405. *Studies in Light Absorption. Part VIII. Dibenzyl and Stilbene Derivatives. Interaction between Unconjugated Chromophores.*

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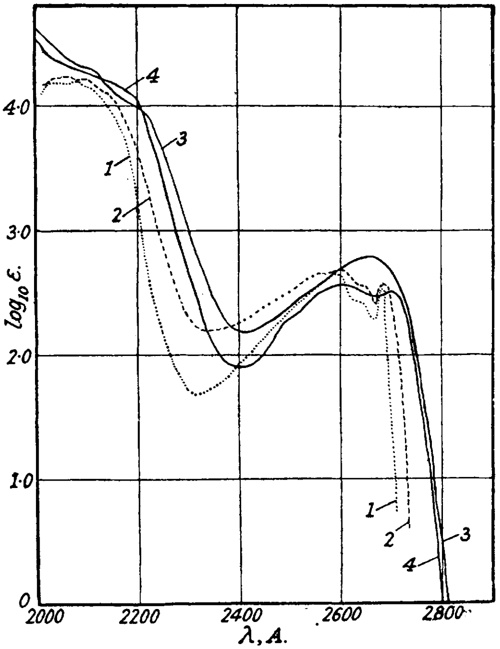
Existing and new spectral evidence for electronic interaction between unconjugated chromophores is reviewed. Examples of interaction in systems of the type $X{\cdot}CH_2{\cdot}Y$ are provided by, *inter alia*, diphenylmethane, 1 : 4-diphenylbut-2-ene, and fluorene. Examples of interaction in systems of the type $X{\cdot}CH_2{\cdot}CH_2{\cdot}Y$ are provided by, *inter alia*, dibenzyl and 9 : 10-dihydrophenanthrene, and by substituted dibenzyls of the type $C_6H_4R'{\cdot}CHR{\cdot}CHR{\cdot}C_6H_4R'$ (R = alkyl and R′ = OH, OMe, or O·CO·Alkyl) the absorption of which differs significantly from that corresponding to a summation of the two $C_6H_4R'{\cdot}CHR$ chromophores. In substituted stilbenes of the type $C_6H_4R'{\cdot}CR{:}CR{\cdot}C_6H_4R'$, electronic interaction between the aryl groups and the ethylenic linkage is largely inhibited by steric interference between the former and the alkyl substituents R, and the absorption is similar to that of the corresponding dibenzyls.

As a result of the interest which attaches to their œstrogenic properties, a wide range of substituted dibenzyl and stilbene derivatives has been prepared within recent years (Dodds, Lawson, Robinson, *et al.*, *Proc. Roy. Soc.*, 1939, *B*, **127**, 140; 1944, *B*, **132**, 83; for summaries see Jones, *Ann. Reports*, 1943, **40**, 137; Solmssen, *Chem. Reviews*, 1945, **37**, 481). The present work was originally undertaken in the hope that ultra-violet-light absorption might prove as valuable a criterion of chemical structure in this as in other fields. It soon became apparent, however, that the relation between structure and spectral properties in this series is one of considerable complexity and presents several features of fundamental interest. The results are now presented from this latter point of view.

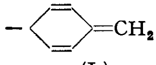
One of the basic principles which has long been accepted in the empirical interpretation of ultra-violet-light absorption is that the absorption due to isolated chromophores is additive, *i.e.*, that the interaction between the unsaturation electrons of groups separated by one or more saturated *carbon* atoms is too weak to affect the spectral properties. This does not, of course, apply to chromophores separated by atoms such as nitrogen, oxygen, or sulphur, which have a definite transmitting (" chromolatory ") effect ascribed to their non-bonded valency electrons (cf. Part III, *J.*, 1946, 948). The experimental evidence on which the principle of complete lack of chromolatory properties of carbon is based is not particularly extensive. Few accurate data are available for systems of the type $X\cdot[CH_2]_n\cdot Y$, where X and Y are single chromophores such as $-C{=}C-$, $-C{\equiv}C-$, $-C{=}O$ and $-CO_2H$, because the characteristic high-intensity absorption of these groups lies in the less readily accessible region below 2000 A. Among the few available examples of this type are diallyl, *cyclo*hexane-1 : 4-dione, and succinic acid which show ultra-violet absorptions corresponding very nearly to that of two propylene, acetone, and acetic acid molecules, respectively (for data and references, see Braude, *Ann. Reports*, 1945, **42**, 105). It will be noted that in all these examples the number (*n*) of methylene groups separating X and Y is two. Most of the studies on the interaction of isolated chromophores, however, relate to systems where X = Ph, as in the work of Ramart-Lucas and her co-workers (*Ann. Chim.*, 1931, **16**, 276; 1932, **17**, 207; **18**, 32; *Bull. Soc. chim.*, 1932, **51**, 965; 1943, **10**, 13; Grignard, " Traité de Chimie Organique," 1936, Vol. II, p. 59) and of Hillmer and Paersch (*Z. physikal. Chem.*, 1932, **161**, 46). These measurements extend only over the region of about 2300 to 3500 A. and therefore refer only to the low-intensity band (subsequently referred to as *B*-band) of the phenyl chromophore near 2600 A. Ramart-Lucas formulated the rule that, in compounds of the type $Ph\cdot[CH_2]_n\cdot Y$, when *n* is 2 or greater, the absorption is practically indistinguishable from that of an equimolar mixture of PhEt and EtY, but that, when *n* is 1, the intensities of absorption are somewhat enhanced, though the wave-length of the band remains unchanged. The deviation from additivity exhibited by derivatives $Ph\cdot CH_2\cdot Y$ depends on the nature of Y and seems to increase in the order $CN < CH{:}CH_2 < CO_2H < CO\cdot NH_2 < CO < I$, which is roughly the expected order of increasing polarisibility. For Y = CN or $CH{:}CH_2$, the deviations in the neighbourhood of the 2600 A. band are very small, and on extending the measurements on allylbenzene to 2000 A. we find that the same applies to the high-intensity band (subsequently referred to as *E* band) near 2100 A., which is practically identical with that of ethylbenzene (see fig.). For Y = CO or I, on the other hand, the deviations are considerable and the shape of the absorption curve is unmistakably altered (Ramart-Lucas *et al.*, *loc. cit.*; Hillmer and Paersch, *loc. cit.*).

Diphenylmethane and Related Systems of the Type $X\cdot CH_2\cdot Y$.—With diphenylmethane (X = Y = Ph), the absorption in the 2600 A. region exceeds only slightly that of an ethylbenzene solution of twice the molar concentration, and the deviation from additivity is only of the same order as in allylbenzene. Accurate measurements extending to 2000 A. (Ley and Specker, *Z. wiss. Photographie*, 1939, **38**, 13) show, however, that in this case there is considerable deviation from additivity in the short-wave-length region (see fig.). Not only are the intensities much increased, but a pronounced inflection, indicating a band partly submerged in the general absorption and not shown by the alkylbenzenes. appears near 2200 A. (In assessing the extent of deviations from additivity, it should be noted that, in the figure, extinction has been plotted on the usual logarithmic scale and that a difference of 0·3 in the ordinates corresponds to a two-fold change in ε.)

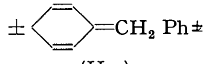
In assessing the significance of relatively small changes in absorption, two complicating factors must be borne in mind. First, absorption curves of solutions represent band envelopes in which the discrete vibrational structure has been largely obliterated by solute–solvent interaction, and the latter will be sensitive to any structural alteration in the molecule. However, the absorption of compounds of the type now considered is not very susceptible to solvent conditions (thus the data for ethanol and hexane solutions are very similar) and any solvation effects due to unconjugated substituents will therefore account only for very small deviations from additivity. Secondly, a substituent may give rise to a change in vibrational levels and hence in the shape of the band envelope of the electronic transition merely by virtue of its weighting effect. However, data for a series of alkylbenzenes (Platt and Klevens, *Chem. Reviews*, 1947, **41**, 301; *J. Chem. Physics*, 1948, **16**, 832) show that the short-wave-length (*E*) bands are almost identical throughout the series toluene to *tert.*-butylbenzene, and any vibrational effect of substituents in this region is therefore also likely to be very small. The conclusion thus seems inescapable that the considerable deviations from additivity in the ultra-violet-light absorption of certain systems of the type X·CH$_2$·Y, and particularly the additional submerged band at 2200 A. exhibited by diphenylmethane are due to electronic interaction between the phenyl groups. Such interaction must take place either by way of the intervening saturated CH$_2$ group, or else spatially between the phenyl groups belonging to the same or different molecules. Intermolecular interaction is excluded in view of the low concentrations employed in absorption measurements and because the absorption of diphenylmethane is independent of concentration. Intramolecular spatial interaction between the two sets of π electrons also seems unlikely in view of the distance between, and the relative position of, the phenyl groups. It therefore appears probable that interaction takes place by way of the intervening methylene group, a conclusion which can be expressed in terms of contributions from resonance forms such as (II*a*) or (II*b*). The effect is closely akin to hyperconjugation in toluene which involves contributions from resonance forms such as (I) and also has a small, but noticeable, influence on the ultra-violet-light absorption due to the phenyl chromophore, though the *B* band alone is affected in this case (Matsen, Robertson, and Chuoke, *Chem. Reviews*, 1947, **41**, 273; Platt and Klevens, *locc. cit.*; Bowden and Braude, forthcoming paper). The same type of resonance effect is also known from chemical evidence to be operative in benzyl halides (Olivier, *Rec. Trav. chim.*, 1922, **41**, 301, 646; 1923, **42**, 516, 757; Hughes, *Trans. Faraday Soc.*, 1941, **37**, 27) and presumably occurs in benzyl derivatives CH$_2$PhR generally, but the fact that it is revealed also in the ultra-violet-light absorption properties does not appear to have been recognised hitherto, except in the case R = H.* From energy considerations, (II*a*) might be expected to make a greater contribution than (II*b*). However, the fact that diphenylmethane is a stronger " acid " than toluene (Conant and Wheland, *J. Amer. Chem. Soc.*, 1932, **54**, 1212) indicates that the resonance form (II*b*) plays some part. The relative importance of contributions



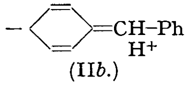
1. *Ethylbenzene* (ϵ × 2).
2. *Allylbenzene* (ϵ × 2).
3. *Diphenylmethane*.
4. *Dibenzyl*.



(I.)



(II*a*.)



(II*b*.)

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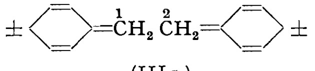
* Since this paper was written, the light absorption of benzyl halides has been discussed in similar terms by Hamner and Matsen, *J. Amer. Chem. Soc.*, 1948, **70**, 2482.

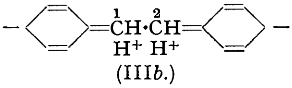
from (II*a*) and (II*b*) to the spectral effect could be tested with 2 : 2-diphenylpropane where resonance forms of the type (II*b*) are excluded, but the relevant data are not at present available.

Some further examples of the interaction of chromophores through a methylene group may be quoted. 1 : 4-Diphenylbut-2-ene exhibits a band at 2200 A., ε 13,000 (Ley and Specker, *loc. cit.*), not found in allylbenzene or toluene. The absorption of fluorene ($\lambda_{max.}$ 2600 and 3000 A., $\varepsilon_{max.}$ 19,000 and 10,000, respectively; Mayneord and Roe, *Proc. Roy. Soc.*, 1937, *A*, **158**, 634) differs significantly from that of diphenyl ($\lambda_{max.}$ 2510 A., ε 17,000). R. N. Jones (*J. Amer. Chem. Soc.*, 1941, **63**, 1658) ascribed the additional 3000 A. band in fluorene and the corresponding 2900 A. band in 9 : 10-dihydrophenanthrene (see below) to the ordinary bathochromic effect of the alkyl substituent, but this suggestion seems hardly tenable in view of the uniformly small effects of alkyl substituents in other aromatic systems. 2 : 2′-Dimethyldiphenyl cannot be used for comparison since it shows abnormal absorption occasioned by restricted rotation, but the absorptions of 3 : 3′- and 4 : 4′-dimethyldiphenyl are very similar to that of diphenyl itself and exhibit only additional *low*-intensity inflexions near 2800 A. (O'Shaughnessy and Rodebush, *J. Amer. Chem. Soc.*, 1940, **62**, 2906). Again, the absorption of *o*-xylene shows only small differences from that of toluene (Conrad-Billroth, *Z. physikal. Chem.*, 1935, **29**, *B*, 170), and the bathochromic effect of alkyl substituents at any positions in 1 : 2-benzanthracene never exceeds 50 A. (Jones, *J. Amer. Chem. Soc.*, 1940, **62**, 148). Thus, the large difference in the absorption of fluorene from that of diphenyl is almost certainly due to interaction through the methylene bridge. Such interaction is of course also indicated by the chemical properties of fluorene, particularly its high methylenic reactivity. Examples of interaction in an isocyclic system are provided by 2 : 5-dihydroacetophenones, data for which have been reported and discussed in Part V of this series (this vol., p. 607). In this case also, interaction is believed to be due largely to enhanced hyperconjugation involving the hydrogen atoms of the methylene group, as in (II*b*).

Dibenzyl and Related Systems of the Type X·CH$_2$·CH$_2$Y.—Turning now to dibenzyl, in which the two phenyl groups are separated by two methylene groups ,we find that only small deviations from additivity occur with the absorption in the 2600 A. region (Ramart-Lucas, *loc. cit.*), but measurements due to Ley and Dirking (*Ber.*, 1934, **67**, 1331) and Ley and Specker (*loc. cit.*) show a new, partly submerged band (subsequently referred to as the *E*′ band) near 2200 A., similar to that exhibited by diphenylmethane. A similar band is also shown by αβ-diethyldibenzyl (3 : 4-diphenylhexane) (Table I). Intramolecular spatial interaction between the π electrons of the two phenyl nuclei is even less likely in dibenzyl than in diphenylmethane in view of the steric configuration of the molecule as determined by *X*-ray analysis (Robertson, *Proc. Roy. Soc.*, 1935, *A*, **150**, 348; Jeffrey, *ibid.*, 1945, *A*, **183**, 388). The planes of the two benzene rings are inclined at an angle of 70° to the central carbon–carbon linkage and the distance between them is nowhere smaller than 4 A. There is no reason to suppose that the configuration of the molecule will be very different in solution, and electronic interaction must therefore again be taking place through the saturated carbon atoms. This is in agreement with Robertson's *X*-ray analysis which indicates a shortening of the Ph–C$_{(1)}$ and C$_{(2)}$–Ph bonds (see III) by 0·07 A. and a lengthening of the central C$_{(1)}$–C$_{(2)}$ bond by 0·04 A., although the latter difference was almost within the limits of experimental error. Such a result could be readily interpreted in terms of small contributions from resonance forms such as (III*a*). The weakening of the central C$_{(1)}$–C$_{(2)}$ bond which it implies is of a type which would increase with the number of phenyl groups and is assumed to be partly responsible for the *ionic* dissociation of hexaphenylethane (cf. Waters, " Chemistry of Free Radicals," Oxford, 1946). The shortening of the Ph–C$_{(1)}$ and Ph–C$_{(2)}$ bonds is confirmed by the more recent analysis of Jeffrey, but, in contrast to the earlier work, a *shortening* of the central C$_{(1)}$–C$_{(2)}$ bond is indicated. In the light of the latter result, the spreading of the π electrons belonging to the phenyl groups over the central carbon chain can no longer be expressed in terms of contributions from resonance forms such as (III*a*). It could be ascribed to less likely structures such as (III*b*) analogous to (II*b*) (cf. Szwarc, Faraday Soc. Discussions, 1947, **2**, 39), but the fact that αβ-diethylbenzyl, in which the likelihood of the incursion of (III*a*)-type hyperconjugation is lessened, exhibits an *E*′ band almost identical with that of dibenzyl, is against such a hypothesis.



(III*a*.)



(III*b*.)

Another interesting example of interaction through two methylene groups is provided by

9 : 10-dihydrophenanthrene. Our data for this compound agree closely with those of Jones (*loc. cit.*). In addition to a band at 2650 A. (ε 17,000) similar to that shown by diphenyl, a further band appears at 2970 A. (ε 4000) almost identical in wave-length with, but less intense than, that found in fluorene. This suggests that interaction is weaker across a $-CH_2{\cdot}CH_2-$ than across a $-CH_2-$ bridge, as might be expected. A further instance of this effect occurs in bisazo-dyes of the type $R{\cdot}N{:}N{\cdot}CH_2{\cdot}N{:}N{\cdot}R$ and $R{\cdot}N{:}N{\cdot}CH_2{\cdot}CH_2{\cdot}N{:}N{\cdot}R$. Piper and Brode (*J. Amer. Chem. Soc.*, 1935, **57**, 135; cf. Lewis and Calvin, *Chem. Reviews*, 1939, **25**, 273) conclude that the absorptions were almost identical with those of two half-molecules $R{\cdot}N{=}N{\cdot}CH_3$, but the curves show considerable deviations from additivity in the short-wave-length region, with maxima near 2500 A. decreasing in intensity on passing from the methylenebisazo- to the ethane-1 : 2-bisazo- and thence to the monoazo-dye. Bateman and Koch (*J.*, 1945, 216) were unable to detect any spectral evidence for interaction in aliphatic compounds containing the system $CR_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CR_2$, but *X*-ray analysis of geranylamine hydrochloride (Jeffrey, *Proc. Roy. Soc.*, 1945, *A*, **183**, 388) indicates that some interaction does occur. It has recently been shown (Barton and Cox, *J.*, 1948, 783) that optical rotation data also provide evidence for the occurrence of interaction through a chain of saturated carbon atoms, and that this effect, like the spectral one, increases with increasing polarisability of the two chromophores.

It will be clear from the above discussion that ultra-violet-light absorption evidence strongly suggests the occurrence of electronic interaction between unconjugated unsaturated groups in systems of the type $X{\cdot}[CH_2]_n{\cdot}Y$, when *n* is 1 or 2, though the mechanism of interaction must still be regarded as unsettled. The fact that allylbenzene exhibits very little deviation from additivity as compared with diphenylmethane, suggests that valency-bond resonance is an important factor.*

TABLE I.*

	E band.		*E′* band.		*B* band.	
	$\lambda_{max.}$, A.	$\varepsilon_{max.} \times 10^{-2}$.	$\lambda_{max.}$, A.	$\varepsilon_{max.} \times 10^{-2}$.	$\lambda_{max.}$, A.	$\varepsilon_{max.} \times 10^{-2}$.
1. $Ph{\cdot}CH_2{\cdot}CH_2Ph$ (52°)	2030	300	*2190*	120	2600	3·6 [1]
2. $Ph{\cdot}CHEt{\cdot}CHEt{\cdot}Ph$ (88°)		†	*2180*	150	2600	3·6 [2]
3. $(p\text{-}HO{\cdot}C_6H_4{\cdot}CHEt)_2$ (188°)		†	2290	215	2800	45 [3]
4. $(p\text{-}MeO{\cdot}C_6H_4CHEt)_2$ (142°)		†	2300	260	2770 2850	30 [4]
5. $(p\text{-}AcO{\cdot}C_6H_4{\cdot}CHEt)_2$ (125°)		†	2220	225	2560	9 [2]
For comparison :						
PhEt	2080	78	—	— ‡	2600	2·2 [2]
$p\text{-}C_6H_4Me{\cdot}OH$	2240	68	—	—	2800	17·4 [2]
$p\text{-}C_6H_4Me{\cdot}OMe$	2240	104	—	—	2800	22 [5]
$p\text{-}C_6H_4Me{\cdot}OAc$	2070	81	—	—	2650	5·4 [2]

* In this and subsequent tables, figures in parentheses refer to m. p.s, and figures in italics to inflexions or " bends."

† Not determined. ‡ $\varepsilon \times 10^{-2}$ at 2190 A. = 13.

[1] Ley and Dirking, *Ber.*, 1934, **67**, 1331; Ley and Specker, *Z. Wiss. Photographie*, 1939, **38**, 13 (in methanol).

[2] This paper. [3] Elvidge, *Quart. J. Pharmacol.*, 1939, **12**, 347; 1940, **13**, 219.

[4] Kharasch and Kleimann, *J. Amer. Chem. Soc.*, 1943, **65**, 11.

[5] Braude, Jones, and Stern, *J.*, 1947, 1087.

Substituted Dibenzyls.—In 4 : 4′-dihydroxy-αβ-diethyldibenzyl (" hexœstrol ") and its dimethyl ether and diacetate (Table I), the interaction of the two benzenoid chromophores is even more pronounced than in the parent hydrocarbon, as shown by comparison of the data with those of *p*-cresol, *p*-tolyl methyl ether and *p*-tolyl acetate. In the tolyl derivatives, the *E* and

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* Since this paper was written, the question of spectral interaction through a $-CH_2{\cdot}CH_2-$ bridge has been examined by Koch (*J.*, 1948, 1111) in the case of dicinnamyl, $CHPh{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CHPh$. The absorption of this compound differs significantly from that corresponding to two molecules of β-methylstyrene, and the deviations are of the same order as in the case of substituted dibenzyls, as would be expected from the above discussion. The hypothesis of electronic interaction is considered by Koch, but rejected in view of the fact that 1 : 6-distyrylhexane(1 : 10-diphenyldeca-1 : 9-diene) also exhibits some, though smaller, deviations from additivity, whereas electronic interaction through a chain of six intervening carbon atoms would be expected to be negligibly small. It seems possible that the abnormal absorption of 1 : 6-distyrylhexane is due to a steric approach of the two styryl groups situated at the overlapping ends of the coiled hydrocarbon chain. Several examples of such effects have been given by Ramart-Lucas (*loc. cit.*; cf. Fulton and Lee, *J.*, 1930, 1057). Further experimental evidence is clearly required in this field, but we consider at present that Koch's data for dicinnamyl provide definite support for the hypothesis of electronic interaction through the $-CH_2{\cdot}CH_2-$ group.

B bands are displaced by *ca.* 100 and 200 A., respectively, towards longer wave-lengths relative to those shown by toluene, owing to the small bathochromic effect of the ·OR substituent. In the dibenzyls, the *E′* band is displaced still further towards longer wave-lengths by 60—100 A., and both the *E* and the *B* bands are intensified considerably beyond the expected factor of 2.

trans-*Stilbene.*—In stilbene, the saturated bridge present in dibenzyl is replaced by an ethylenic group, and the new conjugated system thus created gives rise to an intense long-wave-length band (subsequently referred to as K_3 band) near 2900 A., ascribed to the triple chromophore. In addition, stilbene exhibits shorter-wave-length bands near 2100 and 2200 A.

It is an empirical fact in ultra-violet-light absorption that a multiple chromophore usually gives rise, in addition to its own characteristic band or bands, to subsidiary bands similar to those found with the partial chromophores, and it is natural to associate the subsidiary bands with transitions involving only the unsaturation electrons of these partial structures (cf. Part I, *J.*, 1945, 490). Although the mathematical treatment of conjugated systems has not yet been carried sufficiently far to check these assignments except in a few isolated cases, there can be little doubt that they possess some fundamental significance.

In the case of stilbene, the two obvious partial chromophores are the toluene (*a*) and styrene (*b*) systems. The *E* band of the partial toluene chromophore corresponds to the 2100 A. band of stilbene, whilst the low-intensity *B* band will be masked by the intense absorption in the 2900 A. region (K_3 band).

Ph·C (*a*) Ph·C=C (*b*) Ph·C—C·Ph (*c*)

The partial styrene chromophore appears not to be " active " since no selective absorption appears in the 2500 A. region where styrene shows its characteristic band (subsequently referred to as the K_2 band). The stilbene maximum near 2200 A. has no analogue in either the toluene or the styrene partial chromophores. It bears an obvious similarity, however, to the 2200 A. (*E′*) band exhibited by dibenzyl, and it is tentatively suggested that it is to be ascribed to the partial dibenzyl chromophore (*c*), *i.e.*, that it arises from a transition involving the unsaturation electrons of two phenyl nuclei, but not those of the intervening ethylenic link. The assumption of a partial chromophore involving non-adjacent groups is novel, and may at this stage seem somewhat implausible, but it will be shown that this assignment is strongly supported by a consideration of the data for substituted stilbenes. In terms of molecular-orbital theory, whereas the 2900 A. band in stilbene is assumed to involve the interaction of the π electrons of the two phenyl groups with the π electrons of the ethylenic link, the 2200 A. band is suggested to involve the interaction of the π electrons of the two phenyl groups with the σ electrons of the ethylenic link.

Substituted trans-*Stilbenes.*—In 4-hydroxy- and 4 : 4′-dihydroxy-*trans*-stilbenes (2, 3, Table II) the K_3 bands are displaced by *ca.* 200 A. towards longer wave-lengths as would be expected by analogy with the bathochromic effect of hydroxyl substituents in related conjugated systems (cf. styrene, 4-hydroxystyrene). The displacement of the short-wave-length band near 2200 A., on the other hand, is only small and similar to that observed on passing from dibenzyl to hexœsterol, in agreement with its designation as the *E′* band originating in the partial dibenzyl chromophore.

Introduction of an α-methyl substituent into *trans*-stilbene causes a shift of the *K* band to 2700 A., an effect which has been ascribed to steric interference between the alkyl and the (β) phenyl group, resulting in a displacement of the latter out of the plane of the ethylenic bond (Jones, *J. Amer. Chem. Soc.*, 1943, **65**, 1818). The principles underlying this effect have been discussed in Part VI of this series (this vol., p. 1890). The decrease in co-planarity will result in a decrease in the intensity of the K_3 band at 2950 A. and, at the same time, the appearance of a band near 2500 A., corresponding to the K_2 band of the remaining coplanar styrene chromophore. The very wide band around 2700 A. actually recorded is regarded as due to the superposition of the two, possibly with some true resonance degeneracy of the transitions involved. The *E′* band near 2200 A., on the other hand, is but little affected by the α-methyl substituent, again showing that it is not associated with the stilbene chromophore. Precisely similar relationships obtain in the absorption of 4 : 4′-dihydroxy-α-methylstilbene (5, Table II) as compared with 4 : 4′-dihydroxystilbene. The K_3 band near 3100 A. is replaced by a wide band near 2900 A. regarded as a combination of the reduced 3100 A. band and the 2600 A. (K_2) band expected for the partial 4-hydroxystyren chromophore. The *E′* band, on the other hand, remains unchanged and is practically identical in position with that shown by hexœstrol (Table I).

In αβ-dialkylstilbenes, steric interference occurs between both pairs of alkyl and phenyl

TABLE II.*

	E′ band.		*K* band.		*B* band.	
	$\lambda_{max.}$, A.	$\varepsilon_{max.}$ × 10^{-2}.	$\lambda_{max.}$, A.	$\varepsilon_{max.}$ × 10^{-2}.	$\lambda_{max.}$, A.	$\varepsilon_{max.}$ × 10^{-2}.
1. *trans*-Ph·CH=CHPh (125°)	2260	150	2950 3100	270 [1] 250	— —	— —
2. *p*-HO·C_6H_4CH=CHPh (187°)	2300	175	3040 3160	235 [2] 235	— —	— —
3. (*p*-HO·C_6H_4·CH:)$_2$ (278°)	*2280*	125	3000 3070 3250	285 [2] 285 250	— — —	— — —
4. Ph·CMe=CHPh	*2180*	220	2700	180 [3]	—	—
5. *p*-HO·C_6H_4·CMe=CH·C_6H_4·OH-*p* (175°)	2230	115	2820 2910	270 [2] 270	— —	— —
6. Ph·CMe=CPhMe (107°)	2180 2400	225 120	2800 —	50 [3] —	— —	— —
7. *p*-HO·C_6H_4·CEt=CPhEt	2280	135	—	—	2790	40 [2]
8. (*p*-HO·C_6H_4·CEt:)$_2$ (171°)	2390	180	—	—	2790	70 [2]
9. (*p*-MeO·C_6H_4·CEt:)$_2$ (124°)	2400	210	—	—	2850	50 [4]
10. (*p*-AcO·C_6H_4·CEt:)$_2$ (124°)	2380	130	—	—	*2800*	10 [5]
11. (*p*-EtCO$_2$·C_6H_4·CEt:)$_2$ (107°)	2370	160	—	—	*2800*	15 [2]
For comparison.						
Ph·CH=CH$_2$	—	—	2440	100	2820 2920	6 [6]
Ph·CMe=CH$_2$	—	—	2420	100	*2820*	3 [6]
p-HO·C_6H_4·CH=CHMe	—	—	2590	185	*2890*	28 [2]
p-MeO·C_6H_4·CH=CHMe	—	—	2600	180	*2870*	33 [7]

* All the stilbene derivatives listed in this table are believed to have the *trans*-configuration.

[1] Ley and Dirking, *loc. cit.*; Ley and Specker, *loc. cit.*; cf. Solmssen, *J. Amer. Chem. Soc.*, 1943, **65**, 2370.

[2] This paper.

[3] Arends, *Ber.*, 1931, **64**, 1936.

[4] Kharasch and Kleimann, *loc. cit.*

[5] Solmssen, *loc. cit.*

[6] Ramart-Lucas and Amagat, *Bull. Soc. chim.*, 1932, **51**, 965.

[7] Hillmer and Schorning, *Z. physikal. Chem.*, 1933, **21**, *B*, 389 (in hexane).

groups and the coplanarity not only of the triple (stilbene) chromophore, but also of the remaining double (styrene) chromophore, will be largely destroyed. The main absorption appears in the short-wave-length region near 2400 A. and may be regarded as a slightly displaced *E′* band mainly due to the partial dibenzyl chromophore. As would be expected, this band is little affected by hydroxyl, alkoxyl, or acyl substituents, and the absorption of the substituted dialkylstilbenes (7—11, Table II) is very similar to that of the corresponding dibenzyls. The suggestion made by Jones (*loc. cit.*) that the 2400 A. band in αβ-dimethylstilbene is to be ascribed to the partial styrene chromophore is difficult to reconcile with steric considerations and would appear to be excluded by the insensitivity of the band to substituent effects, which is in contrast to the displacement of the K_2 band at 2470 A. in styrene to 2600 A. in 4-hydroxystyrene and anethole. The substituted stilbenes also exhibit absorption in the 2800 A. region, of considerably higher intensity than the *B* bands shown by the corresponding *p*-tolyl and hexœstrol derivatives. This may be due either to increased dibenzyl-type interaction of the aryl groups, or to the retention of a small degree of triple chromophore character, or both.

cis-Stilbene Derivatives.—*cis*-Stilbene (Table III) exhibits bands near 2200 and 2800 A., analogous to the *E′* and K_3 bands of stilbene. The decreases in $\lambda_{max.}$ and $\varepsilon_{max.}$ of the K_3 band as compared with those of the *trans*-isomer are to be ascribed, respectively, to the shorter length of the conjugated system in the *cis*-configuration and to the decrease in coplanarity owing to steric interference between the *o*-hydrogen atoms of the phenyl groups. In the diacetate and dipropionate (2, 3, Table III), believed to be derivatives of the unknown *cis*-stilbœstrol, the intensity of the K_3 band is still further reduced. In this case, scale models indicate that steric interference will occur between the ethyl and phenyl groups attached to the *same* carbon atom, whereas in the *trans*-derivatives interference is between alkyl and phenyl groups attached to different carbon atoms. The interpretation to be given to the submerged bands near 2500 A. also exhibited by the presumed *cis*-stilbœstrol derivatives, however, is not clear.

ψ-Stilbœstrol and Dienœstrol.—Data for a number of miscellaneous dibenzyl and stilbene derivatives are collected in Table IV. ψ-Stilbœstrol (1) and its diacetate (2), which may be regarded either as substituted dibenzyls or as α-benzylstyrenes, show only dibenzyl-type (*E′*) bands in the 2300 A. region, but no styrene-type absorption, in agreement with their expected non-planar configuration. In dienœstrol (3) and its acetate (4), which may be regarded either as substituted dibenzyls or as 1 : 2-diphenylbutadienes, the 2300 A. band is much enhanced in intensity and is probably a superposition of absorption due to the partial butadiene and dibenzyl chromophores. The isomeric *iso*dienœstrol (5), on the other hand, shows styrene type absorption corresponding almost exactly to the summation of two enol (4-hydroxy-β-methylstyrene) systems. In this compound, the two halves of the molecule appear to be separately coplanar, and a model can be constructed in which this is the case, and in which the two planes containing the enol systems are at approximately right angles to each other.

TABLE III.

	E′ band.		*K* band.	
	$\lambda_{max.}$, A.	$\varepsilon_{max.} \times 10^{-2}$.	$\lambda_{max.}$, A.	$\varepsilon_{max.} \times 10^{-2}$.
1. *cis*-Ph·CH=CH·Ph	2220	230	2800	135 [1]
2. (p-AcO·C_6H_4·CEt:)$_2$ (82°) *	2230	145	*2560* 2780	100 [2] 70
3. (p-EtCO$_2$·C_6H_4CEt:)$_2$ (78°) *	2280	135	2500 2800	105 [2] 80

* Believed to have the *cis*-configuration.

[1] Ley and Dirking, *loc. cit.* [2] This paper.

TABLE IV.

	E′ band.		*K* band.		*B* band.	
	$\lambda_{max.}$, A.	$\varepsilon_{max.} \times 10^{-2}$.	$\lambda_{max.}$, A.	$\varepsilon_{max.} \times 10^{-2}$.	$\lambda_{max.}$, A.	$\varepsilon_{max.} \times 10^{-2}$.
1. p-HO·C_6H_4(:CHMe)·CHEt·C_6H_4·OH-p (151°)	2290	185	—	—	2800	40 [1]
2. p-AcO·C_6H_4·C(:CHMe)·CHEt·C_6H_4·OAc-p (64°)	2230	185 [1]	—	—	—	—
3. p-HO·C_6H_4·C(:CHMe)·C(:CHMe)·C_6H_4·OH-p (230°)	2290	275	—	—	2800	95 [1]
4. p-AcO·C_6H_4·C(:CHMe)·C(:CHMe)·C_6H_4·OAc-p (115°)	2250 2450	260 145	—	—	*2800*	15 [1]
5. *iso*Dienœstrol (189°)	—	—	2590	285	*2950*	50 [1]

[1] This paper.

EXPERIMENTAL.

For the technique of light-absorption measurements, see Parts I (*J.*, 1944, 490) and VII (preceding paper). Data are for ethanolic solutions unless otherwise stated. All the compounds examined are described in the literature, except the diacetate and dipropionate 2 and 3 (Table III), which were very kindly furnished by Dr. E. Walton before publication. Many of the other samples were obtained through the courtesy of Professor E. C. Dodds, F.R.S., Professor E. E. Turner, F.R.S., Dr. W. C. J. Ross and Dr. F. N. Short. Ozonolysis of dienœstrol diacetate (4, Table IV) (1 g.) in acetic acid (50 ml.) for 20 hours (200 mg. of O_3 per hour) and decomposition of the ozonide by the method of Church, Whitmore, and McGrew (*J. Amer. Chem. Soc.*, 1934, **56**, 176) afforded 200 mg. (15%) of the dimedone derivative of acetaldehyde, m. p. 139°, undepressed by an authentic specimen.

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