189. *Studies in Light Absorption. Part X.* Further Observations on Ultra-violet Auxochromes. A Survey of the Effects of Some of the Less Common Elements.*

By K. Bowden and E. A. Braude.

The generalisations previously made (Part III, *J.*, 1946, 948) concerning the spectral effects of covalently saturated substituents on the ultra-violet light absorption of ethylenic and aromatic systems are amplified. Data are presented for 16 phenyl derivates $PhXR_n$ where X represents elements of Groups IV, V, VI, and VII of the Periodic Table and R = alkyl. When X = C, Si, Sn, Pb, or Halogen, the auxochromic effects are relatively small, whereas the elements of Groups V and VI produce large effects. Electronic interaction with the π-electron centre is particularly strong for the substituents NR_2, PR_2, SR, and SeR. These, and some connected observations on the effects of alkyl groups, are discussed in relation to current theories of electronic spectra.

In Part III (*loc. cit.*) a survey was presented of the data then available concerning the auxochromic effects of the commoner types of substituents when directly attached to ethylenic or benzenoid groups. It was shown that the bathochromic displacements due to a covalently saturated substituent X in a system C=C·X could be correlated (i) with the polarisability of the ethylenic group as conditioned by its molecular environment, and (ii) with the position of X in the Periodic Table. Thus, whereas alkyl, alkoxyl, and halogen substituents exert relatively small influences, the conjugating effect of amino and sulphide (thiol) substituents was even greater than that of simple, covalently unsaturated groups, such as a vinyl group; *e.g.*, the characteristic light-intensity absorption of vinylamines ($C=C\cdot NR_2$) and vinyl sulphides (C=C·SR) lies at rather longer wave-lengths ($\lambda_{max.}$ near 2300 Å) than that of conjugated dienes (C=C·C=C; $\lambda_{max.}$ near 2200 Å). The influence of substituents such as NR_2 and SR is ascribed mainly to the interaction of their unshared *p*-electrons with the π-electrons of the adjacent double bond, and it was easily predictable that such interaction, which is conveniently termed π-*p* conjugation, would also be

---

* Part IX, *J.*, 1950, 379.

particularly large in the case of other Group V and VI elements, especially tervalent phosphorus derivatives.

During the last five years, many data have appeared in the literature bearing out the generalisations previously made and many additional examples of the effects of $-NR_2$ substituents (cf. Jones, Shen, and Whiting, *J.*, 1950, 236; Cocker, O'Meara, Schwarz, and Stuart, *ibid.*, p. 2052; Grob, *Helv. Chim. Acta*, 1950, **33**, 1787; Austin, Chanley, and Sobotka, *J. Amer. Chem. Soc.*, 1951, **73**, 5299), $-SR$ substituents (cf. Owen and Somade, *J.*, 1947, 1030; Owen and Sultanbawa, *J.*, 1949, 3109; Koch, *ibid.*, p. 387; Fehnel and Carmack, *J. Amer. Chem. Soc.*, 1949, **71**, 84; Ralls, Dodson, and Riegel, *ibid.*, p. 3320; Rosenkranz, Kaufmann, and Romo, *ibid.*, p. 3689; Price and Zomlefer, *ibid.*, 1950, **72**, 16; Nussbaum, Mancera, Rosenkranz, and Djerassi, *ibid.*, 1951, **73**, 3263), and halogen substituents (cf. Wood and Temin, *ibid.*, 1950, **72**, 139) in open-chain and cyclic ethylenic systems have been described. These, together with some additional data we have determined, make it possible to extend, and fill in several gaps in, the earlier survey of the commoner substituents (Table 1).

Our continuation of the work has been primarily directed towards a study of the less common auxochromes of Groups IV, V, and VI of the Periodic System. No systematic study of the light-absorption properties of organic compounds of the heavier elements has previously been made and the few scattered data available mostly refer to saturated derivatives. For the present purpose, the most suitable derivatives would be the substituted ethylenes of the type $R{\cdot}CH{:}CH{\cdot}XR_n$ where X is the key element and R is alkyl or hydrogen. However, as few such substances are known and as many of them are likely to be very unstable, the corresponding phenyl derivatives, $Ph{\cdot}X{\cdot}R_n$, which have been more fully investigated chemically, were chosen instead, the alkylated derivatives (R = Me or Et) being selected in preference to the parent hydrides (R = H) in view of their superior stability. The present communication deals with the near-ultra-violet absorption of sixteen such derivatives, in which X is C, Si, Sn, Pb, N, P, As, Sb, O, S, Se, Te, and Halogen, and some related compounds. Although the majority of these compounds are known, it became apparent in the early stages of the work that the preparative methods described are frequently unsatisfactory and yield products of doubtful purity. The derivatives of the Group V and VI elements, in particular, are very unstable in air and considerable effort was spent on devising satisfactory methods of preparation and manipulation, which are referred to in the experimental section.

TABLE 1. *Auxochromic effects in different ethylenic systems.* (*Bathochromic shifts in* Å *due to replacement of* H *by* X.)

X =	CR_3	NR_2	OR	SR	Cl	Br
X·C=C	50[1]	400[1]	—	450[1]	50[1]	—
X·C=C·C=C	50[1]	650[1]	—	280[5]	60[1]	100[7]
X·Ph *	80[2]	510[2]	195[2]	550[2]	100[2]	100[2]
X·C=C·Ph	40[3]	580[3]	—	—	—	140[3]
$X{\cdot}C{=}C{\cdot}CO_2H$	50[4]	800[1]	300[1]	700[6]	200[1]	250[1]
X·C=C·C=O	100[1]	950[1]	500[1]	850[1]	200[1]	300[1]

* Displacements of high-intensity *E*-band.

[1] Part III, *loc. cit.* [2] This paper (see Table 2). [3] From comparison of styrene and β-methylstyrene (cf. Braude and Timmons, *J.*, 1950, 2009), β-diethylaminostyrene and β-bromostyrene (see Experimental), respectively. [4] From comparison of crotonic and β-methylcrotonic acid (Braude and Timmons, unpublished). [5] From comparison of the enol ether and benzyl thioenol ether of cholest-4-en-3-one (Rosenkranz, Kaufmann, and Romo, *loc. cit.*). [6] From comparison of acrylic and β-benzylthioacrylic acid (Owen and Sultanbawa, *loc. cit.*). [7] From comparison of hexatriene and 3-bromohexatriene (Woods *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 3394; 1950, **72**, 139).

The principal data are collected in Table 2 and Figs. 1—5. Amongst the compounds studied, earlier measurements were available only for dimethylaniline (Remington, *J. Amer. Chem. Soc.*, 1945, **67**, 1838; Klevens and Platt, *ibid.*, 1949, **71**, 1714), phenetole (Jacobs and Tuttle, *ibid.*, p. 1313), and the halogenobenzenes (Conrad-Billroth, *Z. physikal. Chem.*, 1932, *B*, 19, 76; Doub and Vandenbelt, *J. Amer. Chem. Soc.*, 1947, **69**, 2714), and, in these cases, the agreement between the earlier and present measurements is generally satisfactory. Benzene exhibits two main groups of bands in the near-ultra-violet region, one of moderately high intensity near 2000 Å (ε 8000) which will be referred to as the *E*-

band, and the other of low intensity near 2560 Å (ε 200) which will be referred to as the *B*-band.* A third very intense group of bands near 1800 Å (Platt and Klevens, *Chem. Reviews*, 1947, **41**, 301; Price and Walsh, *Proc. Roy. Soc.*, 1947, *A*, **191**, 22) lies outside the quartz-instrument range, and a fourth group, reported near 3400 Å, is of extremely low intensity (Sklar, *J. Chem. Physics*, 1937, **5**, 669; Lewis and Kasha, *J. Amer. Chem. Soc.*, 1945, **67**, 994). Substituents generally cause a bathochromic displacement and intensification of the *B*-band, as well as the appearance of a new band at longer wave-length than the *E*-band, but of similar intensity. The original *E*-band is just outside the present range of

FIG. 1.

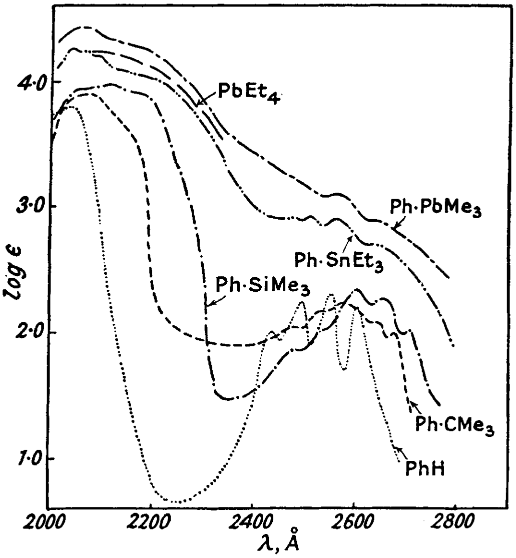


FIG. 3.

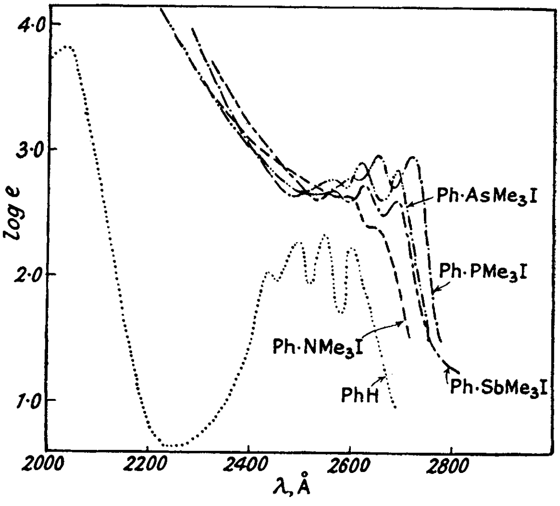
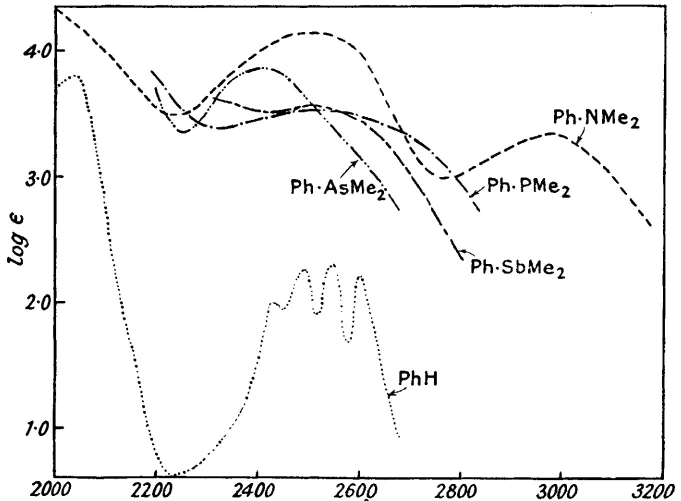


FIG. 2.



---

* These designations were originally based (*Ann. Reports*, 1945, **42**, 105) on the qualitative theoretical interpretation of the bands, regarded as due to transitions of the ethylenic and benzenoid types. Fortunately, they are also indicative of the precise physical descriptions, since the most acceptable symmetry assignments of the excited states are E_{1u} and B_{2u}, respectively (Craig, *Discuss. Faraday Soc.*, 1950, **9**, 5; Burawoy, *ibid.*, p. 78).

measurements, but the vacuum-ultra-violet investigations of Price and Walsh (*loc. cit.*; *Discuss. Faraday Soc.*, 1950, **9**, 53) and Platt and Klevens (*loc. cit.*) and our own data (see Experimental) for methyl phenyl sulphide show that it is also retained in the substituted derivatives. The new high-intensity bands between 2000 and 2500 Å may be regarded as displaced *E*-bands, and the effects observed may be summarised in more detail as follows:

(i) The Group IV substituents CR_3, SiR_3, SnR_3, and PbR_3 cause only small bathochromic displacements which are largest with SiR_3. The substituents $SnEt_3$ and $PbMe_3$ also cause pronounced increases in intensity, but these probably do not arise from interaction with the phenyl ring, but from the metallic groups themselves, since the corresponding tetra-alkyl derivatives also show intense continuous absorption in this region (Fig. 1; cf. Riccoboni, *Gazzetta*, 1941, **71**, 696).

FIG. 4.

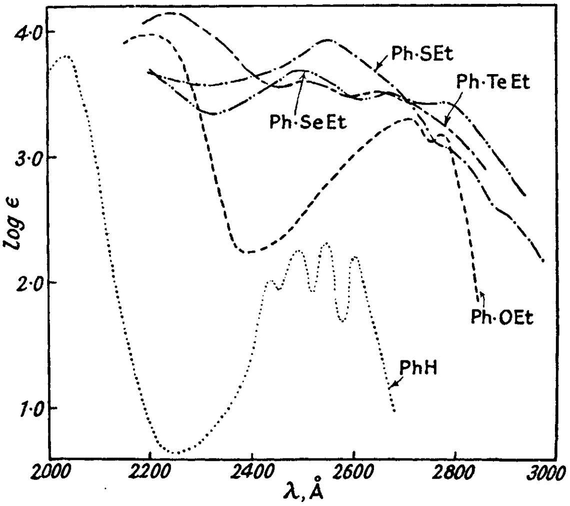
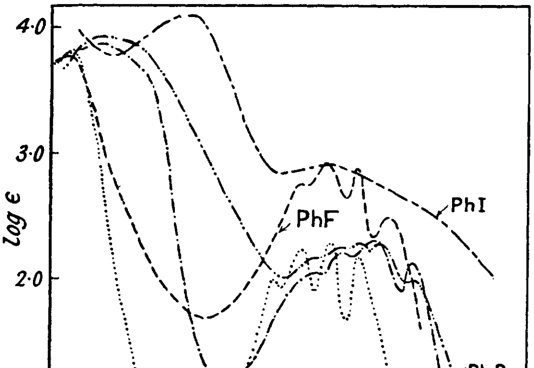


FIG. 5.



(ii) The Group V substituents NMe_2, PMe_2, $AsMe_2$, and $SbMe_2$ cause large bathochromic displacements which decrease as the group is ascended. The substituent NMe_2 also causes a large intensification of the *B*-band, but in $Ph{\cdot}PMe_2$, $Ph{\cdot}AsMe_2$, and $Ph{\cdot}SbMe_2$ this band appears to be submerged. By contrast, the corresponding quaternary substituents NMe_3^+, etc., have only negligible effects; the light absorption of quaternary derivatives (*e.g.*, methiodides) of this group is completely different from that of the parent compounds and resembles that of benzene in the 2500 Å region (Fig. 3). (At shorter wave-lengths, the curves are not comparable because of the superimposed intense absorption of the iodide ion.)

(iii) The Group VI substituents OEt, SEt, SeEt, and TeEt produce similar displacements to those of Group V, except that the effect of OEt is relatively small.

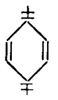
(iv) The Group VII substituents F, Cl, Br, and I cause relatively small effects; as the group is ascended, the *E*-band undergoes increasing bathochromic displacements with but little change in intensity, while the *B*-band undergoes only slight wave-length displacements, but a large increase in intensity in the case of PhF and PhI. The predicted, large auxochromic effect of a PR_2 substituent is confirmed,* but the earlier generalisation (Part III, *loc. cit.*), *viz.*, that the auxochromic effects increase as a Periodic Group is ascended, is now seen to be valid only for the first two rows of the Periodic System and in Group VII.

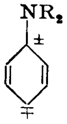
TABLE 2. *Ultra-violet absorption of* $Ph{\cdot}X{\cdot}R_n$.*

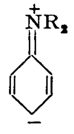
Group IV		Group V		Group VI		Group VII	
$\lambda_{max.}$	ε	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε
$X = CMe_3$		$X = NMe_2$		$X = OEt$		$X = F$	
2075	7800	2050 2510	12000 14000	2195	9500	2040	6200
2570	170	2980	2250	2720	1900	2540	900
$X = SiMe_3$		$X = PMe_2$		$X = SEt$		$X = Cl$	
2110	9300	2510	3500	2050 2550	12500 8600	2100	7500
2600	225	—		2780	1100	2570	170
$X = SnEt_3$		$X = AsMe_2$		$X = SeEt$		$X = Br$	
2040	18000	2390	6800	2500	4900	2100	8600
2510	850	—		2690	3200	2610	200
$X = PbMe_3$		$X = SbMe_2$		$X = TeEt$		$X = I$	
2060	27000	2500	3700	2250	14600	2260	13000
2560	1300	—		2700	4000	2560	800

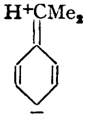
* Data refer to ethanol solutions, except for $Ph{\cdot}PMe_2$ which was measured in *cyclo*hexane. Only the principal data are given in this table; for complete data see the Experimental section.

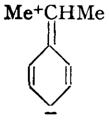
It will be convenient to consider separately the auxochromic effects on the *E*- and *B*-bands. In the terms of valence-bond resonance theory, the *E*-band in benzene may be regarded as arising from transitions to an excited state involving increased contributions from the *p*-dipolar structures † (I) (Craig, *Proc. Roy. Soc.*, 1950, *A*, **200**, 401) and is similar in character to the high-intensity *K*-bands of butadiene and related open-chain conjugated systems which involve dipolar structures such as $\pm CH_2{-}CH{=}CH{-}CH_2\mp$. On this basis, the almost identical *E*-bands near 2000 Å found in substituted benzenes are regarded as "partial" chromophore bands due to transitions involving only the ring and represented by structures such as (II*a*), whereas the new *E*-bands at longer wave-lengths are associated with the new chromophore Ph·X. The bathochromic effects produced by substituents carrying unshared electron pairs are similar in the benzenoid and ethenoid systems (Table 1) and are ascribed to contributions from structures such as (II*b*).


(I)


(II*a*)


(II*b*)


(III*a*)


(III*b*)

---

* Since this paper was written, values similar to those for dimethylphenylphosphine have been reported for 1-phenyl*cyclo*tetramethylenephosphines (Fürst and Horvat, *Science*, 1951, **114**, 330).

† In the wave-mechanical treatment, contributions from *o*-dipolar and homopolar structures are also invoked, but the polarities of the various *o*-dipolar structures in the excited state cancel, whereas those of the *p*-dipolar structures do not.

Such contributions will lower the energies of both the ground and the excited states, and since they will be larger in the more highly polar excited state, the energy of the latter will be lowered more than that of the ground state, *i.e.*, the excitation energy will be decreased and the bands displaced to longer wave-lengths.* The fact that the unshared *p*-electrons of the substituents are involved is borne out by the fact that the bathochromic effects of the Group V substituents disappear almost entirely in the corresponding quaternary derivatives in which the *p*-electron pair is used in bond formation. No simple relation is apparent, however, between the magnitude of the bathochromic effects on the *E*-band and the ionisation potentials of the substituents, or similar parameters which might afford some measure of the availability of the *p*-electrons for electronic displacements of the type involved. Nor is there any exact correspondence between these spectral effects and the so-called " electromeric " effects in chemical reactivity, which are regarded as due to analogous, though less complete, electronic displacements; thus, whereas the bathochromic effects increase in the sequence $F<Cl<Br<I$, the electromeric effects increase in the reverse order (cf. Braude and Stern, *J.*, 1947, 1096; Baker and Hopkins, *J.*, 1949, 1089, and earlier references there cited).

The small, but definite auxochromic displacements produced by Group IV substituents, which do not possess unshared *p*-electron pairs, are less easily accounted for. Three explanations appear possible :

(i) The displacements may be due to interaction between the π-electrons of the ring and the σ-electrons of the substituent, *i.e.*, to contributions from hyperconjugated structures such as (III*a*) and (III*b*). The fact that locations of the *E*-bands are almost identical for toluene, ethylbenzene (Platt and Klevens, *loc. cit.*, 1947), and *tert.*-butylbenzene indicates that, if this mechanism is operative, interaction with the σ-electrons of carbon–hydrogen bonds and carbon–carbon bonds (*i.e.*, III*a* and III*b*) must be of almost equal importance. There is much evidence, however, that $C{=}C{-}C{-}C$ hyperconjugation is much weaker than $C{=}C{-}C{-}H$ hyperconjugation (cf. below) and it seems unlikely that this effect can be solely responsible for the displacements of *E*-bands by alkyl and similar groups.

(ii) A second possibility is that the displacements are due to a " proximity " or " inductive " effect, *i.e.*, to the electrostatic influence of the non-valency electron-cloud of the substituent. If this were the case, the displacements would be expected to *increase* in going from $Ph{\cdot}CMe_3$ to $Ph{\cdot}SiMe_3$, as observed (little significance can be attached to the data for $Ph{\cdot}SnEt_3$ and $Ph{\cdot}PbMe_3$ because of the superposition of absorption due to the metallic moiety itself in the *E*-band range). A similar increase would be expected in the sequence PhMe, PhEt, and PhBu; this, however, is not observed.

(iii) The displacements could arise simply from a " weighting " effect—an alteration in the relative populations of the vibrational sub-levels and of the relative heights of the submerged vibrational peaks, resulting in a shift in the centre of gravity of the band envelope. However, this explanation is again countered by the fact that the displacements actually *decrease* with increasing " weight " in the sequence PhMe, PhEt, and PhBu.

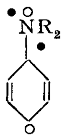
Nevertheless, it is probable that each of the three effects discussed makes some contribution in the case of Group IV as well as other substituents.

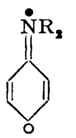
We now turn to the effects of substituents on the *B*-band, which may be ascribed to a forbidden transition involving increased contributions from homopolar excited (Dewar) structures (Sklar, *J. Chem. Physics*, 1937, **5**, 669; cf. Craig, *loc. cit.*). Auxochromic displacements of this band are less amenable to qualitative theoretical discussion, because the influence of substituents on the relative energy levels of Dewar structures is not easy to assess. However, it is clear that a substituent with an unshared electron pair will stabilise a Dewar structure such as (II*c*) in virtue of an electron pairing–unpairing process leading to (II*d*). The ease of the process represented by going from the classical structure to (II*c*) might

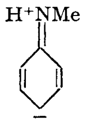
---

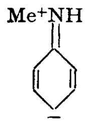
* There has been some controversy concerning the assignment of the high-intensity bands in substituted benzenes. Some authors (*e.g.*, Klevens and Platt, *loc. cit.*, 1949) have regarded the 2510 Å band in dimethylaniline as a strongly intensified *B*-band (2560 Å) of benzene. For reasons which will be apparent from the subsequent discussion, we believe the closeness of the two wave-length locations to be entirely coincidental and that it is the low-intensity band at 2980 Å of the amine which is related to the 2560 Å band of benzene.

be expected to bear some relation to the ease of going from the classical structure to (II*b*); in the valence-bond notation, the former involves the " migration " of *one*, and the latter that of *two* *p*-electrons into the ring. On the other hand, the relation will be modified by the fact that the former process does not, and the latter process does, involve the setting up of a formal charge. There is, in fact, some, though by no means exact, parallelism between the effects of substituents on the *E*- and the *B*-band.


(II*c*)


(II*d*)


(II*e*)


(II*f*)

(• and o represent valency electrons of opposite spin.)

A semi-quantitative molecular-orbital treatment of the effect of substituents on the *B*-band has been given by Sklar (*J. Chem. Physics*, 1939, **7**, 984) and, more recently, by Matsen (*J. Amer. Chem. Soc.*, 1950, **72**, 5243; Robertson and Matsen, *ibid.*, p. 5248, 5252). Sklar dealt primarily with the effect of substituents on intensity, and concluded that a substituent will have a large effect if it has a pair of non-bonded *p*-electrons, a low ionisation potential, and not too large a Ph–X distance. On this basis, SH was predicted to be very effective; in fact, however, the *B*-bands of Ph·SH (Part III, *loc. cit.*; Robertson and Matsen, *loc. cit.*) as well as of Ph·SMe and Ph·SEt are rather less intense than those of Ph·NMe$_2$ or Ph·OMe. Matsen applied molecular-orbital theory to the calculation of wave-length displacements and derived an expression which predicts that the bathochromic shift of the *B*-band will be larger, the smaller the ionisation potential of the substituent X. As already noted by Robertson and Matsen (*loc. cit.*), this prediction is not fulfilled for the sequence Ph·NH$_2$, Ph·OH, and Ph·SH, and the present data for the sequence Ph·NMe$_2$, Ph·SEt, Ph·SeEt, and Ph·TeEt show that the wave-length shift of the *B*-band actually *decreases* with decreasing ionisation potential (NH_3 10·8, H_2S 10·5, H_2Se 9·8, H_2Te 9·14 e.v.; Price, *Chem. Reviews*, 1947, **41**, 257; Price, Teegan, and Walsh, *Proc. Roy. Soc.*, 1950, *A*, **201**, 600). The fact that charged substituents such as NR_3^+ cause displacements of the *B*-band comparable to those produced by a halogen substituent (Fig. 3), and that alkyl groups also have a marked, though smaller, effect, suggests that inductive influences play a considerable part.

Lastly, some interesting facts which emerge concerning the influence of R in Ph·XR_n may be briefly considered. It has long been known (cf. Wizinger, " Organische Farbstoffe," Berlin, 1933) that the bathochromic effect of alkylamino-groups in dyes increases in the order $NH_2 < NHMe < NMe_2$. Similarly, the *E*-band of aniline is shifted by 210 Å towards longer wave-lengths in dimethylaniline compared with that of aniline, and an equal displacement is found in comparing thiophenol and methyl phenyl sulphide (Table 3).

TABLE 3. *Effects of alkyl substituents on band locations* ($\lambda_{max.}$, Å).

R	Ph·NR$_2$		Ph·OR		Ph·SR	
H	2300	2800 [1]	2100	2700 [3]	2350	2690 [1]
Me	2510	2980 [2]	2170	2690 [3]	2540	2790 [2]
Et	2580	3040 [2]	2195	2770 [2]	2550	2780 [2]

[1] Part III, *loc. cit.* [2] This paper. [3] Doub and Vandenbelt, *loc. cit.*

These effects, like those of alkyl groups attached directly to the phenyl ring (cf. p. 1073), could be either inductive or hyperconjugative in character, or both. If they were purely inductive, *i.e.*, due to the displacement of the *p*-electron pair of X towards the ring owing to electrostatic repulsion, they would be expected to increase in the sequence $NH_2 < NHMe < NMe_2 < NEt_2$ and $SH < SMe < SEt$, as observed. If, on the other hand, they were purely hyperconjugative, *i.e.*, due to contributions from structures such as (II*e*) and (II*f*), the displacements would be expected to be *smaller* for NMe$_2$ and SMe than for NH$_2$ and SH since X–H bonds are more polar than X–C bonds; thus, it is well known that

C–H hyperconjugation is stronger than C–C hyperconjugation (cf. Crawford, *Quart. Reviews*, 1949, **3**, 226; Bateman and Cunneen, *J.*, 1951, 2283). It therefore appears that the spectral effect of alkyl groups here is primarily inductive. In the alkylbenzenes, the auxochromic displacements of the *B*-band decrease in the sequence PhMe>PhEt>Ph·CMe$_3$ and this has been ascribed to hyperconjugation (Matsen, Robertson, and Chuoke, *Chem. Reviews*, 1947, **41**, 273). Hyperconjugation would not, however, be expected to exert a dominant influence in the case of *B*-bands which are due to almost non-polar transitions, and an alternative explanation has been given (Hammond, Price, Teegan, and Walsh, *Discuss. Faraday Soc.*, 1950, No. 9, p. 56).

EXPERIMENTAL

tert.-Butylbenzene was prepared in 70% yield from benzene and *tert.*-butanol by Berliner and Bondhus's modification (*J. Amer. Chem. Soc.*, 1946, **68**, 2355) of Huston, Fox, and Binder's method (*J. Org. Chem.*, 1938, **3**, 251). It had b. p. 167—168°/760 mm., $\lambda_{max.}$ in ethanol 2075, 2475, 2520, 2570, 2640, and 2670 Å, ε 7800, 110, 155, 170, 120, and 105, respectively.

Trimethylphenylsilane.—A solution of phenylmagnesium bromide (from Mg, 12 g.) in ether (200 ml.) was added to a stirred solution of silicon tetrachloride (85 g.) in ether (150 ml.) at 0°. After a further 30 minutes' stirring, the mixture was heated under reflux for 3 hours. It was then filtered, the residue was washed with ether, and the combined filtrate and washings were distilled, giving phenylsilicon trichloride (41 g.), b. p. 198—202°, as well as some higher-boiling products, probably diphenylsilicon dichloride. The trichloride (41 g.) in ether (50 ml.) was added dropwise to a solution of methylmagnesium iodide (from Mg, 15·3 g.) in ether (300 ml.) at 0°. The mixture was then heated for 3 hours under reflux and filtered hot. The filtrates were distilled, giving trimethylphenylsilane (21 g., 80%); b. p. 171—172°/760 mm. (cf. Bygdén, *Ber.*, 1912, **45**, 710). It had $\lambda_{max.}$ in ethanol 2110, 2470, 2530, 2600, 2650, and 2700 A, ε 9300, 75, 115, 225, 190, and 105, respectively.

Triethylphenyltin.—Tetraethyltin, b. p. 180°, prepared in 83% yield from stannic chloride (24 g.) and ethylmagnesium bromide (from Mg, 18 g.) in ether (300 ml.) (Pfeiffer and Schnurmann, *Ber.*, 1904, **37**, 320), was treated with the theoretical amount of bromine in carbon tetrachloride solution at 0°, giving triethyltin bromide, b. p. 107°/18 mm. (cf. Cahours, *Annalen*, 1860, **114**, 364). The bromide (18 g.) was added to a solution of phenylmagnesium bromide (from Mg, 1·52 g.) in ether (80 ml.) at 0°, and the whole heated under reflux for 1 hour; ice was added and the ethereal layer was separated and dried (CaCl$_2$). The ether was removed under reduced pressure and the product was distilled over a naked flame, giving triethylphenyltin (11 g., 62%), b. p. 134°/17 mm. (cf. Ladenburg, *Annalen*, 1871, **159**, 251). It had $\lambda_{max.}$ in ethanol 2040, 2060, 2080, 2510, 2560, and 2640 Å, ε 18 000, 17 000, 16 000, 850, 800, and 500, respectively.

Trimethylphenyl-lead.—Lead dichloride (56 g.) was added portionwise to an ethereal solution of methylmagnesium iodide at 0°. The mixture was heated under reflux for 1 hour and excess of ice was then added. The ethereal layer was separated, dried (CaCl$_2$), and treated with a solution of bromine (16 g.) in dry carbon tetrachloride (100 ml.) with external cooling in a carbon dioxide–methanol bath. After the addition, the mixture was allowed to attain room temperature and the solvents were removed under reduced pressure. The residue was extracted repeatedly with hot benzene and the extracts were concentrated under reduced pressure, giving trimethyl-lead bromide, m. p. 133° (Grüttner and Krause, *Ber.*, 1916, **49**, 1425, give m. p. 133°).

The bromide (17 g.) in hot benzene was added to an ice-cold ethereal solution of phenylmagnesium bromide (from Mg, 2 g.). The mixture was refluxed for 1 hour, then cooled to 0° and treated with ice-cold hydrochloric acid. The ethereal layer was dried (CaCl$_2$) and fractionated, giving trimethylphenyl-lead (16 g., 90%), b. p. 104°/15 mm. (cf. Grüttner and Grüttner, *Ber.*, 1918, **51**, 1294). It had $\lambda_{max.}$ in ethanol 2060 Å, ε 27 000; $\lambda_{infl.}$ 2560 and 2640 Å, ε 1300 and 800.

Dimethylaniline.—This had b. p. 79°/15 mm., $\lambda_{max.}$ in *cyclo*hexane 2510 and 2980 A, ε 14 000 and 2250; $\lambda_{max.}$ in ethanol 2510 and 2990 Å, ε 14 000 and 2100. The methiodide had $\lambda_{max.}$ in ethanol 2590 and 2640 Å, ε 430 and 250.

Diethylaniline, b. p. 182°/290 mm., showed $\lambda_{max.}$ in ethanol 2580, 2640, and 3040 Å, ε 16 000, 15 000, and 2250, respectively.

Dimethylphenylphosphine.—Phenyldichlorophosphine was prepared by continuous distillation of a mixture of equal volumes of benzene and phosphorus trichloride through a hard-glass tube heated to dull-red heat and packed with broken porous tile, in an atmosphere of carbon dioxide (cf. Arbuzov, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 395). The heated tube was connected to a water-condenser leading back to the distillation flask. An ethereal solution of phenyldichlorophosphine (36 g.) was added dropwise to an ethereal solution of methylmagnesium iodide (from Mg, 14·4 g.) in an atmosphere of nitrogen. Next day, the solution was heated for 2 hours under reflux and then cooled to 0° and treated with excess of saturated aqueous ammonium chloride solution. The ethereal layer was separated, washed with water, dried (Na_2SO_4), and fractionated in a nitrogen atmosphere, giving dimethylphenylphosphine (12 g.), b. p. 79°/10 mm. (Meisenheimer *et al.*, *Annalen*, 1926, **449**, 227, give b. p. 83—84°/13·5 mm.). The phosphine, which is very readily oxidised in air, had $\lambda_{\text{max.}}$ 2510 Å, ε 3500 in dry *cyclo*hexane. Solutions in ethanol and dioxan gave variable values with lower intensities and were unsuitable for spectral measurements. The methiodide, crystallised from absolute ethanol, had m. p. 231—232° (Michaelis, *Annalen*, 1876, **181**, 363, gives m. p. 226—227°), $\lambda_{\text{max.}}$ in ethanol 2510, 2600, 2650, and 2720 Å, ε 450, 610, 920, and 810, respectively.

Dimethylphenylarsine.—This was prepared from dimethyliodoarsine and phenylmagnesium bromide (Burrows and Turner, *J.*, 1920, **117**, 1378). It was fractionated in a nitrogen atmosphere and had b. p. 85°/14 mm.; $\lambda_{\text{max.}}$ in *cyclo*hexane 2360, 2390, and 2420 Å, ε 6600, 6800, and 6600, respectively; $\lambda_{\text{max.}}$ in ethanol 2415 Å, ε 6800. The methiodide, crystallised from absolute ethanol, had m. p. 250° (Found: C, 38·1; H, 4·8. Calc. for $C_{11}H_{16}AsI$: C, 37·7; H, 4·6%) (Burrows and Turner, *loc. cit.*, give 250°), $\lambda_{\text{max.}}$ in ethanol 2500, 2560, 2620, and 2690 Å, ε 500, 600, 780, and 670, respectively.

Dimethylphenylstibine.—This was prepared by adding an ethereal solution of phenyldichlorostibine (Lecoq, *J. Pharm. Belg.*, 1937, **19**, 133) to an excess of methylmagnesium iodide in ether (cf. Grüttner and Wiernik, *Ber.*, 1915, **48**, 1759). It had b. p. 95—97°/10 mm., $\lambda_{\text{max.}}$ in ethanol 2500 Å, ε 3700. The stibine is rapidly oxidised in contact with air, and all manipulations were carried out in a nitrogen atmosphere. It formed a dibromide, m. p. 112° (from glacial acetic acid), $\lambda_{\text{max.}}$ in ethanol 2650 and 2700 Å, ε 610 and 430; $\lambda_{\text{infl.}}$ 2780 Å, ε 60, and a methiodide, m. p. 212° (decomp.) (from ethanol), $\lambda_{\text{max.}}$ in ethanol 2560, 2620, and 2670 Å, ε 480, 520, and 400, respectively. Phenetole had b. p. 172°/760 mm., n_D^{20} 1·5000, $\lambda_{\text{max.}}$ in ethanol 2195, 2720, and 2770 Å, ε 9500, 1900, and 1500, respectively. Methyl phenyl sulphide had b. p. 191°/760 mm., n_D^{20} 1·5810, $\lambda_{\text{max.}}$ in *cyclo*hexane 2540 Å, ε 9400; $\lambda_{\text{infl.}}$ 2790 Å, ε 1500; $\lambda_{\text{max.}}$ in ethanol 2050 and 2540 Å, ε 12 500 and 9400, $\lambda_{\text{infl.}}$ 2780 Å, ε 1400. Ethyl phenyl sulphide had b. p. 203°/755 mm., n_D^{20} 1·5740; $\lambda_{\text{max.}}$ in ethanol 2550 Å, ε 8600; $\lambda_{\text{infl.}}$ 2780 and 2880 Å, ε 1200 and 400. Ethyl phenyl selenide, prepared by the reaction of phenylmagnesium bromide with selenium, followed by treatment with ethyl iodide (Foster, *J. Amer. Chem. Soc.*, 1933, **55**, 822), had b. p. 216—218°/760 mm., $\lambda_{\text{max.}}$ in ethanol 2500, 2690, and 2790 Å, ε 4900, 3200, and 2600, respectively.

Ethyl Phenyl Telluride.—A suspension of tellurium (25·6 g.) in ether (100 ml.) was added to a stirred ethereal solution of phenylmagnesium bromide (from Mg, 4·8 g.) in a nitrogen atmosphere and the mixture was heated under reflux for 3 hours. Next day, ethyl iodide (31 g.) in ether (50 ml.) was added dropwise and the mixture was heated under reflux for one hour, then cooled; excess of ice-cold hydrochloric acid was added, and the ethereal layer was separated, washed with 30% aqueous sodium hydroxide and then with water, dried (Na_2SO_4), and distilled, giving *ethyl phenyl telluride* (20 g.) as a pale yellow liquid, b. p. 107—108°/22 mm. (Found: C, 41·1; H, 4·9. $C_8H_{10}Te$ requires C, 41·1; H, 4·3%); $\lambda_{\text{max.}}$ in *cyclo*hexane 2250, 2510, 2700, 3300 Å, ε 14 600, 3300, 4000, and 680, respectively; $\lambda_{\text{max.}}$ in ethanol 2240, 2510, and 2650 Å, ε 14 000, 4000, and 3500, respectively. Both solutions undergo rapid change on being kept, probably as a result of disproportionation into diphenyl telluride and diethyl telluride. The *ethiodide* separated from methanol in colourless crystals, m. p. 123° (Found: C, 31·2; H, 4·0. $C_{10}H_{15}ITe$ requires C, 30·8; H, 3·9%), $\lambda_{\text{max.}}$ in ethanol 2200 and 2600 Å, ε 29 500 and 2000; it rapidly darkens on exposure to air.

Fluorobenzene.—This had b. p. 83—84°, $\lambda_{\text{max.}}$ in ethanol 2040, 2480, 2540, 2600, 2660, ε 6200, 600, 900, 800, and 330, respectively; the light-absorption data in *cyclo*hexane were identical within experimental error. Chlorobenzene had b. p. 132°, $\lambda_{\text{max.}}$ in ethanol 2100, 2520, 2570, 2640, 2710 Å, ε 7500, 120, 170, 215, and 145, respectively. Bromobenzene had b. p. 157°, $\lambda_{\text{max.}}$ in ethanol 2100, 2510, 2610, 2640, and 2710 Å, ε 8600, 150, 180, 200, and 105, respectively. Iodobenzene had b. p. 188°, n_D^{24} 1·6162, $\lambda_{\text{max.}}$ in ethanol 2260 and 2560 Å, ε 13 000 and 800.

β-Diethylaminostyrene.—This amine was obtained as a colourless liquid in 80% yield by heating under reflux an ethereal solution of equimolar quantities of phenylacetaldehyde and anhydrous diethylamine in the presence of anhydrous sodium sulphate (cf. Mannich and Davidson, *Ber.*, 1936, **69**, 2106; Krabbe *et al.*, *ibid.*, 1941, **74**, 1892); b. p. 128°/7 mm. (Found: C, 82·1; H, 9·9. Calc. for $C_{12}H_{17}N$: C, 82·2; H, 9·8%) (Mannich and Davidson, *loc. cit.*, give b. p. 147—150°/16 mm.), $\lambda_{\text{max.}}$ in *n*-hexane 2280 and 3000 Å, ε 4900 and 12 800; $\lambda_{\text{max.}}$ in ethanol

2280 and 3050 Å, ε 4600 and 12 600. No reaction appeared to occur between phenylacetaldehyde and diethylphosphine under similar conditions.

trans-β-*Bromostyrene*.—This b. p. 104°/17 mm., m. p. 6° (cf. Wright, *J. Org. Chem.*, 1936, **1**, 459) and showed $\lambda_{max.}$ in ethanol 2530, 2560, and 2600 Å, ε 22 000, 23 000, and 22 000, respectively.

Light-absorption Measurements.—Measurements in the 2200—4000 Å region were made by the photographic method, a Hilger instrument being used (cf. Part I, *J.*, 1945, 490). Measurements in the 2000—2200 region were made by the photoelectric method by means of a Beckman instrument (cf. Part VII, *J.*, 1949, 1898). Contrary to some statements in the literature (cf. Moser, *Nature*, 1951, **167**, 656) absolute ethanol (*e.g.*, fractionated " Burnett's " alcohol) is sufficiently transparent for readings to about 2060 Å by the usual method, in which the instrument is calibrated with the solvent-cell in the beam. Below 2060 Å, a differential method must be used in which the instrument is calibrated without a cell in the beam. The extinctions of the solvent-cell and of the solution-cell are then taken in immediate succession and the reading for the first is subtracted from that for the second. The optical density (E) of a 1-cm. layer of highly purified ethanol at 2000 Å is *ca.* 1·5, corresponding to ε ~0·07, in good agreement with the figures given by Klevens and Platt (*J. Amer. Chem. Soc.*, 1947, **69**, 3059).

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON, LONDON, S.W.7.
THE UNIVERSITY, LEEDS, 2.

[*Received, November 2nd,* 1951.]