84. *Studies in Light Absorption. Part IX. The Relation between Absorption Intensities and Molecular Dimensions, and its Application to the Electronic Spectra of Polyenes and Polycyclic Benzenoid Hydrocarbons.*

By E. A. BRAUDE.

The maximum possible extinction coefficients of molecules can be calculated in a simple manner from the molecular dimensions (cf. Braude, *Nature*, 1945, **155**, 753). The actual extinction coefficients for allowed transitions can be calculated from considerations of the effective " chromophore area " and the polarisation direction of the light absorbed. The values thus obtained for polyenes and polycyclic benzenoid hydrocarbons are in good agreement with those observed.

THE intensities of molecular spectra have received increasing attention within recent years from the experimental as well as from the theoretical point of view. On the one hand, the accurate determination of absorption intensities has become an essential feature of the development of absorption spectroscopy as an analytical tool; and, on the other, the calculation of extinction coefficients by the methods of wave mechanics has been attempted by several authors (Mulliken, *J. Chem. Physics*, 1939, **7**, 14, 20, 339, 353, 356, 364, 570; Sklar, *ibid.*, 984; *Rev. Mod. Physics*, 1942, **14**, 232; Bayliss, *J. Chem. Physics*, 1948, **16**, 287; Kuhn, *Helv. Chim. Acta*, 1948, **31**, 1780; Coulson, *Proc. Physical Soc.*, 1948, **60**, 257). These calculations, whilst of great value in helping to establish the nature of the transitions involved, have not been entirely successful quantitatively since they involve the experimental frequency of the absorption band and lead to absorption-intensity values which generally differ in order of magnitude from those observed unless empirical correction factors are introduced.

The present paper sets out a theory of absorption intensities based solely on considerations of molecular geometry, an approach which appears to have been entirely neglected in the past. It is possible to calculate, in a very simple manner, the maximum possible extinction coefficient of a molecule, the only assumption being that the light must fall within the space of the molecular dimensions in order to be absorbed. Such a calculation is quite independent of the nature of the transition or the frequency of the light. Consider light of intensity I falling on a slice of thickness δl of a cell of unit area filled with the vapour or a dilute solution in a transparent solvent of the absorbent at a concentration of c g.-mol./l. Let the average cross-sectional area of the molecule in the plane perpendicular to the direction of the incident light be $[a]$ and let the thickness of the slice be sufficiently small so that there is no superposition of molecules in the direction of propagation of the light. Then we have

Illumination falling on molecules =
$$(\text{area of molecules/total area}) \times \text{total illumination} = cN[a]\delta l \,.\, I \times 10^{-3}$$

where N is the Avogadro number. Assuming that all the illumination falling on the molecules is absorbed

Illumination absorbed $= -\delta I = cN[a]\delta l . I \times 10^{-3}$

Integrating this between the limits $l = 0$ and $l = l$

$$[\varepsilon] = 1/cl . \log_{10}(I_0/I) = 0.4343N[a] \times 10^{-3} = 2.62 \times 10^{20}[a] \qquad . \quad . \quad . \quad . \quad . \quad (1)$$

where $[\varepsilon]$ is the maximum extinction coefficient. For simple molecules, $[a]$ will be of the order of 10 A.^{2}, *i.e.*, 10^{-15} cm.^{2}, so that $[\varepsilon] \sim 10^5$. This result corresponds in order of magnitude to the highest extinction coefficients which have been observed (cf. below).

According to classical theory, the absorption intensity is determined by the " oscillator strength " (f), *i.e.*, the number of oscillating units per molecule. For electronic transitions

$$f = 2.3 \times 10^3 mc^2/N\pi e^2 \times \int\varepsilon d\nu = 4.32 \times 10^{-9}\int\varepsilon d\nu . \qquad . \quad . \quad . \quad . \quad . \quad (2)$$

where m and e are the mass and charge of the electron, c is the velocity of light, and $\int\varepsilon d\nu$ is the integrated band area (Ladenburg, *Verh. d. physikal. Ges.*, 1914, **16**, 769; *Z. Physik*, 1921, **4**, 451; *Physical Rev.*, 1933, **43**, 320; Mulliken, *J. Chem. Physics*, 1939, **7**, 14; Förster, *Z. Elektrochem.*, 1939, **45**, 548). Approximately, $\int\varepsilon d\nu = \varepsilon_{max}.\Delta\nu$ where $\Delta\nu$ is the " half-width," *i.e.*, the width of the bands at points where $\varepsilon = \frac{1}{2}\varepsilon_{max}.$. $\Delta\nu$ is usually of the order of 5000 cm.$^{-1}$ and for $f = 1$, equation (2) gives $\varepsilon \sim 10^5$. The present treatment thus leads to the same general result as the classical one.

In considering the application of the chromophore-area theory to particular molecules and transitions, at least four factors must be taken into account which will generally reduce the actual extinction coefficient ε considerably below the maximum possible coefficient $[\varepsilon]$. First, in polyatomic molecules the effective chromophore area a will generally be smaller than the maximum cross-sectional area $[a]$ because a given electronic or vibrational transition will be confined to a particular atom or group of atoms and only light falling within the space of the atoms and bonds concerned will be absorbed. Secondly, vibrational and electronic transitions are polarised along a particular axis and only the electric vector of the light in that axis will be effective. For randomly orientated molecules, the statistical factor by which the effective incident intensity, and therefore ε, is reduced, is $\frac{1}{3}$. Thirdly, the ground state of the molecule is usually distributed over a number of vibrational states, and in some cases, over more than one electronic state, and if the transition only take place from a particular sub-level or -levels, the extinction coefficient for a photon of a given magnitude (wave-length) will be further reduced by a fraction (χ) corresponding to the fractional population of the sub-level or -levels concerned. Fourthly, even when other necessary conditions are fulfilled, the interaction probability (κ) may be less than unity. Hence

$$\varepsilon = \kappa \times \chi \times \tfrac{1}{3} \times 2.62 \times 10^{20}a = \kappa \times \chi \times 0.87 \times 10^{20}a \qquad . \quad . \quad . \quad . \quad . \quad (3)$$

In the sequel, discussion will be confined to electronic transitions and we shall assume $\chi = 1$. We shall also assume that, for an *allowed* electronic transition, $\kappa = 1$. Hence

$$\varepsilon = 0.87 \times 10^{20}a \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3a)$$

This extremely simple expression for ε involves only one other parameter, the chromophore area a, and should hold for any allowed electronic transition. On this basis the problem of calculating the absorption intensities due to such transitions therefore reduces to the calculation of the chromophore area a.

The application of (3a) can be well illustrated in the polyene and polycyclic hydrocarbon series. The electronic spectra of these have been thoroughly investigated experimentally, and quantitative data for the parent compounds, ethylene and benzene, have recently become available through the work of Klevens, Platt, and their collaborators in the vacuum-ultraviolet region. It is known that the absorption of ethylenic molecules in the visible and ultraviolet regions is due to transitions of the unsaturation (π) electrons. The effective chromophore area a will correspond to the area occupied by the π-electrons (or, more precisely, the area containing a sufficiently high π-electron density) in the plane perpendicular to the line of propagation (magnetic vector) of the light. In order to calculate a it is necessary to know the polarisation direction of the transition since the cross-sectional area will be different in different axes of the elongated polyene and flat polycyclic-hydrocarbon molecules. It is generally accepted on the basis of molecular-orbital theory that the polarisation direction (electric vector) of transitions involving π-electrons is along the axis of the bond, corresponding to a classical direction of incidence (magnetic vector) at right angles to the bond (cf. Bowen, *Ann. Reports*, 1943, **40**, 12).

The polarisation direction can also be deduced from a consideration of chromophore area and the experimentally observed relationship between chain-length and extinction coefficient in the polyene hydrocarbons, taking into account their elongated zig-zag (*trans*)-configuration. Calling the short and long axes of the molecule x and y, if the electronic oscillation takes place along the x-axis, the required classical direction of incidence of the light would be along the y-axis, and the effective cross-sectional area would be approximately independent of the length of the polyene chain and the number (n) of ethylenic bonds. Hence, by (3a), ε should be largely independent of n. If, on the other hand, the electronic oscillation takes place along the y-axis, *i.e.*, along the axis of the ethylenic bonds, the required classical direction of incidence of the light will be along the x-axis, and the effective cross-section of the molecule will increase with the length of the polyene chain. Hence by (3a), ε should also increase with n. This is the relationship experimentally observed (cf. Hausser, Kuhn, and Smakula, *Z. physikal. Chem.*, 1935, **29**, *B*, 385). On the present interpretation, the increase in ε with increasing length of the polyene chain is therefore simply due to the concomitant increase in chromophore area. It will be noted that the deduced polarisation direction is here quite independent of the numerical magnitude of the extinction coefficients but follows directly from the qualitative relationship between ε and n.

Fig. 1.

Absorption of light by ethylene ($\lambda_{max.}$ *ca.* 1650 a.).
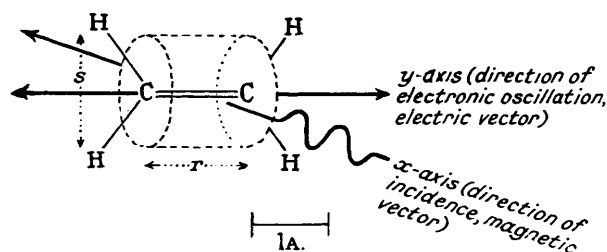
The required direction of incidence for the transitions under discussion having been established, the chromophore area can readily be estimated. Considering first the parent compound, ethylene, it is clear that the space containing an appreciable π-electron density will be considerably smaller than the total space occupied by the molecule; the carbon–hydrogen bonds have no, or very little, double-bond character and the π-electrons can be regarded as confined to the immediate neighbourhood of the carbon–carbon link. For simplicity, they may be imagined to occupy a cylinder of length r and diameter s (Fig. 1) formed by the lateral

Fig. 2.

Absorption of light by polyenes ($\lambda_{max.}$ 2000—5000 a.).
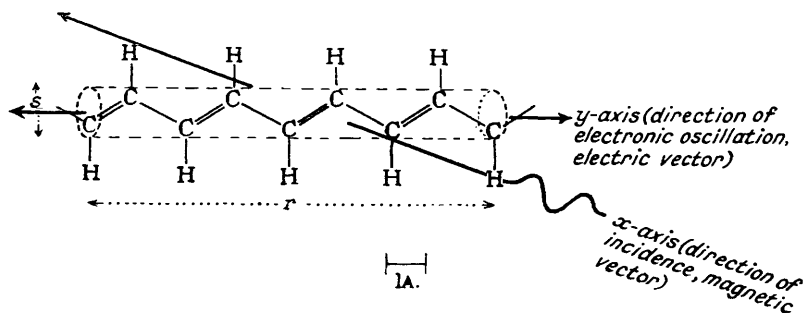
coalescence of the lobes representing the spatial distribution of the p-electrons of the two carbon atoms (cf. Coulson, *Quarterly Reviews*, 1947, **1**, 144). The effective dimensions of the cylinder will depend on the π-electron density required for interaction with a photon. (More precisely, there will be a region in which the interaction probability is unity, or, at any rate, approximately constant, and beyond which κ rapidly falls.) It is reasonable to assume that the necessary electron-density will be of the same order as the electron-density required for interaction with X-rays, and r may therefore be put equal to the carbon–carbon double-bond length 1·35 a.,

whilst s may be estimated from X-ray contour diagrams for substituted ethylenes (*e.g.*, stilbene, Robertson and Woodward, *Proc. Roy. Soc.*, 1937, **162**, *A*, 568) to be about 1·5 A. The required chromophore area will be the rectangular cross-section of the cylinder, *i.e.*, $a = 1·35 \times 1·5 = 2$ A.², whence, by (3a), $\varepsilon = 17,400$. The experimental value, recently determined by Platt, Klevens, and Price (*J. Chem. Physics*, 1949, **17**, 466) is $\varepsilon = 15,000$. The agreement is closer than might be expected in view of the approximations involved in the estimation of a.

In butadiene and the higher members of the polyene series, the conventional carbon–carbon single bonds are known to possess appreciable double-bond character and the π-electron density is distributed over the whole chain of carbon atoms. For simplicity, the π-electrons may again be regarded as occupying a cylinder of diameter 1·5 A. and of length corresponding to the distance r between the terminal carbon atoms, taking into account the zig-zag *trans*-configuration of the polyene chain (cf. Bayliss, *J. Chem. Physics*, 1948, **16**, 287) (Fig. 2). The chromophore area is then given by 1·5r A.², and, by (3a), $\varepsilon = 1·31 \times 10^{20}$ r. The calculated and observed values are shown in the Table. It will be seen that $\varepsilon_{obs.}$ is always somewhat smaller than $\varepsilon_{calc.}$ on this basis and that the ratio $\varepsilon_{obs.}/\varepsilon_{calc.}$ decreases with n. Nevertheless, the agreement is very satisfactory considering the approximate method of estimating a; some reasons for the discrepancies are further considered below.

Calculated and observed molecular-extinction coefficients for polyenes and polycyclic hydrocarbons.

$\varepsilon_{calc.}^{(1)} = 1·31 \times 10^{20}$ r.　$\varepsilon_{calc.}^{(2)} = 1·74 \times 10^{20}$ n　for　polyenes　and　polycyclic　hydrocarbons, $\varepsilon_{calc.}^{(2)} = 1·74 \times 10^{20}$ $(n + 1)$ for diphenylpolyenes.

	$\varepsilon_{obs.}$	r, A.[1]	$\varepsilon_{calc.}^{(1)}$	$\varepsilon_{obs.}/\varepsilon_{calc.}^{(1)}$	$\varepsilon_{calc.}^{(2)}$	$\varepsilon_{obs.}/\varepsilon_{calc.}^{(2)}$
			H·[CH = CH]$_n$·H.			
$n = 1$	15,000 [2]	1·35	17,400	0·86	17,400	0·86
2	21,000 [3]	3·66	48,000	0·44	34,800	0·60
3	53,000 [4]	6·14	81,000	0·65	52,200	1·01
4	64,000 [3]	8·62	113,000	0·57	69,600	0·92
5	51,000 [3]	11·10	145,000	0·34	87,000	0·59
6	70,000 [3]	13·6	178,000	0·39	104,000	0·67
11	65,000 [3]	26·0	340,000	0·19	191,000	0·34
			Ph·[CH = CH]$_n$·Ph.			
$n = 1$	27,000 [4]	3·68	47,000	0·57	34,800	0·78
2	41,000 [4]	6·16	81,000	0·51	52,200	0·78
3	65,000 [4]	8·64	114,000	0·57	69,600	0·93
4	90,000 [4]	11·1	145,000	0·62	87,000	1·03
5	94,000 [4]	13·6	178,000	0·53	104,000	0·90
6	117,000 [4]	16·1	210,000	0·56	122,000	0·96
7	135,000 [4]	18·6	242,000	0·56	139,000	0·97
Benzene ($n = 3$)	46,000 [2]	—	106,000	0·44	52,200	0·88
Naphthalene ($n = 5$)	133,000 [5]	—	176,000	0·76	104,000	1·28
Anthracene ($n = 7$) ...	180,000 [5]	—	248,000	0·72	122,000	1·50
Naphthacene ($n = 9$)...	180,000 [6]	—	320,000	0·56	157,000	1·14

[1] Bayliss, *J. Chem. Physics*, 1948, **16**, 287.　[2] Platt, Klevens, and Price, *ibid.*, 1949, **17**, 466. [3] Data taken from Braude, *Ann. Reports*, 1945, **42**, 105. The data for $n > 3$ refer to alkyl-substituted polyenes.　[4] Hausser, Kuhn, and Smakula, *Z. physikal. Chem.*, 1935, **29**, *B*, 385.　[5] Mayneord and Roe, *Proc. Roy. Soc.*, 1935, **152**, *A*, 299.　[6] Klevens and Platt, *J. Chem. Physics*, 1949, **17**, 470.

In the diphenyl polyenes, the total area containing π-electrons is increased by the terminal phenyl groups, but it is reasonable to assume that transitions involving the polyene chain will only be produced by photons striking the central, acyclic part of the molecule, whereas in the region of the phenyl groups the interaction probability for such transitions will be small. (This is in agreement with molecular-orbital calculations which indicate that the effective length of the conjugated system corresponds to the acyclic portion, cf. Bayliss, *loc. cit.*) Thus, for calculating extinction coefficients of the high-intensity, long-wave-length bands of the diphenylpolyenes, the chromophore area can be taken as approximately the same as for the corresponding unsubstituted polyenes with one extra ethylenic group. The values thus obtained (see Table) are in good agreement with those observed, the ratio $\varepsilon_{obs.}/\varepsilon_{calc.}$ falling consistently within the range 0·5—0·6 for $n = 1$—7.

Benzene exhibits three absorption bands, near 2550, 2000, and 1800 A., ascribed to transitions involving the system of π-electrons. The first two of these are of relatively low intensity and are assigned to " forbidden " transitions, but the 1800 A.-band is of high intensity and must be due to an " allowed " transition (Platt and Klevens, *Chem. Reviews*, 1947, **41**, 301; *J. Chem.*

Physics, 1948, **16**, 832; 1949, **17**, 470; Platt, *ibid.*, p. 484). Similar high-intensity bands of increasing wave-lengths and intensities are exhibited by the higher polycyclic hydrocarbons, and with the first three or four members of the series, the extinction coefficients are approximately proportional to the number of carbon atoms. This means that, as in the acyclic polyenes, the chromophore area also increases approximately linearly with the size of the molecule and indicates that the effective direction of incidence of the light absorbed is at right angles to the plane of the rings, and hence that the electric vector of the transitions lies *in* the plane of the rings (Fig. 3). This is in agreement with molecular-orbital theory (cf. Coulson, *loc. cit.*), and the same has been shown experimentally to apply to the low-intensity bands (Krishnan, *Proc. Indian Acad. Sci.*, 1938, **8**, 487; Scheibe, *Naturwiss.*, 1939, **8**, 478; Scheibe, Hartwig, and Müller, *Z. Elektrochem.*, 1943, **49**, 372). Since the π-electrons are equally distributed over all six carbon–carbon bonds, the chromophore area of benzene will therefore be approximately six times as great as that of ethylene, if any effect due to the thinning-out of the electron density is neglected. Similarly, for the higher members, the chromophore area and $\varepsilon_{calc.}$ will, on this basis, be equal to that of the acyclic polyene with the same number of carbon atoms. As before, the agreement between $\varepsilon_{calc.}$ and $\varepsilon_{obs.}$ is quite satisfactory (see Table). The calculated values are larger than those observed by factors up to about 2. Moecular-orbital calculations for this type of molecule, on the other hand, predict intensities which are smaller than those observed by factors of the order of 10 (Coulson, *Proc. Physical Soc.*, 1948, **60**, 257).

FIG. 3.

Absorption of light by benzenoid hydrocarbons (allowed electronic transition).
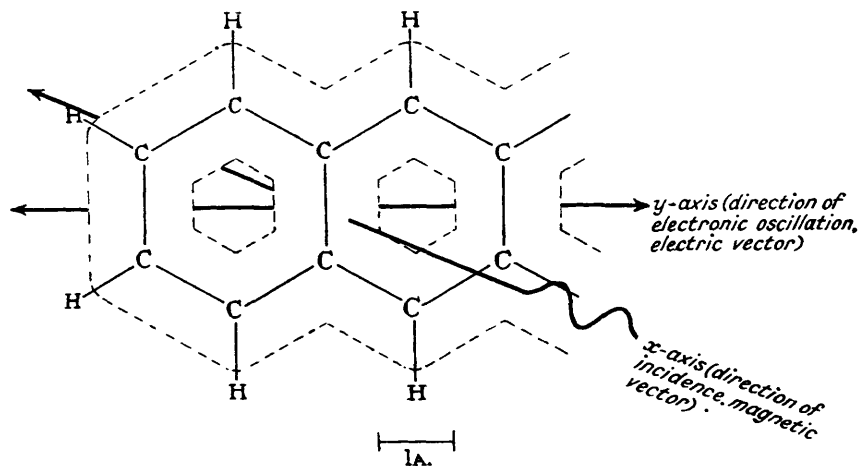
In the preceding discussion of acyclic and cyclic polyenes, the chromophore area has been taken to be proportional to the total number of carbon–carbon bonds in the polyene chain. This involves the assumption that the partial double-bond character of the conventional single carbon–carbon bonds is sufficient to render them as effective as the conventional double bonds for interaction with photons giving rise to π-electron transitions, and, similarly, that the " thinning-out " of the π-electron cloud will not appreciably reduce the effectiveness of the conventional double bonds for interaction with photons. The extent to which these assumptions are justified will depend on the exact relationship between π-electron density and interaction probability, concerning which little is known. An alternative approximation to the above is to assume that the effective chromophore area will be proportional to the *total* π-electron density, *i.e.*, to the number (n) of conventional ethylenic bonds. On this basis, ε should by (3a) also be directly proportional to n, and $\varepsilon_{calc.} = 0.87 \times 10^{20} a_{C=C} \times n$, where $a_{C=C}$ is the chromophore area of an ethylenic bond, *i.e.*, $\varepsilon_{calc.} = 0.87 \times 2 \times 10^{20} n = 1.74 \times 10^{20} n$. The values thus obtained are in better agreement with the experimental data than those calculated previously in the case of the acyclic polyenes, but in less good agreement in the case of the aromatic hydrocarbons (see Table). This indicates that the " thinning-out " effect is more important in the acyclic than in the cyclic series, in agreement with the fact that the effective classical oscillator-strengths per π-electron are also consistently lower in polyenes than in aromatic hydrocarbons (Klevens and Platt, *J. Chem. Physics*, 1949, **17**, 470).

The fact that the observed and calculated values of ε are in fair agreement shows that the assumption made in deriving equation (3a), namely that the interaction probability is approximately unity for allowed transitions, is justified. For forbidden transitions, the interaction coefficient κ will be small and can readily be calculated from the experimental data by means of equation (3). This also provides a useful criterion of whether a transition is allowed or forbidden. Thus for the 2550-A. band of benzene, $\varepsilon_{\text{obs.}} = 200$ and $\varepsilon_{\text{calc.}} \sim \kappa \times 100,000$ (cf. Table), hence $\kappa = 0\cdot002$.

In conclusion, some other factors likely to be responsible for relatively small discrepancies between $\varepsilon_{\text{calc.}}$ and $\varepsilon_{\text{obs.}}$ may be briefly discussed. The data in the Table show that, even for the highest-intensity electronic bands, the observed extinction coefficients are generally slightly lower than those calculated by chromophore-area theory. This is not unexpected in view of the approximations made. In the first place, χ in equation (3) will generally be less than unity since polyatomic molecules usually occupy a number of vibrational levels in the ground state and consequently give rise to an absorption band of considerable width rather than an absorption line. This factor could be accounted for by comparing band areas ($\int \varepsilon d\nu$) rather than extinction coefficients (cf. Mulliken, *loc. cit.*) but the correction is not worth making as the data at present available for $\int \varepsilon d\nu$ are generally less accurate than the values of ε calculated by (3a). Secondly, apart from the intrinsic uncertainty in estimating the dimensions of the π-electron cloud, the effective chromophore area a will generally be smaller than that deduced by the simple considerations outlined above owing to intramolecular shielding effects. These are not easily amenable to quantitative treatment, but a qualitative indication of such effects is provided by the fact that $\varepsilon_{\text{obs.}}$ decreases with increasing substitution in the alkylated olefins (Klevens and Platt, *loc. cit.*). The decrease in absorption intensity usually associated with steric hindrance has been interpreted (Part VI, Braude, Koch, Jones, Richardson, Sondheimer, and Toogood, *J.*, 1949, 1890) as partly due to a decrease in the population of the active vibrational levels, *i.e.* to a decrease in χ, but it is probable that shielding effects are also operative in such cases. The abnormally low value of $\varepsilon_{\text{obs.}}$ in some natural polyenes, *e.g.*, γ-carotene ($n = 11$, see Table) is probably due to similar causes and also suggests the possibility that compounds of this type may not possess the all-*trans*-configuration which has been postulated (Zechmeister, *Chem. Reviews*, 1944, **34**, 267).

Chromophore area considerations are, of course, in no way limited to transitions involving π-electrons, but are equally applicable to other electronic and to vibrational spectra. However, hardly any quantitative extinction measurements in the far ultra-violet or infra-red regions are at present available.