Chromogens based on Non-benzenoid Aromatic Systems. Part III.[1] Synthesis, Spectra, and Molecular Orbital Calculations in the Substituted Fulvene and 6-Azafulvene Series

By **John Griffiths** * and **Martin Lockwood,** Department of Colour Chemistry, The University, Leeds LS2 9JT

The synthesis and electronic absorption spectra of 6-substituted fulvenes and 6-azafulvenes derived from cyclo-pentadiene, 1,2,3,4-tetrachlorocyclopenta-1,3-diene, and fluorene have been examined. Some new syntheses of the tetrachlorofulvenes are described. Spectral studies on twenty derivatives show that mesomeric electron-donating groups at position 6 produce a strong bathochromic shift of the long wavelength absorption band. The tetrachlorofulvenes and tetrachloroazafulvenes are appreciably more bathochromic than their fulvene or fluorene counterparts, whereas the fulvenes and fluorenes absorb at similar wavelengths. The PPP molecular orbital method, with limited configuration interaction, has been applied to these compounds, by use of a combination of conventional and empirically modified parameters. The calculated spectra are in excellent agreement with experiment. In all cases a high degree of electron transfer from the donor atom to the five-membered ring was indicated for these transitions.

SIMPLE resonance theory suggests that intense visible absorption bands should occur in the spectra of fulvene derivatives if the system contains a mesomeric electron donor group capable of resonance interaction with the five-membered ring, *i.e.* (Ia) ⟷ (Ib). Various compounds of this type have been described which confirm this prediction, and dyes of commercial significance have been reported.[2] Resonance theory is, however, notoriously unreliable for predicting subtle structural effects, and it was of interest to examine the spectra of a wide range of coloured fulvene and azafulvene systems in order to compare the results with those of a more sophisticated theoretical treatment.

(Ia)   (Ib)

Three series of compounds have been examined, namely the parent fulvenes (II), the tetrachlorofulvenes (III), and the fluorene analogues (IV). In each series, the effects of electron-donating groups and of aza-substitution at the 6-position have been studied, and the spectral perturbations have been compared with those predicted by a Pariser–Pople–Parr (PPP) MO treatment.

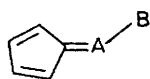Although many of these compounds have been described previously, certain important members were

unknown, and methods for their preparation are described. Where spectroscopic data were not available, the relevant compounds were prepared by published procedures. The MO procedure was of the usual PPP type with limited configuration interaction, within the fixed β approximation. The calculations were compared with the results of experiment, and the charge redistributions in the excited state were examined for each compound. It was found necessary to evaluate certain of the parameters empirically in order to obtain close agreement between calculated and experimental transition energies, but this was only necessary when strong inductive substituents were attached to the atom concerned.

RESULTS AND DISCUSSION

Synthesis of Fulvenes.—Derivatives of particular interest because of their potentially deep colours were (IIIf—h), and as they have not been reported previously, synthetic approaches were examined. Three independent routes to (IIIh) were established. In the first, use was made of the known nucleophilicity of 1,2,3,4-tetra-chlorocyclopentadiene when it was condensed with *NN*-dimethyl-*p*-nitrosoaniline, with a tertiary amine as basic catalyst. The reaction in ethanol was rapid at room temperature, the solution turning deep blue on mixing the two components. The azafulvene (IIIh) was isolated in 36% yield after chromatography over silica
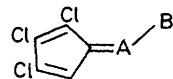
[1] Part II, J. Griffiths and M. Lockwood, *J.C.S. Perkin II*, 1973, 1155.

[2] F. Ramirez and S. Levy, *J. Amer. Chem. Soc.*, 1957, **79**, 6167; G.P. 1,296,289/1969; U.S.P. 3,385,874/1968.

gel. The compound formed dark blue, rather unstable crystals, and its structure was confirmed by elemental analysis and ^1H n.m.r. spectroscopy.
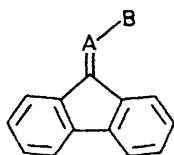

	A	B			A	B
a;	CH	H		a;	CH	Ph
b;	CH	NH_2		b;	CH	p-HO·C_6H_4
c;	CH	NMe_2		c;	CH	p-Me_2N·C_6H_4
d;	CH	p-Me_2N·C_6H_4		d;	N	NH_2
e;	N	NH_2		e;	N	NMe_2
f;	N	NMe_2		f;	N	Ph
				g;	N	p-HO·C_6H_4
				h;	N	p-Me_2N·C_6H_4

	A	B
a;	CH	Ph
b;	CH	p-MeO·C_6H_4
c;	CH	p-$Me_2NC_6H_4$
d;	N	Ph
e;	N	p-HO·C_6H_4
f;	N	p-Me_2N·C_6H_4

An alternative synthesis involved condensation of p-dimethylaminoaniline with hexachlorocyclopentadiene. The dihydrochloride of the amine was dissolved with hexachlorocyclopentadiene in ethanol and treated with aqueous alkali at room temperature. Again a rapid blue colouration was observed, and after 2 h the reaction was complete. The fulvene (IIIh) was isolated in 80% yield. Although this method was evidently the most suitable for preparing (IIIh) and its analogues, a third method was examined because of its relevance to dye-image formation in colour photography. Oxidation of p-dimethylaminoaniline with silver salts produces the highly electrophilic species (V). By analogy with known coupling reactions used in coloured-image formation, it was thought that this species might react with tetra-chlorocyclopentadiene to give the blue dye (IIIh) (see Scheme 1). When a suspension of silver chloride in aqueous gelatin was added to a solution of tetrachloro-cyclopentadiene and p-dimethylaminoaniline in ethanol under alkaline conditions, an immediate deep blue colour was produced. After removal of metallic silver, (IIIh) was obtained in 25% yield. Although of little preparative value, this reaction could be of practical importance in colour photography, particularly as the dye (IIIh) has a very intense colour (log ε 4.45).

The p-hydroxyphenyl derivative (IIIg) was prepared

in 14% yield from p-aminophenol by the second procedure. Attempts to improve the yield were unsuccessful The product was obtained as a red solid, giving blue solutions in alkali, and was characterised by elemental analysis.

The tetrachlorofulvene (VI) was prepared by treating Michler's ketone with phosphoryl chloride to give the addition complex, and condensing this with tetrachloro-cyclopentadiene (Scheme 2). Although the complex is known to react with arylamines to give triarylmethanols, it was not certain whether the diene would be sufficiently nucleophilic in the absence of base to take part in the reaction. In the event, the reaction proceeded smoothly, and the fulvene (VI) was obtained in 50% yield. The stable red crystals were very soluble in benzene and methylene chloride.

Electronic Absorption Spectra.—Many of the fulvene derivatives showed a pronounced bathochromic shift of the first absorption band in polar solvents, and thus for comparison with calculated values the maxima were determined for solutions in non-polar solvents. Literature data were used for spectra recorded in cyclohexane, n-hexane, n-heptane, or dioxan; otherwise the requisite compounds were prepared in this laboratory and their spectra measured in cyclohexane. The spectra of all new compounds were measured in this solvent. The results are summarised in Table 1.

Molecular Orbital Calculations.—One of the most convenient methods for calculating the absorption spectra of large, unsaturated molecules is the Pariser–Parr–Pople (PPP) SCF method. Although this procedure is based on the σ–π separation approximation, it has proved very successful for planar molecules. The

SCHEME 1

$R = p$-Me_2N·C_6H_4
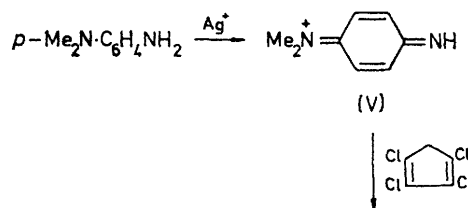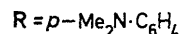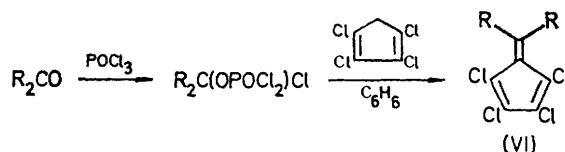
SCHEME 2

heavy dependence of the method on empirical parameters can be advantageous, particularly if calculations are confined to a relatively narrow class of compound. Within such a class, the appropriate parameters can lead

to reliable predictions of quite small spectral shifts, a particularly valuable feature for coloured systems, where the prediction of colour is rendered difficult by the

TABLE 1

Experimental [a] and calculated spectral data for fulvene derivatives

Compd.	$\lambda_{max.}$ (exp.)/ nm	$\log_{10}\varepsilon$ (exp.)	f(exp.) [b]	$\lambda_{max.}$ (calc.)/ nm	f(calc.)
(IIa) [c]	242	4.1	0.38	241	0.64
	362	2.33	0.005	379	0.04
(IIb)				292	0.85
				338	0.04
(IIc) [d]	316	4.49	0.94	312	0.82
				336	0.04
(IId) [e]	390	4.52	0.31	395	0.99
(IIe) [f]	307	4.16	0.37	307	0.86
(IIf) [f]	327	4.41	0.71	341	0.80
(IIIa) [g]	340	4.31	0.45	343	0.83
(IIIb) [g]	370	4.44	0.56	371	1.03
(IIIc) [g]	461	4.69	0.57	451	1.13
(IIId) [h]	325			327	0.86
(IIIe) [h]	361			372	0.80
(IIIf) [i]	445			450	0.40
(IIIg) [i]	483	4.02	0.23	490	0.89
(IIIh)	575	4.45	0.30	590	1.11
(IVa) [j]	260	4.48	0.65	229	1.02
	326	4.17	0.33	337	1.16
(IVb) [j]	348	4.29	0.44	354	1.09
(IVc) [j]	398	4.49	0.89	390	1.09
(IVd)	394	4.20	0.44	380	0.45
(IVe)	416	4.24	0.41	423	0.61
(IVf)	476	4.65	0.92	502	0.64

[a] Unless otherwise stated, spectra were recorded in cyclohexane. [b] Oscillator strength, evaluated from the relationship $f = 4.32 \times 10^{-9}\varepsilon_{max.}\Delta\nu_{\frac{1}{2}}$, where $\Delta\nu_{\frac{1}{2}}$ is the band width at $\varepsilon_{max.}/2$, in cm^{-1}. [c] Ref. 6. [d] Solvent n-hexane; see ref. 10. [e] Solvent n-heptane (G. Kresze and H. Goetz, *Chem. Ber.*, 1957, **90**, 2161). [f] Solvent n-hexane (K. Hafner, G. Schulz, and K. Wagner, *Annalen*, 1964, **678**, 39). [g] Method of preparation: E. T. McBee, R. K. Meyers, and C. F. Baranauckas, *J. Amer. Chem. Soc.*, 1955, **77**, 86. [h] Method of preparation: H. Disselnkötter, *Angew. Chem.*, 1964, **76**, 433. [i] Solvent light petroleum (b.p. 40—60°). [j] Solvent dioxan (E. D. Bergmann, Y. Hirshberg, D. Lavie, Y. Sprinzak, and J. Szmuskovicz, *Bull. Soc. chim. France*, 1952, 703)

sensitivity of the eye to small wavelength changes. Surprisingly, the PPP method has not been applied widely to coloured molecules, and this is presumably because of the need for special parameter evaluation. The parameters available from the literature are of limited scope, and rarely take into account the effect of chemical environment.

The fulvenes and azafulvenes seemed particularly appropriate for examination by the PPP method. Thus most of the compounds were expected to be planar, and a sufficient number of examples was available to facilitate the evaluation of new parameters. The presence of a non-alternant ring system and various heteroatomic substituents was expected to provide a useful test of the reliability of the method.

For the calculations, structural and energy parameters were required. The former, *i.e.* bond lengths and bond angles, were obtained from literature data for model systems as closely representative as possible. A planar geometry was assumed in all cases. The bond lengths used are summarised in Table 2.

The one-centre electron repulsion integrals, γ_{rr}, were

determined from the relationship $\gamma_{rr} = VSIP_r - A_r$, where $VSIP_r$ and A_r are the valence state ionisation potential and electron affinity of atom r, respectively. The two-centre repulsion integrals γ_{rs} were calculated from the Nishimoto–Mataga relationship,[3] and the $\alpha_r{}^{core}$ terms were evaluated in the usual way from the

TABLE 2

Two-centre parameters for fulvene derivatives

Bond type	$r/Å$ [a]	β^{core}/eV [b]	Bond type	$r/Å$ [a]	β^{core}/eV [b]
C(1)–C(2)	1.435	−2.30	C(6)–N	1.38	−2.50
C(2)–C(3)	1.346	−2.60	N(6)–N	1.40	−2.39
C(3)–C(4)	1.435	−2.30	N(6)–C	1.395	−2.48
C(1)–C(6)	1.343	−2.70	Ar–C	1.395	−2.39
C(1)–N(6)	1.26	−2.80	Ar–N	1.38	−2.75
C(6)–C	1.395	−2.33	Ar–O	1.36	−2.60

[a] Bond distance estimated from related compounds of known geometry. [b] From the values given by the Nishimoto–Forster relationships [4] modified slightly to give the best empirical fit with experimental data.

VSIP and γ_{rs} integrals. The $VSIP_r$ and A_r values for each atom were treated as two independently variable parameters, and it can be seen that variation of these has a fairly complex effect on the calculations. Trial-and-error calculations enabled the best values for these parameters to be determined, by using the predicted absorption maxima as criteria. The parameters are summarised in Table 3. The final modified values were

TABLE 3

One-centre parameters used in PPP calculations

Group	Atom	Z [a]	VSIP [b,c]	A [b,d]
CH,CC,CN	C	1	11.16 [e]	0.03 [e]
CCl	C	1	12.0	2.0
C=N–	Ṅ	1	14.12 [e]	1.78 [e]
C₄Cl₄C=N–	Ṅ	1	15.0	5.50
C=C–NH₂	N̈	2	21.0	9.26
C=N–NH₂	N̈	2	21.0	9.26
C=C–NMe₂	N̈	2	16.0	9.26
C=N–NMe₂	N̈	2	16.0	9.26
Ar–NMe₂	N̈	2	12.0	9.26
Ar–OH	Ö	2	32.9 [f]	11.43 [f]

[a] Number of π electrons contributed by the atom. [b] Unless otherwise stated, parameters have been determined empirically for the fulvene derivatives of Table 1. [c] Valence state ionisation potential (eV). [d] Electron affinity (eV). [e] J. Hinze and H. H. Jaffé, *J. Amer. Chem. Soc.*, 1962, **84**, 540. [f] See ref. 4.

qualitatively acceptable, and took into account in the correct manner the effect of inductive substituents attached to the atom concerned. Further modification of the 6-nitrogen parameters were found to be necessary for the tetrachlorofulvene series, and the dimethylamino-parameters also required modification when this group was attached to an aromatic ring. Where strong inductive effects were absent, the normal literature values for the relevant atoms were satisfactory.

The chloro-substituents in compounds of general structure (III) should strictly be included in the π-electron framework, each halogen atom donating two electrons to the system. However, calculations of this

[3] K. Nishimoto and N. Mataga, *Z. phys. Chem.*, 1957, **12**, 335.

type involved an additional increase in the number of parameters, and the results were generally unsatisfactory. Thus the effect of the halogen atom was assumed to be principally inductive, and the carbon parameters were modified appropriately; otherwise the halogen atoms were ignored.

The β_{rs}^{core} integrals were evaluated empirically, but in the event corresponded closely to the values calculated from the data of Nishimoto and Forster [4] for benzene derivatives, on the assumption of a linear relationship between bond order and β_{rs}^{core}. The values used throughout these calculations are given in Table 2. In general, the choice of the correct two-centre core integral was not as critical as in the case of the VSIP$_r$ and A_r parameters.

The one-electron orbital energies were calculated after the required degree of self-consistency was reached, and the electron densities and bond orders were determined from the eigenvectors. Transition energies were calculated after configuration interaction between the first nine singly excited singlet configurations. In general, the inclusion of configuration interaction had a small effect on the first transition, but a more significant effect on higher energy transitions. Oscillator strengths and polarisation directions were calculated after configuration interaction.

The theoretical absorption wavelengths and intensities are compared with the experimental values in Table 1: the agreement is remarkably good for the twenty compounds studied. As is usual, the calculated intensities are generally larger than the observed values, but the relative values are satisfactory. The PPP method, involving use of a frankly empirical approach, is evidently of considerable predictive value in the series studied. The general applicability of some of the parameters used was illustrated by calculation of the spectrum of the cyclopentabenzoxazine (VII): good agreement between theory and experiment was observed.[5] This system shows no spectral similarities to the azafulvenes and fulvenes.

(VII)
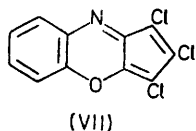
Comparison of Experimental Results with Theoretical Predictions.—Fulvene (IIa), the parent of the compounds studied, shows two principal absorption bands in cyclohexane at 362 (log ε 2.33) and 242 nm (4.1).[6] Straub et al.[7] have shown that the effect of 6-substituents cannot be explained by simple HMO theory if all bond lengths are assumed equal, although Weiss and Murrell [8] found that this inadequacy could be corrected by introducing a reasonable degree of bond alternation into the fulvene structure. In this way, the latter workers were able to account satisfactorily for the spectra of a number

of 6-substituted fulvenes within the HMO procedure. Their calculations suggested that the highly allowed transition of fulvene corresponded to a build-up of electron density at positions 2 and 5, with a small decrease at position 6. This contrasted with the results of Straub et al., who found a large increase in electron density at the 6-position. The general bathochromic effect of electron-donor 6-substitutents was more in qualitative agreement with the conclusions of Weiss and Murrell.

It was of interest to compare the results of a PPP calculation on fulvene, using bond lengths and bond angles determined experimentally for 6,6-dimethylfulvene,[9] with the results of the latter authors. Weiss and Murrell used an empirical approach to the problem of bond fixation. In our calculations, the two-centre core integrals, β_{rs}^{core}, were calculated from the bond length relationships of Nishimoto and Forster,[4] and the normally accepted VSIP parameters for all carbon atoms were used (Table 3). The predicted transition wavelengths, after a configuration interaction treatment over all singly excited states, (λ_{max} 241 and 379 nm) compared very favourably with the experiment values, as did the relative band intensities (Table 1). The two bands were due to transitions approximated by electron excitation between orbitals 2 ⟶ 4 and orbitals 3 ⟶ 4, respectively. The predicted electron density changes, before configuration interaction, are shown in Figure 1.

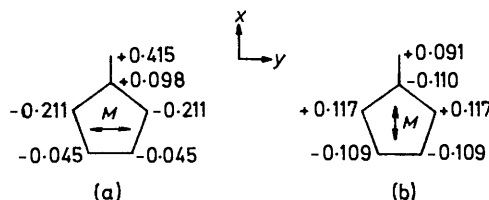FIGURE 1 π-Electron density changes and transition moment directions for (a) the 3 ⟶ 4 (362 nm), and (b) the 2 ⟶ 4 (242 nm) transitions of fulvene; a positive sign indicates an increase, and a negative sign a decrease, in electron density

The general electron redistribution pattern for the 2 ⟶ 4 transition resembles that predicted by Weiss and Murrell,[8] and within the ring there is a general depletion of electron density at positions 1,3, and 4, and a build-up of electron density at positions 2 and 5. However, whereas Weiss and Murrell found a small degree of electron migration from position 6, we find a small, though significant, migration of electron density to this position. There appears to be little point in predicting structural effects from the electron redistribution patterns, since the attachment of a mesomeric electron-donor substituent to position 6 of fulvene produces a completely different orbital picture.

The yellow colour of fulvene is due to tailing of the weak absorption band into the visible region of the spectrum. Electron-donor-substituted derivatives [e.g. 6-dimethylaminofulvene (IIc)] are generally more

[4] K. Nishimoto and L. S. Forster, *Theor. Chim. Acta*, 1966, **4**, 155.

[5] J. Griffiths and M. Lockwood, *Chem. and Ind.*, 1974, 379.

[6] D. Meuche, M. Neuenschwander, H. Schaltegger, and H. U. Schlunegger, *Helv. Chim. Acta*, 1964, **47**, 1211.

[7] P. A. Straub, D. Meuche, and E. Heilbronner, *Helv. Chim. Acta*, 1966, **49**, 517.

[8] R. Weiss and J. N. Murrell, *Tetrahedron*, 1970, **26**, 1131.

[9] N. Norman and B. Post, *Acta Cryst.*, 1961, **14**, 503.

intensely coloured, but this is due more to the bathochromic shift of the intense band than to any alteration of the weak band, and in most cases the latter is completely obscured by the former. Thus (IIc) shows a single band at 316 nm (log ε 4.49) in hexane. In the majority of cases, our attention will be directed towards the highly allowed transition. The computed absorption data for (IIc) show the intense and weak bands at 312 and 336 nm, respectively, and their greatly reduced separation relative to fulvene suggests that overlap will occur, as observed experimentally. The electron-density changes in the excited state for the 312 nm band are typical for fulvenes and azafulvenes with mesomeric electron-donating groups attached to the 6-position, and these changes are shown in Figure 2 for (IIc). The transition may be described reasonably well as a one-electron excitation from orbital 4 to orbital 5, and is polarised along an axis roughly parallel to the 2,3-bond (Figure 2). There is a significant migration of electron density from the donor nitrogen atom into the ring, at positions 2 and 5, and thus there is some justification for the resonance picture of the absorption process [cf. (Ia) ◄─► (Ib)]. However, there is an even greater build-up of negative charge at position 6, which suggests that an electronegative atom at this point would give a bathochromic shift of the band. In agreement with this the 6-azafulvenes (IIe and f) absorb at longer wavelengths than their fulvene counterparts. The general direction of charge transfer in all these compounds indicates that the excited state should have a higher dipole moment than the ground state, and thus a positive solvatochromism should be observed. This is found experimentally; for example the absorption band of (IIc) at 316 nm in hexane is displaced to 322 nm in methanol.[10]

One would expect tetrachloro-substitution, as in (IIIe), to lead to a net bathochromic shift of the principal band. A bathochromic shift is in fact observed, from $\lambda_{max.}$ 327 to 361 nm in hexane, for tetrachloro-substitution of (IIf). The calculated maximum for (IIIe) is 372 nm. The electron migration pattern and polarisation direction found for (IIIe) resemble those calculated for (IIf).

Large bathochromic shifts are to be expected for 6-arylfulvenes, where the phenyl ring contains a mesomeric electron-donor group in the *para*-position, *e.g.* (IId). The increased conjugation should generally lower the energy of the π* orbitals, and the charge-transfer transition should move to longer wavelengths. This was found experimentally for several derivatives: for example 6-(*p*-dimethylaminophenyl)fulvene (IId) absorbed at 390 nm in n-heptane, whereas (IIc) absorbed at 316 nm in n-hexane. The calculated value for (IId) was in close agreement with experiment (395 nm). The charge migration pattern (Figure 3) showed the expected transfer of electron density from the NMe₂ group into the five-membered ring, but unlike the situation in Figure 2, carbon atoms 1—5 all show an increase in electron density. This suggests that tetrachloro-substitution should

¹⁰ K. Hafner, K. H. Hafner, C. König, M. Kreuder, G. Ploss, G. Schulz, E. Sturm, and K. H. Vopel, *Angew. Chem.*, 1963, **75**, 35.

lead to larger shifts in the 6-aryl series of fulvenes and azafulvenes in comparison with those compounds with the donor substituent directly attached to position 6. The bathochromic shift accompanying tetrachloro-substitution of (IId) is *ca.* 500 cm⁻¹ greater than for similar substitution of (IIc).
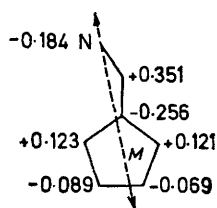

FIGURE 2   π-Electron density changes and transition moment direction for the long wavelength absorption band of 6-dimethylaminofulvene (IIc)
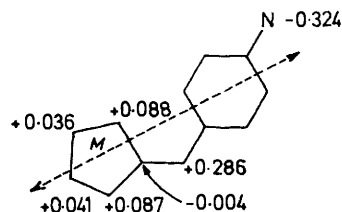

FIGURE 3   π-Electron density changes and transition moment direction for the long wavelength band of 6-(*p*-dimethylaminophenyl)fulvene (IId)

MO Calculations concerning the effect of 6-aza-substitution on 6-(*p*-dimethylaminophenyl)tetrachlorofulvene (IIIc) were particularly interesting, and predicted an unusually large bathochromic shift of *ca.* 140 nm (5 200 cm⁻¹). A large shift was observed experimentally, and the aza-derivative (IIIh) was blue in colour, in contrast to the red compound (IIIc). The calculated maximum at 590 nm (experimental value 575 nm) correctly predicted a blue colour for (IIIh). The *p*-hydroxyphenyl derivatives in the tetrachloro-series showed the expected hypsochromic shifts relative to the dimethylamino-analogues, the fulvene (IIIb) absorbing at 370 and the azafulvene (IIIg) at 483 nm. Again aza-substitution produced a dramatic red shift, which was well accounted for theoretically (Table 1). The hydroxy-compounds were soluble in alkali, giving deeply coloured solutions of the anions absorbing at even longer wavelengths than the dimethylamino-derivatives.

In the fluorene series (IV), two effects might be considered to operate. In the resonance interpretation, the five-membered ring will lose much of its cyclopentadiene character, and the decrease in electron-acceptor ability should cause a general hypsochromic shift of the charge-transfer band. On the other hand, the additional conjugation from the annelated benzene rings should lead to bathochromic displacements. From the only pair of compounds suitable for comparison, *i.e.* (IId and IVc), it appears that these two effects are roughly comparable, as there is little difference between the absorption maxima of these compounds (390 and 398 nm, respectively). Despite the large increase in molecular size, the PPP method gave an excellent prediction of this effect,

indicating a theoretical value of 390 nm for (IVc). The fluorene derivatives (IVa—c) showed a second absorption band of similar intensity to the long-wavelength band, in the region 250—290 nm. This was also predicted well by theory. As in the simpler series (II) and (III), the long-wavelength band of the fluorene derivatives was essentially of the charge-transfer type.

All the derivatives considered so far would be expected to have reasonably planar structures, and this accounts, at least in part, for the considerable success of the PPP calculations. However, the derivative (VI) will certainly not be planar, and could adopt various conformations depending on the correct formulation of the ground state. For example, if charge transfer to the five-membered ring were complete, as in (VIII), the cyclopentadienide anion residue would rotate out of plane, leaving a planar bis-(p-dimethylamino)diphenylmethane system bearing a delocalised positive charge. This would resemble the ferrocene analogue of Malachite Green (IX).[11] On the other hand, the fulvene structure

(VIII) R =

(IX) R = ferrocenyl
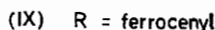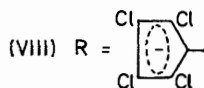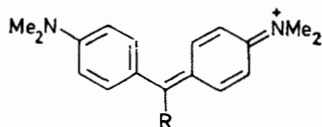
(VI) would require rotation of both phenyl rings out of plane. By analogy with Malachite Green, Michler's Hydrol Blue, and (IX), a structure such as (VIII) should absorb intensely in the region of 600 nm. In fact the compound absorbs at 490 nm in ethanol, and is thus best represented by (VI). If steric factors were sufficiently dominant, the resonance formulations (VI) and (VIII) could correspond to a true chemical equilibrium, each conformer corresponding to a different resonance form. This phenomenon has been observed previously in systems closely related to (VIII), and has been termed allopolar isomerism.[12] Since the two resonance formulations should have different light absorption properties, this effect is characterised by two absorption maxima which are both solvent- and temperature-dependent. The fulvene (VI) however showed no properties of this type, although in cyclohexane the broad visible band did appear as two peaks of similar intensity (452 and 478 nm). The ^{1}H n.m.r. spectrum (CDCl$_3$) showed no splitting of the NMe$_2$ signal. The MO calculations based on a planar fulvene structure predicted two transitions of similar intensity, at 425 and 430 nm, polarised perpendicularly to each other. The absence of allopolar isomerism in the case of (VI) could be attributed to the low tendency of the five-membered ring to form the tetra-chlorocyclopentadienide anion unit.

[11] C. C. Barker, G. Hallas, and M. N. Thornber, *J. Chem. Soc.*, 1965, 5759.

The successful application of the parameters in Tables 2 and 3 to the PPP calculations for the fulvenes suggests that these parameters might be useful in other systems. Calculations of the spectra of other non-benzenoid chromogens are being examined in this context.

EXPERIMENTAL

U.v. and visible spectra were recorded with a Unicam SP 800 spectrophotometer and n.m.r. spectra were determined at 100 MHz. M.p.s are corrected.

2,3,4,5-Tetrachloro-6-(p-dimethylaminophenyl)-6-azafulvene (IIIh).—*Method* 1. To a mixture of 1,2,3,4-tetrachloro-cyclopentadiene (1.02 g, 5 mmol) and *NN*-dimethyl-*p*-nitrosoaniline (0.75 g, 5 mmol) in ethanol (25 ml) was added 1,4-diazabicyclo[2.2.2]octane (0.56 g, 5 mmol) over 30 min. The mixture was stirred at room temperature for 2 h and the deep blue solution evaporated to dryness under reduced pressure. The residue was dissolved in a small volume of benzene and chromatographed over silica gel, with benzene as eluant. The first blue fraction afforded (IIIh) in 36% yield as a dark blue solid, m.p. 118—119° (Found: C, 46.6; H, 3.0; Cl, 41.95; N, 8.5. C$_{13}$H$_{10}$Cl$_4$N$_2$ requires C, 46.5; H, 7.0; Cl, 42.2; N, 8.35%); τ (CDCl$_3$) 6.96 (6 H, s), 2.88 (2 H, d, *J* 4.5 Hz), and 3.32 (2 H, d, *J* 4.5 Hz).

Method 2. To a stirred solution of hexachlorocyclo-pentadiene (1.37 g, 5 mmol) and *p*-dimethylaminoaniline dihydrochloride (1.04 g, 5 mmol) in a mixture of water (5 ml) and ethanol (45 ml) was added a solution of sodium hydroxide (0.4 g, 10 mmol) and 1,4-diazabicyclo[2.2.2]octane (1.12 g, 10 mmol) in water (25 ml) dropwise over 30 min. The mixture was stirred for a further 2 h, more water was added, and the solution was extracted with methylene chloride. Chromatographic separation of the dried concentrated extracts as in method 1 afforded (IIIh) in 80% yield.

Method 3. A suspension of silver chloride was prepared by adding a solution of silver nitrate (7.5 g, 44 mmol) in water (40 ml) to a well stirred solution containing sodium chloride (2.92 g, 50 mmol) and gelatin (0.06 g) in water (40 ml). To this suspension was added sodium carbonate (4.0 g) in water (20 ml), followed by a solution of tetrachloro-cyclopentadiene (1.02 g, 5 mmol) in ethanol (20 ml). After thorough mixing, a solution of *p*-dimethylaminoaniline dihydrochloride (1.35 g, 6.4 mmol) in water (40 ml) was added in one portion. The mixture was stirred for 30 min at room temperature. An equal volume of methylene chloride was added, and the organic layer was isolated. Chromatographic separation of the concentrated extracts as in method 1 afforded (IIIh) in 25% yield.

2,3,4,5-Tetrachloro-6-(p-hydroxyphenyl)-6-azafulvene (IIIg).—A solution of hexachlorocyclopentadiene (1.37 g, 5 mmol) in absolute ethanol (25 ml) and a solution of sodium ethoxide (0.68 g, 10 mmol) in the same solvent (25 ml) were added simultaneously over 15 min to a stirred solution of *p*-aminophenol (0.54 g, 5 mmol) in absolute ethanol (25 ml). An immediate blue colour was formed, and after 5 h stirring at room temperature the colour was deep red. After removal of the solvent under reduced pressure, the product was isolated in 14% yield as red *crystals* (decomp. 220°) by chromatography over silica gel (Found: C, 42.7; H, 1.75; N, 4.45. C$_{11}$H$_5$Cl$_4$NO requires C, 42.75; H, 1.6; N, 4.55%).

[12] L. G. S. Brooker, *J. Photographic Sci.*, 1953, 83; S. Hunig, H. Schweeburg, and H. Schwarz, *Annalen*, 1954, **587**, 132; S. Hunig and H. Schwarz, *ibid.*, 1956, **599**, 131.

2,3,4,5-*Tetrachloro*-6,6-*bis*-(p-*dimethylaminophenyl*)*fulvene* (VI).—A solution of Michler's ketone (1.34 g, 5 mmol) and phosphoryl chloride (1.15 g, 7.5 mmol) in dry benzene (40 ml) was heated under reflux for 30 min. Tetrachlorocyclopentadiene (1.02 g, 5 mmol) was added and refluxing continued for 15 min. The resultant deep red solution was washed with dilute sodium hydroxide solution, followed by water, dried (MgSO$_4$), concentrated, and chromatographed over silica gel in benzene. The main red fraction afforded (VI) in 50% yield, as red *crystals* (decomp 200°) (Found: C, 58.4; H, 4.55; Cl, 31.05; N, 6.4. C$_{22}$H$_{20}$Cl$_4$N$_2$ requires C, 58.15; H, 4.4; Cl, 31.2; N, 6.2%); τ (CDCl$_3$) 6.92 (12 H, s), 2.8 (4 H, d, *J* 4.5 Hz), and 3.35 (4 H, d, *J* 4.5 Hz).

Condensation of Fluorenone with Arylamines.—Fluorenone (5 mmol), the amine (10 mmol), and anhydrous zinc chloride (0.15 g) were heated for 30 min at 170 °C in a flask fitted with an air condenser. The residue was digested with water and extracted into methylene chloride. Chromatography of the concentrated extracts over silica gel in benzene gave the requisite azafulvene derivative; yields (m.p.): (IVd), 76% (82—83°); (IVe), 67% (192—193°); (IVf), 47% (100—101°).