Ultra-violet Absorption Spectra of 9-Substituted Fluorenes.

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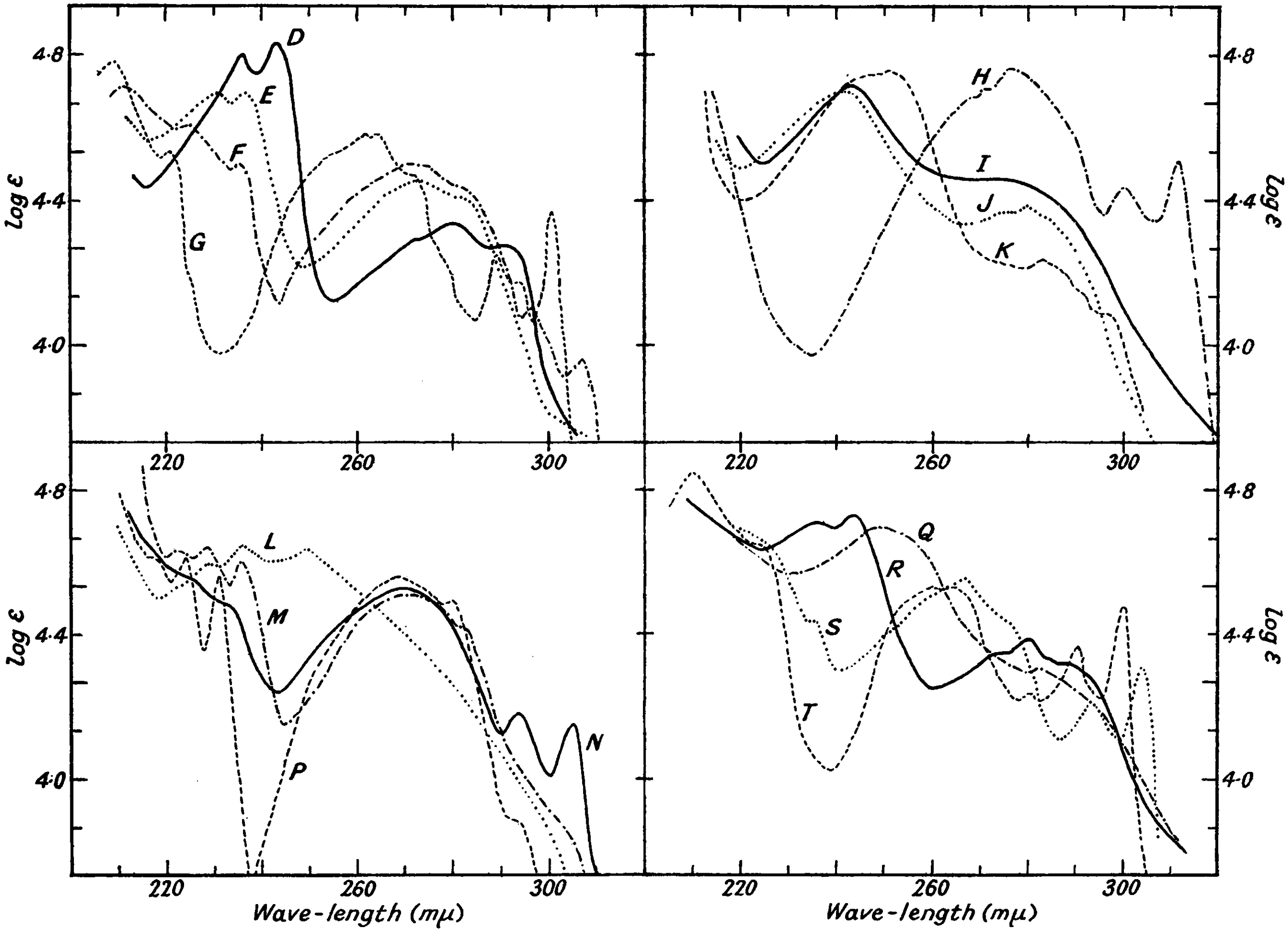
Some electronegative substituents in the 9-position of fluorene cause significant changes in the ultra-violet absorption spectrum.

DATA previously available in the literature seemed to indicate that simple substituents attached by a single bond at the 9-position of fluorene cause little change in the ultra-violet absorption, and thus Miller and Wagner (*J. Org. Chem.*, 1951, **16**, 279) conclude: "it appears that simple substituents in position-9 of fluorene, and the presence of an α,β-double bond, do not greatly alter the absorption of the fluorene system." Results now presented show that some electronegative substituents in the 9-position cause marked changes in the absorption spectrum.

If the three absorption regions in the fluorene system (200—225, 245—275, and 285—305 mμ) are designated A, B, and C bands, respectively (cf. Clemo and Felton, *J.*, 1952, 1658) it will be seen from the figures that a chlorine atom in the 9-position moves the A and B bands by *ca.* 12 mμ towards the visible, flattens the B band, and eliminates the C band. Bromine produces a bathochromic shift of *ca.* 25 mμ (in this case the two maxima of the A band have merged), and the intensity of the B band is further depressed. The shift is even greater for iodine, and the B band becomes only a plateau (partly because of broadening of the A band). Introduction of a second chlorine or bromine atom in the 9-position causes further changes of the same kind, and halogens have a similar effect when they replace



D, 9 : 9-Dichlorofluorene; *E*, 9-chlorofluorene; *F*, 9-ethoxyfluorene; *G*, fluorene; *H*, 2 : 7-dibromofluorene (in EtOH); *I*, 9-iodofluorene; *J*, 9-bromofluorene; *K*, 9 : 9-dibromofluorene; *L*, 9-bromo-9-nitrofluorene; *M*, 9-azidofluorene (in EtOH); *N*, 9-aminofluorene (in EtOH); *P*, 9-aminofluorene (in acidified ethanol); *Q*, 9-bromo-9-phenylfluorene; *R*, 9-chloro-9-phenylfluorene; *S*, 9-phenylfluorene; *T*, 9-trimethylsilylfluorene.

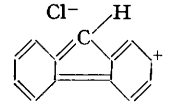
hydrogen in the 9-positions of 9-trimethylsilyl- and 9-phenyl-fluorene and of di-9-fluorenyldimethylsilane. Related, but smaller, changes were noticed when halogen replaced hydrogen in what was believed to be the quaternary carbon position of 9-phenyl-1 : 2-3 : 4-7 : 8-tribenzofluorene (R. N. Jones, *J. Amer. Chem. Soc.*, 1945, **67**, 2025). The changes in spectrum produced by one or two halogen atoms in the 9-position are markedly greater than those produced by halogens in the most sensitive aromatic positions of fluorene, where they cause small bathochromic shifts with very little change in shape of the absorption curve.

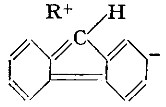
Other electronegative substituents in the 9-position cause similar changes in the absorption spectrum of fluorene, and the order of effectiveness of single substituents in causing bathochromic shifts, accompanied by flattening of the B band and suppression of the C band, is $H < NH_2,OEt < N_3,Cl < Br < I$. The most marked change in shape of the curve is found with 9-bromo-9-nitrofluorene, in which the B band appears to have been submerged and the C band eliminated.

There are distinct differences between the absorption curves of 9-aminofluorene in neutral and acidified ethanol, respectively, and the absorption of the ammonium-ion compound is somewhat similar to that of 9-azido- and 9-chloro-fluorene. Since the positive nitrogen atom does not have a greater effect than the halogens on the absorption, electron-withdrawal by an inductive mechanism seems not to be a major factor in the influence of 9-substituents on the spectrum of fluorene.

Detailed explanation of the spectral changes described must await assignment of the bands of the fluorene spectrum, but we suggest that the effects may originate in negative hyperconjugation (cf. Hughes, Ingold, and de la Mare, *J.*, 1948, 17; Braude and Coles, *J.*, 1951, 2085; Armitage and Whiting, *J.*, 1952, 2005), involving contributions to an excited state of structures such as (I). Resonance stabilisation of the excited state relative to the ground state would account for the bathochromic shifts. and the polarizability of the C–X bonds would explain the order of effectiveness of various groups X given above. In agreement with this, trimethylsilyl, methyl, and phenyl groups in the 9-position cause slight bathochromic shifts below 250 mμ, but little change in the position and shape of the B and C bands. In these cases hyperconjugation would presumably lead to structures of type (II) ($R = Me_3Si$, Me, or Ph) similar to those expected to contribute to the structure of fluorene itself ($R = H$).

(I)



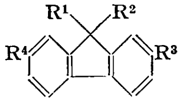


(II)

In view of the ease with which halogen may be introduced into the 9-position of fluorene and analogous positions of more complex compounds, the spectral effects described could help in determinations of structure.

EXPERIMENTAL

Materials.—The following fluorene derivatives were prepared by established methods: 9-bromo-, m. p. 104·5° (from acetone) (Wittig and Felletschin, *Annalen*, 1944, **555**, 133); 9-iodo- (from light petroleum), m. p. (rapid heating) 107—108°, with decomp. at 125° (Wanscheidt, *Ber.*, 1926, **59**, 2092); 9-chloro-, m. p. 91·5° (from glacial acetic acid containing hydrochloric acid) (Staudinger, *Ber.*, 1906, **39**, 3060); 9-azido-, m. p. 44° (from aqueous ethanol) [Arcus and Mesley's method (*J.*, 1953, 178) was modified by using 9-bromo- in place of 9-chloro-fluorene and boiling for 2 hr.]; 9-amino-, m. p. 62° (from light petroleum) (Ingold and Wilson, *J.*, 1933, 1493); 9 : 9-dibromo-, m. p. 118° (from *cyclo*hexane) [Wittig and Vidal's method (*Chem. Ber.*, 1948, **81**, 368) was modified by illumination with a 150-w lamp during reflux for 6 hr.]; 9-bromo-9-phenyl-, m. p. 99° (from light petroleum) (Buu-Hoï, *Annalen*, 1944, **556**, 1); 9-chloro-9-phenyl-, m. p. 78° (from light petroleum) (Staudinger, *loc. cit.*); 9 : 9-dichloro-, m. p. 103° (from ether) (Schmidt and Wagner, *Ber.*, 1910, **43**, 1796); 9-bromo-2-nitro-, m. p. 143·5° (from ethanol) (Anantakrishman and Hughes, *J.*, 1935, 1607); 9-bromo-9-nitro-, m. p. 108° (decomp.) (from ethanol) (Wislicenus and Waldmüller, *Ber.*, 1908, **41**, 3334); 2-nitro-, m. p. 156° (from ethanol) ("Org. Syntheses," Chapman and Hall, London, Coll. Vol. II, p. 447).



Methods of preparation of other compounds will be described in a separate communication.

Spectra.—Solutions in *n*-hexane or (where indicated) 95% ethanol were examined with a Unicam S.P. 500 Spectrophotometer, usually not below 215 mμ.

Absorption data tabulated refer to fluorene derivatives not included in the diagrams. The letter under "Shape" indicates which curve in the diagram the absorption resembles.

R^1	R^2	R^3	R^4	$\lambda_{max.}$ (mμ) with log ε in parentheses					Shape
[a] Me_3Si	Me_3Si	H	H	255 * (4·10)	264 (4·19)	291·5 (4·04)	300 (4·02)	—	*T*
Me	Me_3Si	H	H	262 (4·16)	267 (4·18)	290·5 (3·95)	301 (4·07)	—	*T*
OEt	Me_3Si	H	H	213·5 (4·26)	273 (4·14)	282 * (4·01)	293·5 (3·81)	305 (3·82)	*F*
[b] Br	Me_3Si	H	H	245 (4·40)	279 (4·00)	—	—	—	*J*
Cl	Me_3Si	H	H	223 * (4·41)	232 (4·40)	238·5 (4·39)	275 (4·08)	284 * (4·02)	*E*
[ab] H	Me_3Si	Br	H	270·5 (4·32)	289 * (3·96)	294 (4·04)	299·5 (4·05)	305·5 (4·11)	*H*
[a] H	Me_3Si	Br	Br	272 * (4·39)	276 (4·42)	299·5 (4·17)	302 * (4·14)	311 (4·35)	*H*
[b] H	H	Br	H	270 (4·39)	295 (3·90)	298 * (3·88)	306 (3·98)	—	*H*
[c] —	—	—	—	227 * (4·69)	261 (4·49)	265·5 (4·49)	278 (4·09)	290 (4·24)	*T*
[d] —	—	—	—	245·5 (4·60)	280 * (4·14)	—	—	—	*J*
H	H	NO_2	H	233 (4·00)	331 (4·26)	—	—	—	—
Br	H	NO_2	H	225 (4·35)	256 (4·01)	263·5 * (3·95)	268 (3·96)	322 (4·23)	—
[b] Br	H	NO_2	H	225·5 (4·30)	271 * (3·81)	274 * (3·82)	330 (4·19)	—	—
Br	Me_3Si	NO_2	H	229 (4·23)	262·5 (3·94)	316 * (4·19)	326·5 (4·23)	—	—
[b] H	H	NO_2	NO_2	~247 (3·90)	331 (4·43)	—	—	—	—

* Inflexion. [a] Not studied below 230 mμ. [b] In ethanol. [c] Di-(9-bromo-9-fluorenyl)dimethylsilane; there is also a band at 300 mμ (log ε 4·39). [d] Di-9-fluorenyldimethylsilane.

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