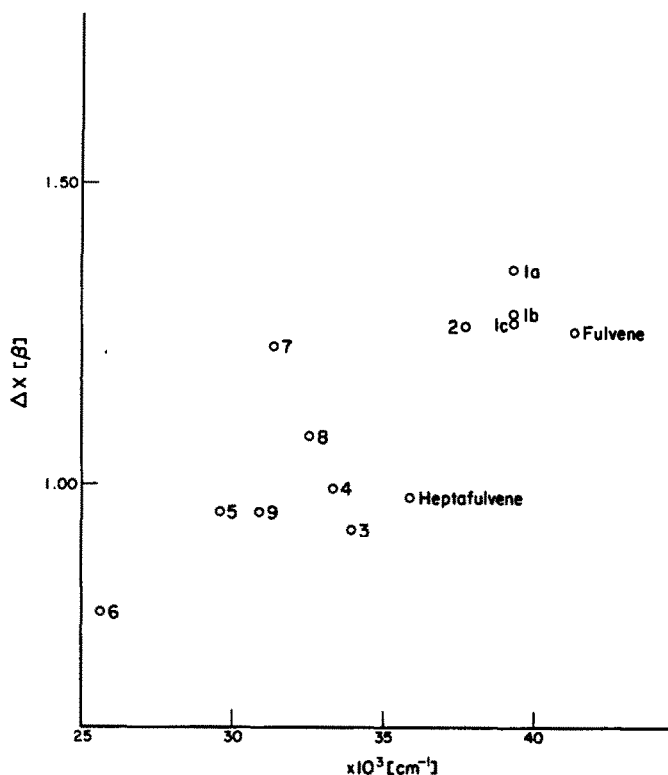


FIG. 1 HMO-correlation for 6-substituted fulvenes (A_1 -band); $a = 0$.

physical significance of the bond alternation parameter a , derived from these correlations.

To examine (a) we first look at the electronic rearrangements that occur on excitation for $a = 0$ and $a = 0.3$. We show changes in electron density $\Delta(C_p^2)$ on excitation $b_1 \rightarrow b_1^*$ (a positive sign is an increase in electron density):



There is a considerable difference between these two results. The most important feature is that the large migration of electrons to the 6 position is entirely removed by the measure of bond fixation which was found to optimize the results. Bond fixation clearly goes some way to give the situation typical of an alternant hydrocarbon where excitation is accompanied by no charge migration at all. However the effect is most noticeable at the 6 and 3(4) positions, the migration from the 1 to the 2(5) positions being almost the same in the two calculations.

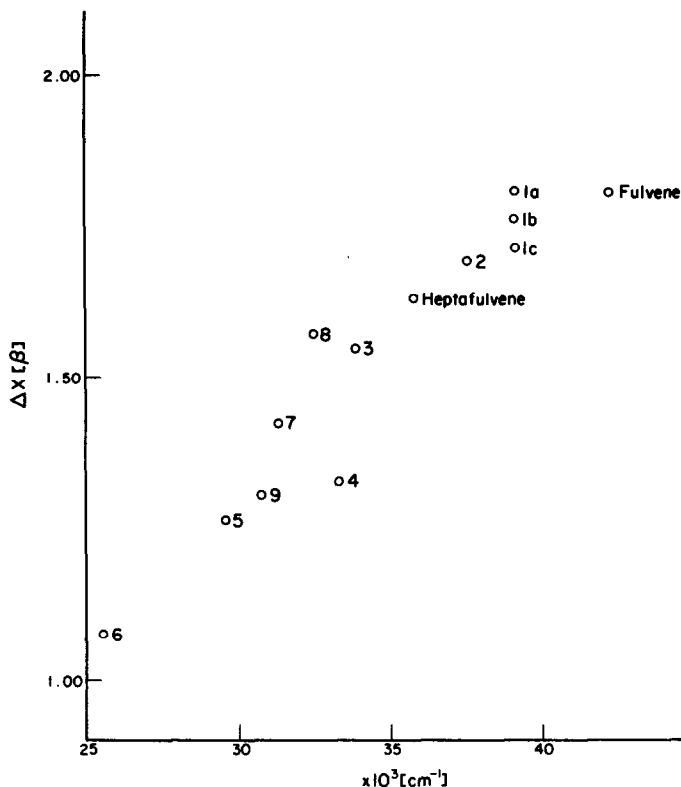


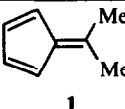
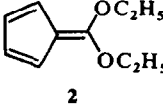
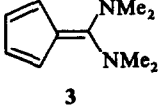
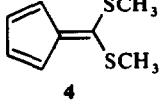
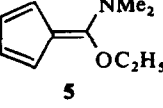
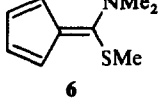
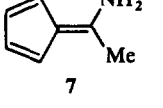
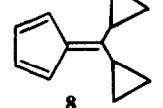
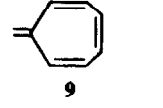
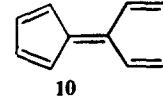
FIG. 1a HMO-correlation for 6-substituted fulvenes (A_1 -band); $a = 0.3$.

In principle one should be able to test our deduction that there is little change in electron density at the 6-position by introducing a suitable inductive perturbation. The most unambiguous way of doing this is by aza-substitution. Unfortunately 6-aza-fulvene has not yet been prepared, but if we compare compounds 7 and 9 of Table 1, we have an inductive perturbation of the required kind although on a compound already having a terminal substituent. The magnitude of the observed red-shift (only 500 cm^{-1}) is much better accounted for if one assumes strong bond fixation (cf. Table 1). Moreover, if we use the value of the inductive perturbation ($\alpha_N - \alpha_C$) deduced from the spectral shifts of other hydrocarbons¹⁷ ($\approx 18,000 \text{ cm}^{-1}$), we then can deduce the appropriate change in electron density from the first-order perturbation expression:

$$\Delta E_\mu = \Delta(C_\mu^2)(\alpha_N - \alpha_C)$$

and find it corresponds to an increase in charge density with excitation of only 0.03 units, in good agreement with our deduction. From these results we have some justification for saying that there should be almost no first order inductive effect for this particular electronic transition for substituents in the 6-position and that therefore their shifts should be dominated by the mesomeric effects alone. Second-order inductive shifts are usually much smaller than these.

TABLE 2. EXPERIMENTAL* AND CALCULATED ENERGIES FOR THE A₁-BAND† OF 6,6-DISUBSTITUTED FULVENES

Compound	Δx [β] $a = 0$	Δx [β] $a = 0.3$	ΔE exp. nm (cm ⁻¹)	log ϵ	Ref.
 1	1.49 (a) 1.29 (b) 1.34 (c)	1.82 (a) 1.72 (b) 1.67 (c)	269 (37,200)	4.30	3
 2	1.37	1.67	293 (34,150)	4.26	6
 3	1.40	1.44	342 (29,250)	4.44	6
 4	1.32	1.36	353 (28,350)	4.20	11
 5	1.34	1.47	328 (30,500)	4.41	6
 6	1.35	1.39	355 (28,200)	4.35	12
 7	1.33	1.61	316 (31,600)	4.30	6
 8	—	—	289 (34,600)	4.29	14
 9	0.99	1.63	280 (35,800)		10
 10	1.04	1.27	395 (25,300)	4.23	13

* Except for 4(CCl₄), 6 (EtOH) and 10 (dioxan), the solvents were hydrocarbons.

† cf. footnote below Table 1.

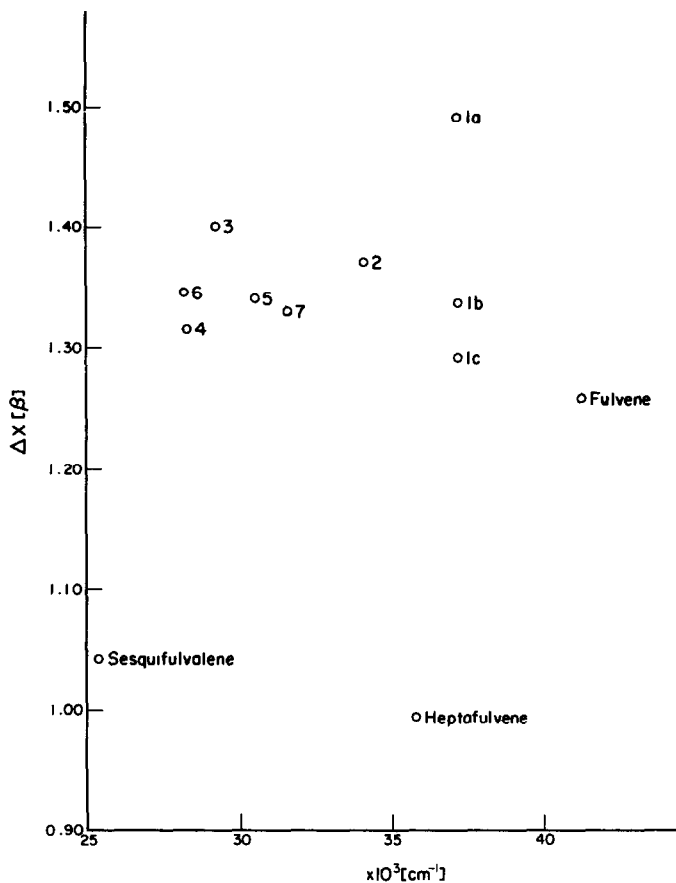
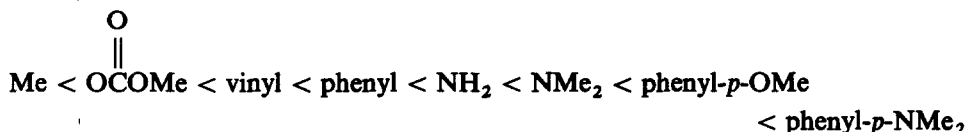


FIG. 2 HMO-correlation for the A_1 -band of 6,6-disubstituted fulvenes; $a = 0$.

This offers an opportunity to comment on the relative effects of the various substituents given in Table 1. As it has been shown, with the degree of bond fixation we have derived, the $b_1 \rightarrow b_1^*$ transition is associated with a charge transfer from the exocyclic double bond into the ring; more precisely from the 1 to the 2(5) positions. We may therefore anticipate that the red shifts caused by the various substituents will depend largely on their relative electron-releasing capacity. It follows that the physical interpretation of the correlation shown in the Figs would be that there is increasing charge-transfer character in the $b_1 \rightarrow b_1^*$ transition if one goes from $-\text{Me}$ to $-\text{phenyl-}p\text{-NMe}_2$ as substituents. This is borne out by examining the coefficients of the Hückel orbitals of our calculations. From the *experimental* data we therefore can derive the following sequence of substituents according to increasing $+M^*$ -effects (where the superscript * refers to the electron releasing power of the substituents in the *electronically excited state*; the $+M$ and $+M^*$ -effects of substituents must not necessarily run parallel):



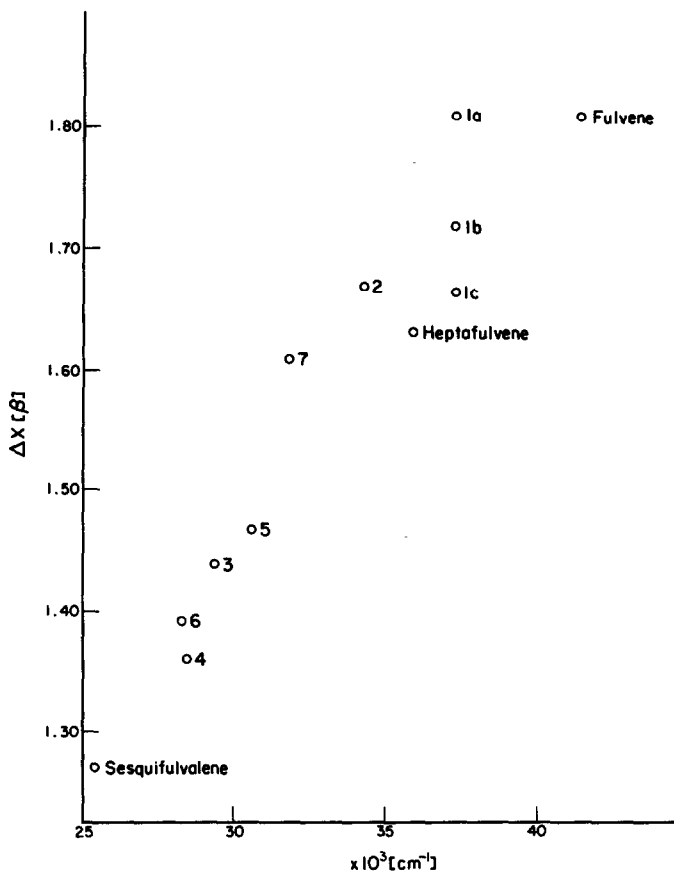


FIG. 2a HMO-correlation for the A_1 -band of 6,6-disubstituted fulvenes; $a = 0.3$.

The model used for the Me group in our calculations requires some further comment. Three methods of treating the Me group within a Hückel framework have been proposed:^{5a} (a) assuming a purely inductive effect; (b) mainly mesomeric effect combined with a small inductive effect and (c) solely mesomeric effect.

Given our earlier discussion it does not come as a surprise that the inductive model (a) even qualitatively fails to predict the observed bathochromic shift, giving at best zero shift for $a = 0.3$. Models (b) and (c) also give the wrong direction to the shift for $a = 0; 0.1$ but for $a \geq 0.2$ the observed trend is given correctly, with optimal results for $a = 0.3$ and model (c). Thus we understand the Me group as a substituent which exerts a *weak* mesomeric effect on the A_1 -band of fulvene. It has been shown¹⁷ that weak mesomeric effects of substituents should be additive with respect to the shift of a given band of a parent compound. This view is fully supported by the experimental results (cf. Tables 1 and 2) that introduction of two Me groups in the exocyclic position of fulvene gives rise to a red shift of the A_1 -band (4000 cm^{-1}) which is exactly twice that for one Me group. On the other hand this additivity is

expected to break down¹⁷ if the first substituent introduced exhibits a *strong* mesomeric effect, which may no longer be regarded as a small perturbation. Such is the case e.g. with the —NMe_2 group, which, when attached to the exocyclic position of fulvene, shifts the A_1 -band of the parent compound $10\,000\text{ cm}^{-1}$ to the red, whereas a second group of that kind has only the additional effect of further 2000 cm^{-1} .

An alkyl-substituent with special properties is the cyclopropyl group. For cyclopropane itself, it is well established by NMR¹⁸ and near-IR¹⁹ spectroscopy that the exocyclic σ -orbitals of the C atoms have virtually sp^2 -character. De Meijere and Lüttke²⁰ have recently analysed vinylcyclopropane by electron diffraction and have shown that the C—C single bond linking the ethylene and cyclopropyl units has a bond length of 1.475 \AA —which is a normal $C(sp^2)\text{—}C(sp^2)$ single-bond length. One would therefore expect that the inductive effect* of the cyclopropyl group is distinctly smaller than that of a normal alkyl group, for which the +I effect arises because an $sp^3\text{-C}$ atom is less electronegative than an $sp^2\text{-C}$ atom.² We may therefore assume that the mesomeric effect is dominant for the cyclopropyl group, and if we compare compounds 1 and 3 of Table 1 with compound 8 of Table 2, we deduce that the +M* effects of alkyl:cyclopropyl:vinyl are roughly in the ratio 1:2:4.

It is perhaps puzzling that the alkyl group in some situations produces an inductive perturbation (e.g. the spectral shifts of the first band of azulene) and in others produces an mesomeric perturbation (the situation for the A_1 -band of fulvene). Dewar has pointed out that in the HMO framework the only acceptable model for the +M-effect of a Me group is one which treats it as a pseudo-unsaturated group²¹ which possesses an antibonding orbital. If we accept the usual parametrization for that model²² we then have in a perturbation approach a very low-lying bonding orbital and an anti-bonding orbital at very high energy interacting with the various π -levels of the parent compound. The size of the interaction will be governed by the separation of the orbitals concerned. The inductive effect of a group is independent of the position of its orbitals relative to those of the parent compound but depends on the potential field exerted by the group.

As can be seen from Fig. 3, the separation between the a_1 and b_1^* orbitals of azulene and the pseudo- π -orbitals of the Me group is extremely large, with a resulting small +M-effect on the 1L_b -band. Of primary importance however is the +I-effect of the Me group which is extremely efficient in shifting the band, because azulene exhibits a maximum degree of non-alternant character as a result of its aromaticity (e.g. drastic changes in electron density in the $a_2 \rightarrow b_1^*$ transition). Thus the net result of this situation can be approximated with a mere inductive model. In fulvene the situation is to some extent complementary. The effect of bond fixation is twofold: firstly, as demonstrated for the A_1 -band, it leads to a stronger separation of the b_1, b_1^* orbitals, thus furthering the mesomeric effect (cf. Fig. 3), and secondly, the introduction of some amount of alternant character connected with it, reduces the effectiveness of a substituent to influence the transition energy by an inductive mechanism. For the special case of 6-methylfulvene we have demonstrated that this may result in a situation where there is no first order inductive effect operative. For substituents attached (or inserted) to the 5-membered ring of fulvene we may expect intermediate situations. Future publications will deal with a number of new compounds of this type and their spectral properties will be discussed.²³

* Defined as a σ -bond-relayed effect, according to reference 2.

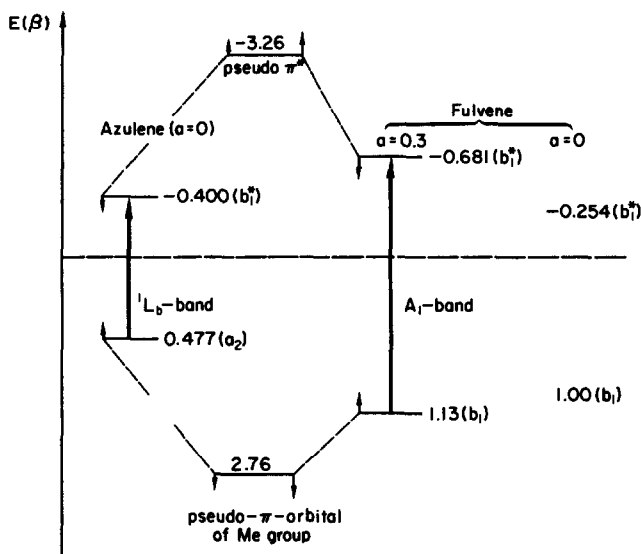


FIG. 3 The mesomeric effect of the Me group on the 1L_b -band of azulene and the A_1 -band of fulvene.

The consideration of Fig. 3 has demonstrated that there is neither need nor justification to use models (a), (b) or (c) for the Me group as *alternatives* (cf. 5^a). Clearly, a satisfactory model has to take into account the +M and -I effect of the Me group simultaneously. Model (b) comes closest to that postulate, but it seems that the parameters involved need to be reconsidered.

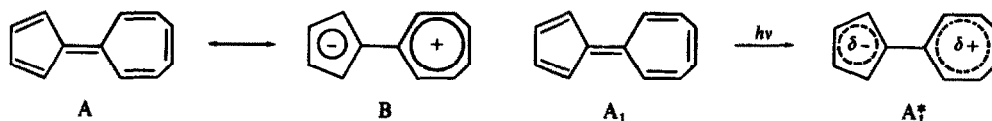
For the strong mesomeric substituents and symmetrical disubstitution at the 6-position of fulvene a new band is expected to appear in the spectrum, which corresponds to a pure charge transfer from the π -orbitals of the substituents to the hydrocarbon. This arises because the antisymmetric combination of the substituent π -orbitals (a_2) will not, in the Hückel model, interact with the a_2 -orbitals of the hydrocarbon* (the interaction is found to be very small also in the Pariser-Parr-Pople model⁴). Within the HMO-model the energy of this orbital depends solely on $h_{\bar{x}}$. If its energy could be determined by photoelectron-spectroscopy it would be a good measure of the relative coulomb integrals $h_{\bar{x}}$ of various substituents \bar{x} . The spectrum of 6,6-bisdimethylamino-fulvene shows in fact a band (251 nm; $\log \epsilon$ 3.87), which is absent in the spectrum of the corresponding mono-substituted compound.⁹ The disubstituted sulphur compound 4 (cf. Table 2) also shows a band of this type (240 nm, $\log \epsilon$ 3.60¹¹).

Finally we turn to a comparison of our deduced level of bond fixation ($a = 0.3$) with that obtained by other methods. The phenomenon of bond fixation depends on a balance between π -electron delocalization energy and σ -bond compression energy. Several methods of treating this have been described.²⁴⁻²⁶ The results of Nakajima *et al.*²⁵ may be most readily compared with ours, because their bond fixation is also introduced by the simple expedient of having a specified ratio of π -electron resonance integrals for formal double and single bonds: $k = \beta_u/\beta_D$. For fulvene the lowest energy

* The reason for this is that the a_2 -orbitals of fulvene possess a nodal plane which contains the twofold axis.

of the ground state molecule was obtained with $k = 0.56$, which is close to our value ($a = 0.3$ corresponds to $k = 0.54$). Similar calculations on butadiene, heptafulvene and sesquifulvalene gave comparable k -values, ranging from 0.54 to 0.60.²⁵ These results were obtained using the Wheland–Mann method for computing π -electron energies, but Binsch *et al.*²⁶ have shown that it is not a serious simplification to use the Hückel method. It is also perhaps worth emphasising that the type of bond fixation deduced by Nakajima is essentially first-order in the terminology of ref. 26. The conclusion that fulvene should exhibit the same order of bond fixation as butadiene has been supported by zero-overlap SCFMO-calculations which include both σ - and π -electrons.²⁷ The fact that our predicted substituent shifts agree well with experiment for a fixed value of k suggests that all these substituted fulvenes have a similar degree of bond fixation (and therefore geometry of the 5-membered ring), even if the ring contains a larger negative charge for the strong donor substituents.

Sesquifulvalene can formally be looked upon as a special case of a disubstituted fulvene. From Fig. 2a and the interpretation we gave to the red-shifts of the A_1 -band we can deduce that the 7-membered ring should be the strongest $+M^+$ -substituent in this series. This is born out by the calculations. We have therefore shown that the much-disputed²⁸ ‘Hückel-rule’ resonance $A \leftrightarrow B$ is of no importance for the description of the ground state of sesquifulvalene but that there exists a low-lying electronically excited A_1 -state which is polarised in a similar manner as the hypothetical species B:



One may expect that the correspondingly high polarizability of the molecule along the two-fold axis will be a dominant effect in chemical reactivity. These conclusions will to a smaller extent be relevant for all donor-substituted fulvenes.

If the bond fixation parameter $a = 0.3$ is used for heptafulvene and sesquifulvalene, then the predicted bands lie on the same correlation line as the substituted fulvenes (Fig. 2a). If on the other hand the normal Hückel model is taken ($a = 0$) this correlation is absent (Fig. 2). This emphasises that UV data on compounds of this type are a valuable test of structure. The Nakajima results were obtained using an exponential relationship between β and bond length r :

$$\beta_{(r)} = \beta_0 \exp [b(1.397 - r)]; b \approx 4.6 \text{ \AA}^{-1}$$

We would like to support the use of this relationship for carbon-carbon bonds when molecular geometries are known.

CONCLUSION

Dewar has claimed²⁹ that the application of HMO-theory to *non-alternants* and systems containing *heteroatoms* and/or *strong bond alternation* leads in practice to results which are unreliable “even in a qualitative sense”.

The molecules discussed in this paper possess these three features simultaneously. The results obtained encourage one to believe that the HMO model is just as useful a tool to interrelate chemical facts in the field of non-alternants as it has shown to be the case with alternants.

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