The Triplet–Triplet Absorption Spectra of Some Aromatic Hydrocarbons and Related Substances.

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[Reprint Order No. 4818.]

The absorption spectra of molecules, excited to the metastable lowest triplet state by irradiation of dilute rigid solutions, have been measured by means of a single-beam recording spectrophotometer. The extreme spectral range studied was from 7500 to 2650 Å or to the onset of ordinary electronic absorption. Triplet–triplet spectra are given, plotted on an arbitrary extinction scale, for naphthalene, fluorene, and 7 larger hydrocarbons, and the assignment of the bands observed is discussed. However, the expected $^3E_{2g} \longleftarrow {}^3B_{1u}$ transition in benzene was not detected, nor could the corresponding absorption be found in four related compounds. Spectra are also given for quinoline and *iso*quinoline, together with observations on some larger mono-nitrogen heterocyclics in which there is evidence of photolysis, especially in solvents containing alcohol or ether; triplet absorption was not found in pyridine or acridine. Solvent effects in these spectra are illustrated.

From the rate of decay of triplet–triplet absorption, values of the triplet-state lifetime were found in substantial agreement with those found from the rate of decay of phosphorescence. The concentration of triplet molecules under the experimental conditions used was found, from observations on the ground-state population, to be very small (<5% conversion); this conflicts with McClure's conclusion (*J. Chem. Phys.*, 1951, **19**, 670) that under even milder irradiation, the bulk of the solute molecules are converted into the metastable state. (The remainder of McClure's investigations, where overlapped by the present work, is however confirmed.) Finally, an unusual effect encountered here, which is probably due to photodecomposition, was a marked diminution of triplet–triplet absorption intensity during prolonged continuous irradiation.

(1) The best obeyed of all the selection rules which govern electronic transitions in molecules composed of the lighter elements is the intercombination selection rule, which prohibits transitions between molecular states of different multiplicities. In the vast majority of organic molecules—namely, those which contain an even number of electrons and have ground states with zero total electron spin (singlet states)—the more conventional methods of spectroscopy can hence only provide information regarding the location and vibrational structure of excited *singlet* states. Nothing is revealed concerning the equally interesting triplet (or diradical) states, or, *a fortiori*, of states of higher multiplicity. Experimental access to these states was only made possible comparatively recently through the work of G. N. Lewis and his associates on the mechanism of the fluorescence and phosphorescence which most covalent molecules can be induced to show under suitable conditions. The essence of this work was the demonstration of the rôle played by triplet states in the deactivation of a molecule excited by light absorption, and in particular that phosphoresence, the long-lived emission of energy lower than that absorbed, was in fact emission from the lowest triplet state. The long lifetime of such emission and the extreme weakness of the corresponding singlet–triplet absorption is due to the improbability of the intercombination transition, as prescribed by the selection rule.

To prevent the excited molecule's losing its energy entirely by radiationless collisional and interaction processes, it is usually necessary to disperse the substance as a dilute solution in a rigid solvent; the best glasses from an optical point of view are mixtures of various organic solvents, frozen in liquid nitrogen. The processes known to participate in the luminescence phenomena which may be observed in such solutions are shown in Fig. 1 (cf. Kasha, *Discuss. Faraday Soc.*, 1950, **9**, 14) which refers specifically to naphthalene. The most significant feature of this scheme is the possibility of inter-system crossing between the first excited singlet state S' and the triplet state T. From T both radiative and non-radiative (quenching) processes combine to return the molecule to the ground state S, the mean lifetime of the state T being in this case 2·6 sec. While the molecule is in the state T it may be regarded as a distinct, if metastable, molecular species, having physical properties of its own. In particular, it should be possible to excite the molecule, by passing light of suitable wave-length, to higher triplet states T', T'', . . . (Fig. 1, process 6). This possibility was realized at the very beginning of the systematic investigation of the phosphorescence of organic molecules, by Lewis, Lipkin, and Magel (*J. Amer. Chem. Soc.*, 1941, **63**, 3005), who measured the triplet–triplet (T–T) absorption spectrum of fluorescein. Lewis and Lipkin (*ibid.*, 1942, **64**, 2801) made measurements on diphenylamine, and Grubb and Kistiakowsky (*ibid.*, 1950, **72**, 419) on certain dianthrones. McClure (*J. Chem. Phys.*, 1951, **19**, 670) reported on the first systematic investigation of the T–T spectra of 14 hydrocarbons and related molecules. Our work, which was initiated before Dr. McClure's publication, has been greatly assisted by it. Where the results overlap there is generally good agreement; we have extended the range of compounds examined, located additional bands in some of McClure's compounds, and obtained more precise estimates of T–T intensities.

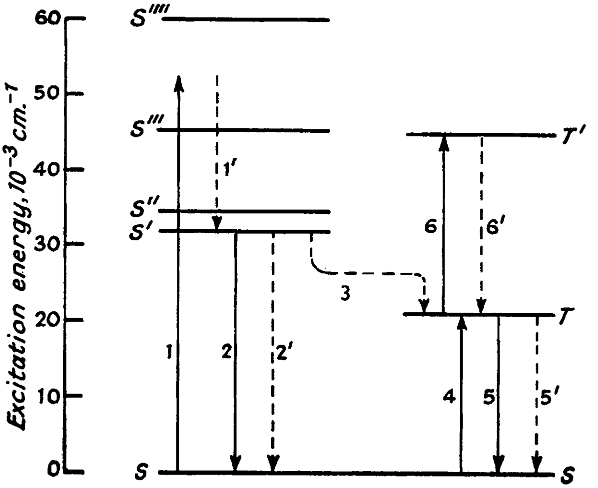

Fig. 1. Known radiative (full lines) and radiationless (broken lines) processes in naphthalene. 1, Excitation to S', S'''', . . .; 1', rapid internal conversion from S'', . . . to S'; 2, fluorescence; 2', fluorescence quenching; 3, inter-system crossing; 4, (weak) singlet–triplet excitation; 5, phosphorescence; 5', phosphorescence quenching; 6, triplet–triplet absorption; 6', internal conversion to T.

(2.1) *Detection and Measurement of Triplet–Triplet Absorption.*—Consideration of Fig. 1 suggests that a triplet–triplet spectrum should be found by measuring the absorption spectrum of a solution in which a steady triplet-state concentration is maintained by simultaneous intense irradiation in the region of ordinary (singlet–singlet, or S–S) absorption. Success in detecting the triplet spectrum will depend, *inter alia*, on the number of triplet molecules which it is possible to generate in the light path. A favourable arrangement therefore is to pass the measuring beam along the axis of a cylinder of rigid solution, which is subjected to crosswise irradiation along its length (cf. Fig. 2). If it is assumed that the molecule has a sufficiently intense T–T absorption in the accessible wave-length range [2600—7500 Å; see (5·3), p. 1603] there are a number of conditions that limit the observation of the spectra. These are listed below and discussed in following sections: (i) A total number of triplet molecules must be maintained sufficient to give measurable absorption. (ii) The triplet molecules must be distributed in the solution so that the spectrophotometer light beam is effectively intercepted. (iii) The T–T bands must not be masked by S–S bands in the same region. The usually overwhelming preponderance of singlet molecules will, in this case, make detection of T–T absorption impossible.

(i) and (ii) both affect the degree to which the illumination from the spectrophotometer source is absorbed by the triplet molecules. For a given distribution of triplet molecules, the absorption is proportional to their number; hence it is important to make this as large as possible by having an intense exciting source and by using high concentrations; intense exciting sources are readily available for substances which absorb at wave-lengths longer than 2500 Å. The effect of concentration in the apparatus of Fig. 2 is, however, complicated by the fact that, with lateral excitation, the triplet molecules are concentrated in the outer regions of the solution. In a too concentrated solution the triplets form in a thin cylindrical annulus in the outermost zone, and therefore present to the spectrophotometer a narrow ring of high optical density surrounding a circular area containing almost no triplet molecules : the apparent average optical density in such a case is thus almost zero. The selection of the most suitable concentration for the solution is thus an important question, and is referred to again in (2.3).

Apart from these controllable factors, high percentage conversions into the triplet state are favoured by long triplet lifetimes and high probabilities of inter-system crossing (Fig. 1, process 3) compared to fluorescence and fluorescence quenching (processes 2 and 2′). Many triplet lifetimes are known but an *a priori* assessment of these other factors usually requires a knowledge of the ratio of luminescence mechanisms more detailed than is at present available.

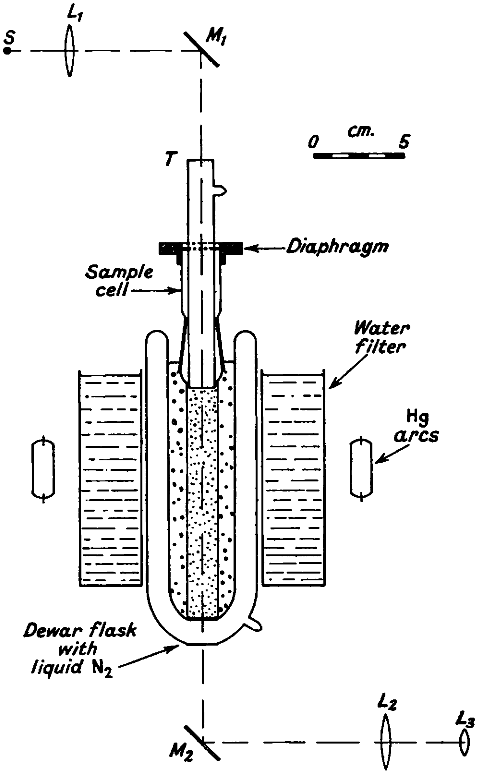

FIG. 2. Apparatus for the measurement of triplet–triplet absorption. S, light source; L_1, L_2, silica collimating and focusing lenses; L_3, entrance lens of Cary spectrophotometer; M_1, M_2, front-aluminized mirrors; T, evacuated tube.

(2.2) *Apparent Optical Density and Extinction Coefficient for Triplet–Triplet Absorption.*—For an absorbing system of non-uniform optical density, the measured density (the light-sensitive element being assumed faithfully to integrate the input energy) is the apparent optical density, ρ_A. We define this to be $\rho_A = -\log_{10}I/I_0$, where I is the total light flux emerging from the specimen, and I_0 the incident flux. If the mean concentration of triplet molecule is c_t, then we arrive at the apparent extinction coefficient ε_A : $\rho_A = \varepsilon_A c_t l$, l being the cell length in cm. In our experiments we have not directly measured c_t. We shall, however, infer an upper limit to c_t in various ways, the corresponding ε_A being then a lower limit to the apparent extinction coefficient for triplet–triplet absorption.

(2.3) *Selection of Concentrations of Solutions.*—The rôle of solute concentration in determining the intensity of triplet–triplet absorption has been described in (2.1), and the selection of the optimum concentration is of obvious importance. Moreover, the distribution of absorbing molecules across the path of the measuring light being non-uniform, apparent and true extinction coefficients are not the same, nor will the ratio of two apparent extinction coefficients be the same as the ratio of the two corresponding true extinction coefficients. However, if the non-uniformity of the triplet distribution is not too great, the difference between such ratios will be very small. Under such conditions, then, even when the mean triplet concentrations are left undetermined, a plot of apparent optical densities against wave-length will differ from a plot of true extinction coefficients only by a constant scale factor. It is important then to use concentrations for which the differences between true and apparent optical densities are minimal, compatibly with the triplet–triplet absorption's being sufficiently intensely developed.

The formal analysis of this question is given by one of us elsewhere (Ross, *J. Opt. Soc. Amer.*, in the press). It is there shown that, with the experimental arrangement used here and with monochromatic irradiation, the apparent optical density of triplet–triplet absorption is a maximum when the optical density for the exciting wave-length is approximately unity; the corresponding concentration may be called the " optimum " concentration. A change in concentration either way by a factor of 2 does not greatly decrease the intensity of excitation-induced absorption. Finally, apparent optical densities are very nearly proportional to true extinction coefficients (for triplet absorption) at solute concentrations up to about 80% of the optimum.

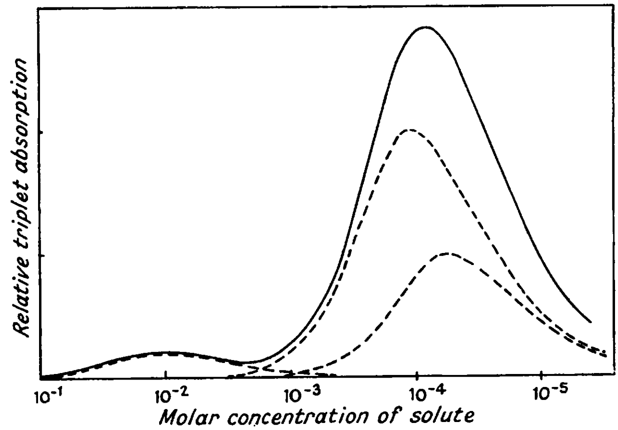

FIG. 3. Relative intensity of triplet–triplet absorption as a function of solute concentration, calculated for a hypothetical solute with three-line exciting source. The broken curves are the contributions to the absorption intensity due to the separate lines, the full curve is their sum. The rigid solution was taken to be in the form of a plane slab, 1 cm. thick, normally and uniformly irradiated from both sides.

It remains to consider briefly the case of irradiation by non-monochromatic light. A specific, hypothetical, example will serve. Suppose the sample is simultaneously irradiated at wave-lengths λ_1, λ_2, λ_3, the relative intensities of these lines being I_1, I_2, I_3, and the extinction coefficients of the solute for the three wave-lengths ε_1, ε_2, ε_3. Now, for monochromatic irradiation (λ_1 alone, say), if the calculated triplet optical density, for measuring light of a given wave-length λ, is plotted against the logarithm of solute concentration, a bell-shaped curve is obtained with the maximum at the optimum concentration for the exciting line.

The height of this maximum is approximately equal to the product $kI_1\varepsilon_t(\lambda)$, $= \beta$ say; the factor k may be taken as being proportional to the triplet-state lifetime. The optimum concentration for simultaneous irradiation at three wave-lengths can then be predicted by adding together three such curves, one for each exciting line. Thus, suppose $I_1 : I_2 : I_3 = 2 : 2 : 1$, that $\varepsilon_1 = 10^{-2}$, $\varepsilon_2 = 10^{-4}$, $\varepsilon_3 = 5 \times 10^{-5}$, and the thickness of the sample is 1 cm. The factor k is virtually constant at low concentrations but falls off in concentrated solutions owing to self-quenching; hence we may take, in this illustration, $k_1 : k_2 : k_3 = 1 : 10 : 10$. Then $\beta_1 : \beta_2 : \beta_3 = 2 : 20 : 10$.

The three curves, and their sum, calculated for this particular situation, are shown in

Fig. 3. It is seen that the optimum concentration is determined very largely by the intense line, but that the maximum of the intensity curve is even flatter than when monochromatic radiation is used. This is clearly a general result, and may be extended to cover irradiation by a many-line or a continuous source, and the optimum concentrations may be calculated, given the source characteristics and the absorption spectrum of the solute. Mostly this information will *not* be available, but it is clear that a concentration unimportantly different from the optimum will have been used if a series of solutions are examined whose concentrations differ from each other by a factor of about four.*

In the present work triplet–triplet spectra were sought in this fashion, and the intensity of triplet absorption, when found at all, was indeed observed to vary with concentration roughly as predicted here.

(3.1) *Apparatus and Accuracy of Results.*—Fig. 2 illustrates the apparatus and method of measurement of *T–T* spectra. A full description is given in (5.1). The apparatus differs from that of McClure in some small but important respects; but in principle it is the same. We recorded the focused light beam after its passage through the frozen sample on a Cary Recording Spectrophotometer. The traces are compared with spectra taken without excitation and with others taken with excitation but without source illumination. The apparent optical density curves shown hereafter are constructed from such sets of three traces. The reproducibility of traces was, in all cases upon which our results are based, better than 5% and rarely worse than 2%. Uniform drifts caused deviations of this kind, due to voltage fluctuations which were ultimately eliminated; or to softening of the glassy solutions by the absorbed light, which appears to be an intrinsic difficulty. Wave-lengths have a probable error not greater than 5 Å, although the maxima of broad peaks are not known so precisely as this. The relative extinction coefficients involve many uncertainties, but comparison of spectra calculated from different experiments with the one substance suggest that, for spectra which were intensely developed (maximum optical density >1), errors in the relative extinction coefficient should not exceed 0·05 unit. The error should vary smoothly with wave-length, so that the shape of a curve is more reliable than the quoted error suggests. Exceptions to this statement are marked in the spectra by dotted lines. Here there are special disturbing factors making precise measurement difficult, such as strong sample fluorescence, discontinuity in the source spectrum, or *S–S* absorption showing structure. Mercury lines occur, as shown in the spectra, by scattering of the exciting light. The spectra are interpolated in these regions, which are usually so narrow that the error introduced is insignificant.

(3.2) *Choice of Rigid Solvents.*—Triplet–triplet absorption spectra were measured in two kinds of glass, consisting of mixed solvents frozen in liquid nitrogen. The mixtures are denoted as EPA (ether–*iso*pentane–alcohol) and PMh (*iso*pentane–methyl*cyclo*hexane).

Triplet spectra measured in the two solvents are not often materially different, there being only a modest wave-length displacement, and perhaps slight modification of the vibrational structure. In other cases, however, there is an important effect. Thus Lewis and Lipkin (*loc. cit.*) as mentioned in (1), found excitation-induced absorption in diphenylamine, our measurement of which is shown in Fig. 4; it is extremely intense, and can be obtained with quite feeble irradiation, the solution turning deep red-purple. Yet in PMh we were unable to find any sign of triplet–triplet absorption. In EPA, however, irradiation of diphenylamine induces a complex series of photoreactions, as Lewis and Lipkin discussed, and the solution after irradiation is found to have acquired a green colour which is permanent as long as the solution remains frozen. It seems likely that the excitation-induced absorption is not due, as Lewis and Lipkin supposed, to diphenylamine itself, but to the green substance, which they concluded was the ion $[(C_6H_5)_2NH]^+$ produced by photo-ejection of an electron. In PMh solution, where there is no potential electron-acceptor present, such photo-oxidation does not occur, and no green coloration is found. No photo-oxidation was detected in any of the hydrocarbons studied, or in the smaller hetero-aromatic compounds. The angular benzoquinolines and benzacridines gave definite evidence,

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* This discussion assumes (*a*) that the ground state is not significantly depopulated [cf. (4.1)] and (*b*) that the exciting wave-lengths are not absorbed by the triplet molecules. In the former case the optimum concentration is higher, but even less critical, than that predicted here; in the latter it is lower.

however, of such an effect in EPA solutions, and with such molecules it appears essential that triplet spectra be measured with hydrocarbon solvents.

(3.3) *Results.*—The spectra measured in this way are shown in Figs. 4—7. The numerical values are in Tables 1 and 3, and the properties of the triplet levels are given in Table 2. The relative intensities of absorption maxima shown in the Figures and Tables and denoted by $\rho_{\text{rel.}}$ are the extinctions relative to the most intense observed band; they also denote, subject to the considerations discussed in (2.3), ratios of extinction coefficients.

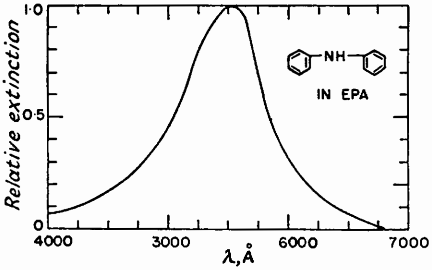
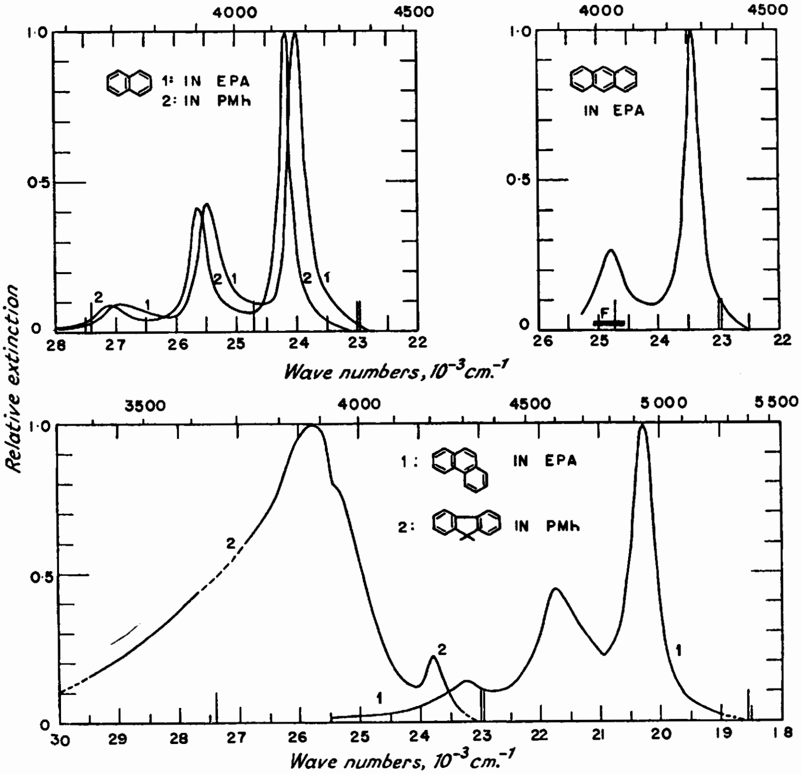


FIG. 4. Irradiation-induced absorption of diphenylamine in ether–*iso*pentane–alcohol (EPA) at 77° K.

FIG. 5.



Triplet–triplet absorption spectra of naphthalene, anthracene, phenanthrene, and fluorene. Temperature 77° K. Curves are broken where their accuracy is reduced. Long vertical lines along the bases of the figures show the positions of mercury lines. Solid bars above the base lines indicate the location of simple fluorescence (*F*) and ordinary absorption (*A*), when present.

The data in the frequency column of Table 1 overlap the results of McClure (*loc. cit.*) in part, and the agreement throughout is good. The intensity of excitation was greater than McClure's, which, together with our ability to distinguish bands overlaid by sample luminescence, accounts for the additional peaks found. McClure recorded two measurements of relative extinction coefficient : he found 0·45 (present work 0·43) for the second peak of naphthalene, and 0·56 (present work 0·45) for the second peak of phenanthrene. In the latter case his result lies outside the probable error of our measurement.

TABLE 1. *Characteristics of observed triplet–triplet absorption spectra.*

Obs. triplet bands cm.$^{-1}$	$\rho_{\text{rel.}}$
Naphthalene in EPA	
*24,000 ± 25	1·00
*25,465 ± 30	0·43
26,950 ± 100	0·10
Naphthalene in PMh	
24,185 ± 25	1·00
25,675 ± 30	0·41
27,175 ± 150	0·09
Anthracene in EPA	
*23,420 ± 30	1·00
24,750 ± 50	0·27
Phenanthrene in EPA	
*20,280 ± 30	1·00
*21,730 ± 50	0·45
23,200 ± 50	0·14
Fluorene in PMh	
23,750 ± 50	0·23
25,300 ± 100	S
25,800 ± 100	1·00

Obs. triplet bands cm.$^{-1}$	$\rho_{\text{rel.}}$
Chrysene in EPA	
*15,900 ± 100	0·11
17,150 ± 50	1·00
17,750 ± 150	S
18,500 ± 150	S
24,630 ± 150	0·18
26,000 ± 250	0·15
1 : 2-*Benzanthracene in EPA*	
*20,450 ± 20	1·00
*21,100 ± 100	S
*21,700 ± 75	0·58
23,050 ± 100	0·54
1 : 2-*Benzanthracene in PMh*	
20,550 ± 20	1·00
21,200 ± 100	S
21,800 ± 100	0·62
23,250 ± 150	0·55

Obs. triplet bands cm.$^{-1}$	$\rho_{\text{rel.}}$
1 : 2-5 : 6-*Dibenzanthracene in EPA*	
*17,100 ± 30	1·00
*18,280 ± 30	0·67
*19,700 ± 100	0·39
*20,000 ± 100	0·40
21,200 ± 150	0·30
23,350 ± 150	0·24
Pyrene in EPA	
19,050 ± 100	0·20
19,400 ± 100	S
20,450 ± 100	0·15
24,070 ± 30	1·00
26,900 ± 200	0·10
3 : 4-*Benzopyrene in EPA*	
19,850 ± 100	0·31
20,950 ± 50	0·95
21,370 ± 50	1·00
22,500 ± 100	0·76

Obs. triplet bands cm.$^{-1}$	$\rho_{\text{rel.}}$
Quinoline in EPA	
20,550 ± 100	0·40
21,050 ± 100	S
21,850 ± 100	0·59
23,400 ± 200	0·98
24,850 ± 300	1·00
~26,300	S
Quinoline in PMh	
(19,000	0·04)
20,600 ± 150	0·22
22,200 ± 150	0·42
23,800 ± 150	0·97
25,300 ± 150	1·00
~26,800	S
iso*Quinoline in EPA*	
20,500 ± 200	0·03
21,800 ± 200	0·09
23,720 ± 50	1·00
25,000 ± 250	0·66
iso*Quinoline in PMh*	
24,150 ± 50	1·00
25,500 ± 150	0·50

S denotes an unresolved shoulder. * Position of band also recorded by McClure (*loc. cit.*).

TABLE 2. *Collected data on triplet states.*

Compound	Lowest triplet (cm.$^{-1}$) [a]	Excited triplets (cm.$^{-1}$) [b]	Max. obs. ρ_A [c]	Lifetime τ_P^0 (sec.) [d]	Triplet colour
Naphthalene	21,300	45,000	>1	2·5 ± 0·1	Yellow
Anthracene	14,700	38,120	1	<0·1	—
Phenanthrene	21,600	41,880	>1	3·3 ± 0·2	Yellow
Fluorene	23,750	47,500	1	5·7 ± 0·3	Yellow
Chrysene	19,800	35,700 44,430	≫1	2·6 ± 0·2	Red
1 : 2-Benzanthracene	16,500	36,950	≫1	0·3 ± 0·1	Yellow
1 : 2-5 : 6-Dibenzanthracene	18,300	35,400	≫1	1·4 ± 0·1	Red-purple
Pyrene	16,800	35,850 40,870	0·4	0·7 ± 0·2	Yellow
3 : 4-Benzopyrene	—	—	0·3	<0·1	Yellow
Quinoline	21,700	42,250	0·3	0·5 ± 0·2	Yellow
*iso*Quinoline	—	—	0·3	1·3 ± 0·3	Yellow

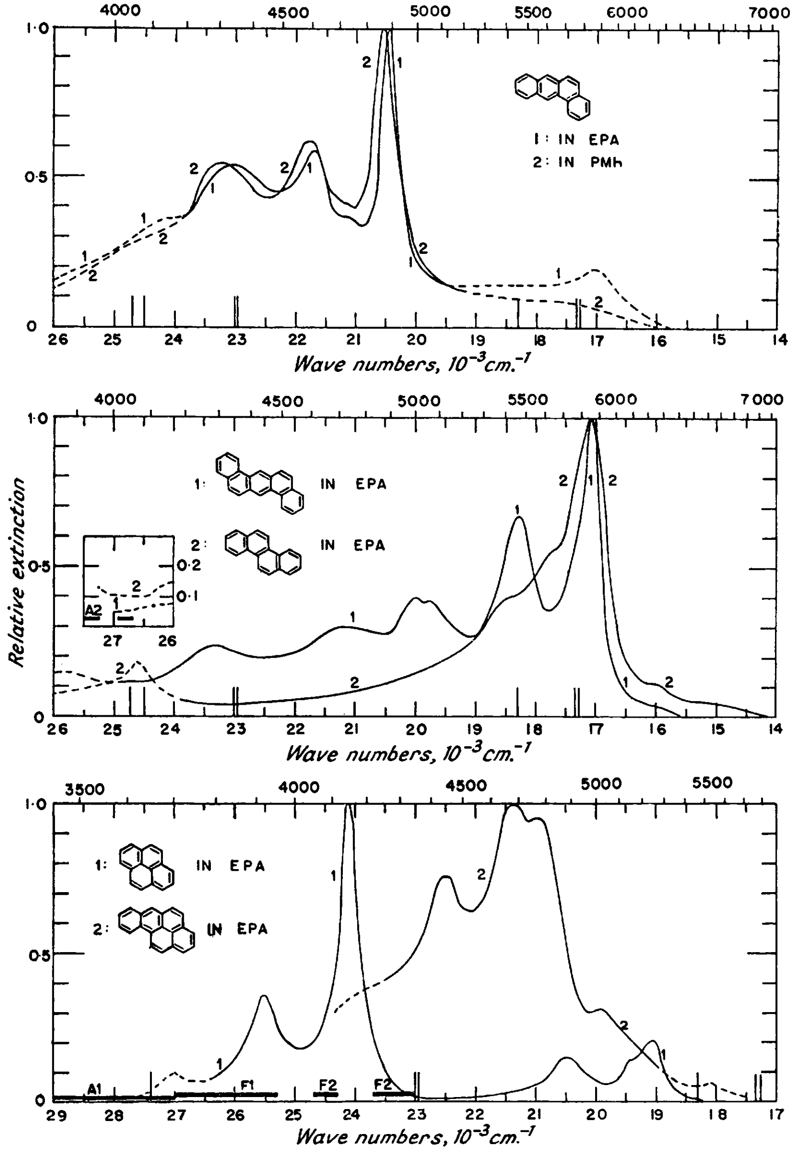
[a] McClure, *J. Chem. Phys.*, 1949, **17**, 905. [b] *I.e.*, total energies calculated from apparent origins of triplet–triplet transitions. [c] Optical densities of strongest bands under maximum available excitation. [d] Measured from rate of decay of triplet absorption.

Tables 2 and 3 contain, as well as quantitative information, a list of the colours of the triplet states. These colours are visible along the length of the irradiated cell, and are a striking feature of the experiments.

(3.4) *Naphthalene, Anthracene, and Phenanthrene.*—Discussion of the negative result in benzene being deferred, we deal with the three simplest aromatic hydrocarbons first. They show very similar, and simple, spectra. Naphthalene and phenanthrene give stronger spectra than anthracene, probably because the last emits absorbed light very efficiently as fluorescence, and also has a short-lived triplet state. The band groups appearing as peaks are all distinctly narrow (300—500 cm.$^{-1}$), and complex structure as found in other molecules is missing. The peaks fall into progressions with spacings approximately :

Naphthalene : 1490, 1500 cm.$^{-1}$ (in PMh) ; 1465, 1515 cm.$^{-1}$ (in EPA)
Anthracene : 1330 cm.$^{-1}$ (EPA)
Phenanthrene : 1450, 1470 cm.$^{-1}$ (EPA)

FIG. 6.

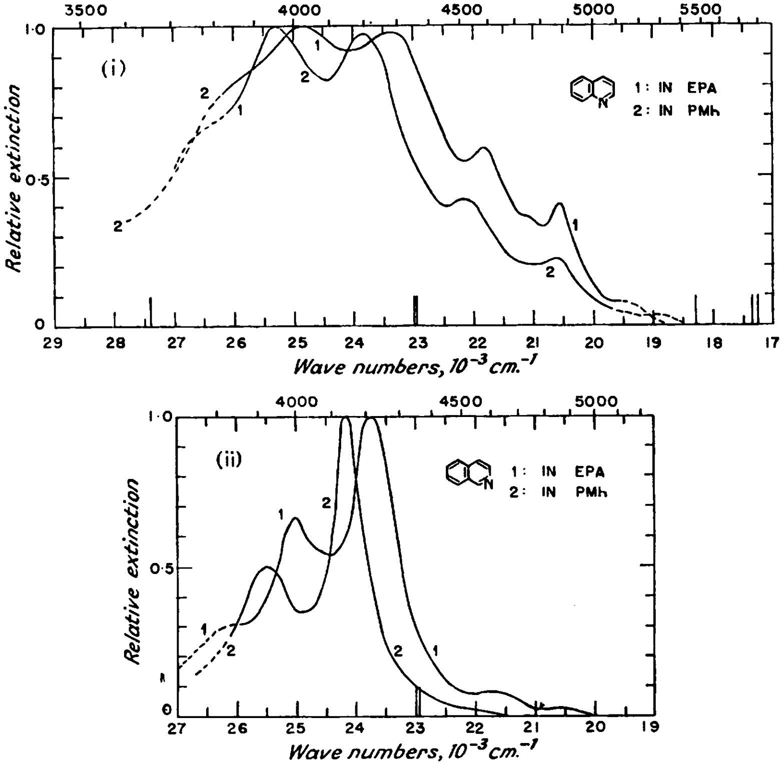


Triplet–triplet absorption spectra of 1 : 2-benzanthracene ; 1 : 2 : 5 : 6-dibenzanthracene and chrysene ; and of pyrene and 3 : 4-benzopyrene. See also notes to Fig. 5.

These frequencies are close to totally symmetric frequencies of about 1400 cm.$^{-1}$ which are a prominent feature of the singlet spectra of these and many other condensed hydrocarbons, and we may assume that similar vibrational modes are involved. These modes involve principally the carbon skeleton (Dr. H. McConnell, personal communication) though their precise nature, and the reason for their prominence, are not yet understood.

The intensity of the band systems must be measured indirectly. The method is described in (4.1); it allows a lower limit to be set to the extinction coefficients from an estimate of the upper limit of the triplet concentration. In naphthalene the extinction coefficient is not less than 10,000 and in anthracene not less than 50,000, leading to oscillator strengths not less than 0·05 and 0·25, respectively. These values, coupled with the simple vibrational pattern, suggest an allowed transition; and one polarized in the molecular plane. Now, powerful theoretical arguments indicate that the lowest triplet levels of naphthalene and anthracene belong to $^3B_{2u}$ of point group D_{2h}; allowed in-plane transitions from this state end at states belonging to $^3B_{1g}$ (long-axis polarized) or ^3A_g (short axis). In the alternative notation which Platt (*J. Chem. Phys.*, 1949, **17**, 484) has recently introduced for use with condensed aromatic molecules, these two possibilities would be described as $(^3K_a$ or $^3K_b) \longleftarrow {}^3L_a$. Experimental evidence does not yet allow a choice to be made between these two. We do, however, believe that McClure's assignment to a forbidden transition is untenable in view of the intensities mentioned above and discussed in (4.1).

FIG. 7.



Triplet–triplet absorption spectra of quinoline and *iso*quinoline. See also notes to Fig. 5.

(3.5) *Fluorene.*—Compounds with less than two fused benzene rings, have not, with this one exception, so far yielded *T–T* spectra. Fluorene gives a poorly resolved spectrum, almost certainly with less structure than the *S–S* spectrum would show at equally low temperatures.

(3.6) *Larger Condensed Hydrocarbons.*—The triplet absorption of the benzanthracenes and chrysene are very intense, and are developed sufficiently for measurement with only about one-tenth of the irradiation intensity necessary for the 2- and 3-ring hydrocarbons. These spectra show considerable vibrational structure with, at the same time, insufficient regularity in the band-spacings to justify attempting vibrational analyses. In the benzanthracenes, the principle bands are well resolved, but in chrysene the resolution is surprisingly poor, the difference being enough to suggest that the transitions belong to different series, in Platt's sense (*loc. cit.*). Chrysene is further distinguished by showing in the region examined two electronic transitions, the second occurring around 25,000 cm.$^{-1}$ with about one-fifth of the intensity of the first. This transition overlaps the intense singlet-absorption spectrum and is overlaid by two strong mercury lines; the measurements here are therefore somewhat qualitative, although the existence of the new transition is definite.

It is necessary to comment on our spectra of 1 : 2-benzanthracene. To the long-wave-length side of the principal absorption band there was found in EPA solution another band at 17,000 cm.$^{-1}$; in PMh there was marked absorption with no positive maximum. No absorption in this region was reported by McClure. In our measurements, absorption in this region was observed to decay at about one-quarter of the rate of the rest of the spectrum [cf. (3·9)], and is consequently rejected as spurious. Whether it is due to a photo-oxidation product or to impurity (possibly dibenzanthracene, from the nature of this absorption) we are unable to say. The chromatographic purification was reported as " difficult " but this absorption was the same both before and after such refinement.

Chrysene and possibly dibenzanthracene are distinguished from the previous compounds by showing at least one weak vibrational band on the long-wave-length side of the strongest peak. These bands are unusually weak to be accounted for simply by the Franck–Condon effect, but the transitions themselves appear to be so intense that it is most unlikely that the long-wave-length bands are the origins of forbidden transitions made feebly allowed by solvent perturbations.

In contrast to the intense absorption of the three cata-condensed hydrocarbons above, pyrene and 3 : 4-benzopyrene absorbed only comparatively weakly under full irradiation. Pyrene shows two distinct absorption systems which must correspond to two distinct upper triplet levels. The principal bands in each system are spaced at around 1400 cm.$^{-1}$, and in view of the high molecular symmetry this could be a single predominant totally-symmetric frequency. Again, the lowest energy band in each transition is the most intense. It is not surprising that the comparatively unsymmetrical benzopyrene should show a completely different spectrum with no apparent vibrational progression and reaching maximum intensity only with the third or fourth vibrational band.

In none of these five compounds do we suggest assignments for the electronic levels concerned, except to note that the transitions are almost certainly allowed.

(3.7) *Quinoline,* iso*Quinoline, and Other Nitrogen Heterocycles.*—No spectra were found in pyridine [see (3.8)] or acridine, but both quinoline and *iso*quinoline gave weak absorption. These differ markedly from naphthalene, having an extended series of poorly resolved vibrational bands. The spectra differ somewhat according as they were measured in EPA or PMh solutions, but in interpreting the curves of Fig. 7 it is to be recognized that these spectra were weakly developed, and that errors in the intensity scale could be as large as 0·2 unit. For this reason the failure to find in PMh solutions of *iso*quinoline the long-wave-length bands just detectable in EPA is not proof positive of their non-existence, while in the spectrum of quinoline in EPA it would be premature to speculate on the curious structure in the region 20,000—21,000 cm.$^{-1}$. A definite effect of change of solvent, however, is a blue shift in each case of about 400 cm.$^{-1}$ on passing fron EPA to PMh; there is no evidence of photolysis in solutions in EPA.

Allowance being made for the difficulty in locating the band maxima, it appears that both quinolines show long progressions in a single frequency of about 1400 cm.$^{-1}$, about the same as the only frequency observed in naphthalene. Compared with those of naphthalene, the maxima are shifted slightly towards long wave-lengths, but the first band is no longer the strongest. This change is much more marked in the α-hetero-molecule, quinoline, than in the β-isomer. Presumably at the comparatively high energy of the upper triplet state (total about 41,000 cm.$^{-1}$) the unbound electrons of nitrogen are interacting significantly with the π-system. This interaction might be expected to manifest itself also in the ordinary singlet absorption to levels of the same or higher energy, but although the singlet spectra of the two quinolines show less structure in the 2500 Å region than does naphthalene, the required measurements at low temperatures have not been made.

With the four non-linear benzoquinolines and benzacridines, photoreactions occur in EPA, and irradiation-induced absorption is greater in that solvent than in PMh. All absorption bands, in either solvent, were no better resolved than those of quinoline. We record in Table 3, as preliminary results only, the features of the observed spectra; the lifetime measurements in that Table were determined from the rate of decay of absorption.

TABLE 3. *Triplet–triplet absorption of* N-*heterocyclics.*[a]

Solute	Solvent	Intensity of absorption	Absorption maxima (Å)	$\rho_{\text{rel.}}$	$\tau_P{}^0$ (sec.)	Remarks
7 : 8-Benzoquinoline	PMh	Weak	5050	1·0	1·4	—
			~4650	0·9		
	EPA	V. strong	5000	1·0	2·1	Colour during irradiation deep orange. Permanent change suspected
			4650	0·8		
			~4400	0·5		
5 : 6-Benzoquinoline	PMh	Weak	5100	1·0	1·8	—
	EPA	V. strong	5170	1·0	2·6	Colour during irradiation deep orange; after irradiation, permanently pink, bands at 5600 and 5100 Å
			4820	0·8		
			~4520	0·5		
1 : 2-Benzacridine	PMh	V. weak	4970	1·0	<0·5	—
	EPA	V. strong	4970	1·0	0·3	Colour during irradiation deep orange; afterwards solution showed one very weak permanent absorption band at 4270 Å
			4700	0·9		
3 : 4-Benzacridine	PMh	None	—	—	—	—
	EPA	Moderate	5100	1·0	0·4	Colour during irradiation yellow. No evidence of permanent change
			4800	0·9		

[a] All solutions of approx. concentration 2×10^{-4}M. Spectra examined from 7000 Å to the onset of ordinary absorption around 4000 Å. Below 4300 Å most records showed intense fluorescence. All absorption bands detected were very broad, and in most cases absorption extended over most of the spectral range examined.

(3.8) *Benzene and Other Monocyclic Compounds.*—*T–T* absorption was sought, under widely varying conditions, in solution of benzene, hexamethylbenzene, diphenyl, diphenylamine, and pyridine. With use of the " Pointolite " hot tungsten light source, solutions of each substance were scanned between 7500 and 3050 Å; benzene and pyridine were further examined between 3500 and 2650 Å, the carbon arc being used. In no case was *T–T* absorption by these molecules found. The absorption in EPA solutions of diphenylamine is considered to be due to a photochemically derived substance [see (3.3)]. These negative results, added to those of McClure (*loc. cit.*) for aniline and phenol, call for some discussion.

Every theoretical and analogical consideration suggests that there should be at least one absorption band, and probably more, in the spectral region examined. Specifically a non-empirical calculation of the energy levels of benzene by Parr, Craig, and Ross (*J. Chem. Phys.*, 1950, **18**, 1561) predicts an allowed in-plane $^3E_{2g} — ^3B_{1u}$ transition at 18,500 cm.$^{-1}$. Forbidden bands are predicted at 5000 and 33,000 cm.$^{-1}$. The precision of these calculations is not great—comparison with available experiment shows up errors of as much as +15,000 cm.$^{-1}$—but in these cases there are definite reasons why the calculated levels should be too high (they are levels whose wave functions, in the language of the valence-bond theory, are expressible only in terms of polar structures—cf. Craig, *Discuss. Faraday Soc.*, 1950, **9**, 5); these considerations do not apply to either the $^3B_{1u}$ or $^3E_{2g}$ levels. Moreover, and probably more convincingly, the existence of transitions at 24,000 and 23,420 cm.$^{-1}$ in naphthalene and anthracene naturally suggests that there should be a triplet transition around 25,000—30,000 cm.$^{-1}$ in benzene.

Failure to detect absorption bands may result from too low a concentration of triplet molecules, or intrinsic weakness in the bands themselves. A forbidden *T–T* absorption of about the same strength as the benzene *S–S* system at 2600 Å might well escape detection. In naphthalene we obtained a *T–T* optical density of 1·0 in an allowed transition by intense irradiation of a 0·0004M-solution. An optical density of about one-fiftieth of this was detectable in our experiments, so that with an equal concentration of benzene triplets a transition less than one-fiftieth of the naphthalene strength might have escaped detection.

In the singlet series the ratio of forbidden to allowed intensities is usually 1/100 or less, so that from considerations of oscillator strength the possibilities are marginal. On the other hand, if the transition in benzene is allowed then its non-appearance must be due to too low a steady concentration of triplet molecules.

This question of the steady concentration of triplet molecules has been analysed by McClure (*loc. cit.*) in terms of the processes depicted in Fig. 1, for cases in which there is no photochemical decomposition. Such an analysis was applied here, the data on triplet lifetimes, quantum yields of phosphorescence, and concentration quenching given by Gilmore, Gibson, and McClure (*J. Chem. Phys.*, 1952, **20**, 829) being used with appropriate data on the extinction coefficients for the exciting light. This led to the expectation that, possibly in benzene, and certainly in some of its derivatives, triplet concentrations should be achieved higher than were found with naphthalene.

The details of this argument we omit, since very recently Gibson, Blake, and Kahn (*ibid.*, 1953, **21**, 1000) have shown that under our experimental conditions, benzene is fairly rapidly decomposed to hexatriene by light of wave-length 2537 Å. This product is formed in the outer layers of the rigid solution, and its high extinction coefficient at 2537 Å would effectively filter out the exciting light and prevent the formation of triplets, or further hexatriene, within the bulk of the solution. This photoreaction, which may be related to some of our own observations on higher hydrocarbons [cf. (4.2)], could well account for the failure to find triplet–triplet absorption in benzene and its derivatives. The most reasonable alternative explanation for this failure is that the benzenoid compounds have strong triplet–triplet absorption at 2537 Å; the triplet molecules themselves would then absorb the exciting light.

(3.9) *Measurement of Phosphorescence Lifetimes.*—The mean lifetime of the triplet state (or observed phosphorescence lifetime, $\tau_P{}^0$) has hitherto always been determined from measurement of the rate at which phosphorescence intensity decays after the cessation of irradiation. The decay is strictly of first order, and the reciprocal of the rate constant is the mean lifetime, as normally defined. Lifetimes can also be determined from the rate of decay of triplet–triplet absorption, again after the cessation of irradiation. The method is less general than the phosphorescence-decay technique, but is useful when the phosphorescence is particularly feeble or occurs in the infra-red where intensity measurements are difficult. This is so, for example, with anthracene, for which even the wave-length of the phosphorescence is not definitely known (cf. Reid, *ibid.*, 1952, **20**, 1214). Triplet-state lifetimes were here measured by setting the spectrophotometer at fixed wave-length, usually the peak of a triplet absorption band, and recording intensity as a function of time. During the course of the record, the lamps were switched off, and the intensity transmitted by the frozen solution rose to its limiting value corresponding to no triplet absorption. In calculating the decay constants due account was taken of the fluorescence and scattered light whose decay was instantaneous. It will be noticed that the method is valid even if singlet–singlet absorption is present and the ground state is measurably depopulated, since increase in the singlet absorption intensity will take place at precisely the same rate as that at which the triplet absorption decays. The accuracy obtainable by this method depends on the response of the recorder. The use here of a mechanical recorder meant that only mean lifetimes greater than 0·1 sec. could be distinguished from zero. The accuracy of the measurements determined from the constancy of the rate constants during the decay was at best of the same order.

For accurate measurements of this kind it is essential that triplet–triplet optical densities be as nearly as possible proportional to extinction coefficients. Because of the non-uniform distribution density to triplet molecules across the cell the relation between optical density and number of triplets is non-linear. Serious deviations from linearity will lead to rate constants for the decay which apparently increase with time. This was in fact observed in some solutions of concentration well above the " optimum " [the word being used in the sense defined in (2.3)], but mostly the calculated rate constants remained sensibly constant throughout the decay. Indeed, we have taken this observed constancy to justify the assumption of proportionality between optical density and extinction coefficients in the corresponding solutions.

The rate constants thus measured are included in Tables 2 and 3. In Table 2, seven of the deduced lifetimes can be compared with those measured by McClure (*ibid.*, 1949, **17**, 905), by the phosphorescence-decay method. Agreement is excellent, except for fluorene and pyrene for which McClure's figures are 4·9 ± 0·2 and *ca.* 0·2 sec., respectively. A decision between the values offered must await remeasurement, although possibly those found from phosphorescence decay, being subject to fewer complicating factors, are to be preferred. Of the remaining lifetimes given, that of anthracene is particularly interesting in view of the long lifetimes of benzene, naphthalene, and phenanthrene. The lifetimes of the heterocyclics confirm McClure's qualitative observation that such compounds appear to have the relatively long lifetimes characteristic of the parent hydrocarbons.

(4.1) T–T *Extinction Coefficients and the Concentration of Triplet Molecules.*—The steady concentration of solute molecules in their triplet states depends, *inter alia*, on the intensity of irradiation, and must be separately measured if the arbitrary intensity states of Figs. 4—7 are to be replaced by scales of extinction coefficients. McClure (*loc. cit.*) measured *T–T* optical densities as a function of excitation intensity and deduced the extinction coefficient by a relation, theoretically derived, between the reciprocal optical density and the reciprocal excitation-intensity. Values obtained by this method are, we believe, much too low.

Since population of the triplet state implies depopulation of the singlet state, the intensity of the *S–S* spectrum must diminish under conditions in which the *T–T* spectrum is observed. In principle, measurement of the intensity decrease in the *S–S* spectrum should give an accurate value of the population of the triplet state. In practice, under our conditions of excitation, the depopulation is undetectably small, so that only an upper limit can be given to it, and consequently only an upper limit assigned to the triplet concentration. The method is particularly simple for molecules having an *S–S* absorption system in a spectral region clear of *T–T* absorption. This occurs in naphthalene, for which we also have values of extinction coefficient at low temperature (Passerini and Ross, *J. Chem. Phys.*, in the press). At 3110 Å, the position of the 1 $\longleftarrow$ 0 band of the first singlet sytem, the extinction coefficient is about 400. A solution of naphthalene of concentration 0·0002M (calculated after allowance for contraction on freezing) gave a *T–T* optical density of 1·08 at its maximum at 4160 Å. At 3110 Å the *S–S* optical density was 0·8 and no difference in transmission could be detected with and without the excitation. Thus the number of molecules converted to give a *T–T* optical density of unity formed so small a fraction of the total as to remain undetected. A conservative estimate, allowing for the fact that not all of the cell was illuminated, is that not more than 5% of molecules were in the triplet state; the minimum value of the triplet extinction coefficient is 10,000. It is to be noted that the *T–T* optical density is an apparent density, in the sense of (2.2), and leads to a small extinction coefficient; for the same reason, that the singlets lost by depopulation are not uniformly spread across the cell, the *S–S* intensity change is ***more*** sensitive than expected on the basis of calculation we have used. We believe therefore that 10,000 for the *T–T* extinction is conservative to an extreme degree, and that this lower limit might be increased by at least a factor 2. In a similar study of phenanthrene the *T–T* optical density was 1·8 and no depopulation could be detected. A lower limit deduced as in naphthalene is 18,000. In anthracene a solution of $5{\cdot}9 \times 10^{-6}$M was examined in the same way. Its *T–T* optical density was 0·13. Its singlet spectrum showed no difference under excitation throughout the whole of the region 3850—3500 Å, which includes three strong maxima (3785, 3735, and 3595 Å). The extinction coefficient for *T–T* absorption at the 23,420 cm.$^{-1}$ maximum is not less than 45,000.

McClure's values for naphthalene, anthracene, and phenanthrene are 480, 2800, and 1560. In further support of our much higher values we refer briefly to two other lines of evidence. At low triplet concentrations, concentration increases almost linearly with increasing excitation, but falls off as saturation is approached. In a solution of anthracene $7{\cdot}8 \times 10^{-5}$M (run 1, Table 4) the optical densities at the wave-length of maximum absorption produced separately by three 125-w mercury lamps were 0·39, 0·41, and 0·25, all ±0·02. The sum of these figures is 1·05 ± 0·06. The three lamps operating simultaneously gave 1·02 ± 0·03 which, within experimental error, shows that the triplet concentration is still in the linear region of its dependence on excitation, implying the very low conversion of 1 or 2% at most. Finally, a number of EPA solutions of naphthalene and anthracene of steadily decreasing concentration were examined under the maximum available excitation. Considerable *T–T* absorption was shown by solutions so dilute that, even assuming *complete* conversion into triplet state, values of extinction coefficient are implied greater than those of McClure. These are summarised in Table 4. These lower limits are of course less than those in the penultimate line of Table 4 derived from depopulation measurements.

TABLE 4. *Lower limits to extinction coefficients of strongest triplet–triplet bands.*

Solute	Naphthalene		Anthracene		
Run No.	1	2	1	2	3
Concn. c (mole/l.)	$4{\cdot}4 \times 10^{-5}$	$2{\cdot}2 \times 10^{-5}$	$7{\cdot}8 \times 10^{-5}$	$2{\cdot}0 \times 10^{-5}$	$5{\cdot}9 \times 10^{-6}$
Irradiated path-length l (cm.)	5·0	5·0	6·0	5·0	5·5
T–T optical density ρ_A	0·90	0·70	1·20	0·31	0·13
Minimum extinction coeff., min. $\varepsilon = \rho_A/cl$	4000	6400	2200	3100	4000
Min. ε from ground-state depopulation	10,000		45,000		
ε (McClure, *loc. cit.*)	480		2,800		

(4.2) *The Slow Decrease in Triplet–Triplet Absorption under Continuous Irradiation.*—The estimates at which McClure, on the one hand, and the present authors, on the other, have arrived at the triplet state concentrations produced by irradiation of frozen solutions could hardly be more different.* The difference is far greater than can be accounted for by experimental errors, and can only be due to unsuspected complications in the two different methods used. The technique here of observing the ground-state population with and without excitation leads directly to an upper limit for the triplet concentration. McClure's method, outlined in (4.1), was much more inferential, and depended for its reliability on the transition scheme of Fig. 1 being complete and particularly on the absence of photodissociation, etc. Indeed, McClure was careful to point out that, in the event of such additional processes actually occurring his estimates of concentration and extinction coefficients could be greatly in error.

What the precise nature of these additional processes might be we do not understand at all fully. By far the most probable complication is photodecomposition, as referred to earlier (3.8) in connection with benzene. In the present work this was indicated especially in measurements on fluorene and naphthalene. The observations were in the nature of a slow but steady decrease in the overall intensity of triplet–triplet absorption under continued irradiation. The intensity of the singlet spectrum remained unaltered during the same experiments, showing that the effect of the irradiation, whatever its nature, did not permanently involve the bulk of the solute molecules in the measuring light-path.

We can illustrate this with a specific example. A naphthalene solution of concentration $1{\cdot}9 \times 10^{-4}$M was irradiated for a total of 95 min. Initially, the optical density of triplet absorption (strongest band) was 1·12; after 20 min. this had decreased to 0·38. With further irradiation the decrease continued, reaching apparently a limiting value of 0·25 (22% of the initial optical density) towards the end of the experiment. The rate of decrease of absorption intensity was approximately exponential. Interruption of the irradiation for periods up to 30 min. did not cause any recovery of the diminished absorption although our experimental technique did not allow the interesting experiment to be performed of melting and refreezing the glass to see whether the diminished absorption was then restored.

With more dilute solutions, the fall was even more striking. Thus, in the naphthalene solutions of runs 1 and 2 of Table 4, only 20 minutes' total irradiation was enough to reduce intensity of triplet absorption to 14% and 11%, respectively, of the initial value.

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* The present demonstration of a low triplet concentration does not conflict with the high concentrations (up to 89%) of total solute found by Lewis, Calvin, and Kasha (*J. Chem. Phys.*, 1949, **17**, 804) in their work on the paramagnetism of acid fluorescein ($\tau_p{}^0 = 2{\cdot}8$ sec.) in boric acid glass, for in their measurements a much greater irradiation intensity was used.

This kind of effect should be accompanied by a diminution in the intensity of phosphorescence, and this was indeed noticed by Nauman (Thesis, University of California, Berkeley, 1947) in respect of toluene and numerous other substances. The original intensity of phosphorescence was restored by melting and refreezing the solutions. The light-filtering effect of the slowly-formed photodecomposition products could well cause our observed diminution in triplet absorption, and hence account for the failure of McClure's inferential method of arriving at extinction coefficients. This explanation is not unique, however, and has some difficulties. Thus, with anthracene, for which McClure again obtained low extinction coefficients, the triplet–triplet absorption did *not* fall off demonstrably. Again, it is not clear why this absorption should fall to a limiting value distinctly in excess of zero. A final decision concerning this effect must await further study.

EXPERIMENTAL

(5.1) *Absorption Cell.*—In order to transmit short-wave-length radiation, the cell containing the sample, and the Dewar vessel in which it stands, must be largely constructed of silica; for the same reason, liquid nitrogen is the only convenient refrigerant. The cell containing the solution was a silica tube terminating in a flat silica disc. At the top of the tube was a ground cone, over which fitted a Pyrex socket with a short length of tube attached. Across the top of the socket was stretched between steel flanges a Neoprene diaphragm with a circular hole in the centre; metal and glass were bonded with Araldite resin. Through the hole in the diaphragm there penetrated an evacuated Pyrex tube with flat silica end-plates, the lower plate providing a flat top surface for the solution. The lower part of this tube was externally platinized to prevent stray light from being scattered into the system from the surface of the quietly boiling refrigerant. The evacuated tube could slide through the diaphragm, so allowing the cell length to be varied. The cell stood in an unsilvered silica Dewar vessel, having flat inner and outer bottom surfaces. The contact between the bottom of the cell and the floor of the Dewar vessel was never precise enough to exclude liquid nitrogen, and without further precautions the light path would thus have been interfered with by streams of nitrogen bubbles. These were excluded by pushing the end of the cell through a hole in a small square of cloth, and later packing the cloth down firmly round the bottom of the cell. It was then almost always possible so to adjust the location and tilt of the cell so that no bubbles crossed the light path. The cloth packing served also to prevent ice crystals in the nitrogen from drifting under the cell. In use, hot air was directed against the lower surface of the Dewar flask, and ice-free liquid nitrogen was supplied every few minutes.

(5.2) *Irradiation of Rigid Solutions.*—As shown in Fig. 2 the cell was irradiated around the circumference. Excitation was provided either by up to three Osram type-MB/V 125-w medium-pressure mercury arcs (from which the glass envelopes had been removed), with reflectors, or by the spiral, low-pressure mercury–neon arc described by Ingold and Wilson (*J.*, 1936, 944) placed alongside the cell. The former lamps emit chiefly in the visible, and at 3346 and 3650 Å (these last lines being used for the excitation of most of the substances examined); the latter is an exceedingly intense source of the 2537 Å line, but its emission could not be very efficiently concentrated on the cell. The medium-pressure lamps were the more commonly used. Their infra-red emission being considerable, it was essential that they be shielded from the sample by a suitable heat filter, since neither nitrogen nor silica absorbs in the near infra-red. An annular silica filter cell was used, shown in section in Fig. 2; it was filled with distilled water.

The length of the cell actually irradiated was at most 10 cm.; the medium-pressure lamps being only 3 cm. long, this illumination was not uniform along the length of the cell. As far as possible the exciting lamps were screened to prevent stray light from entering the spectrophotometer; a small amount of such exciting light was found useful, however, the mercury lines thus detected being used for wave-length calibration.

(5.3) *Light-absorption Measurements.*—The source *S* (Fig. 2) was usually a 1000 c.p. " Pointolite " lamp. Light from *S* was collimated, passed downwards through the sample, and then reflected along the optic axis of a Cary Recording Spectrophotometer (Model 10). It was focused at the focus of the entrance lens of the spectrophotometer, *i.e.*, at the point normally occupied by the light sources in the conventional use of this instrument. The spectrophotometer was used on *single-beam* operation, recording intensity against wave-length. The intensity at a wave-length λ depended on the brightness of the lamp, the slit widths, and the alignment of the optical system. A typical trace of the recorder pen deflection, $I_0(\lambda)$ against λ, for light passing through a rigid glass without irradiation is shown in Fig. 8; the curve has a flat maximum at about 5500 Å and falls off rapidly to the red and less rapidly toward the violet. Below 4050 Å gaseous emission bands become increasingly prominent and, near the glass cut-off at 3000 Å, they provide most of the intensity. With one single instrument setting a spectrum could be measured over about 500 Å; settings were then changed and a further stretch was measured until the whole spectrum was covered. The focused light beams gave pen deflections comparable to those obtained in normal Cary operation with the tungsten lamp. Typical slit widths are given in Table 5.

TABLE 5. *Typical working slit widths using* 1000 *c.p. light source.*

Wave-length (Å)	7600	7000	6000	5000	4000	3600	3200
Linear slit width (mm.)	0·27	0·075	0·016	0·014	0·027	0·054	0·20
Spectral slit width { (Å)	97	23	3·4	1·8	1·7	2·4	6·0
Spectral slit width { (cm.$^{-1}$) ...	168	47	9·4	6·8	11	19	59

For measurements below 3000 Å, and in some cases below 3500 Å, the positive crater of a carbon arc gave a continuous source of high brightness. Fluctuations were somewhat troublesome but qualitative observations were possible with it, and moderately strong *T–T* bonds would undoubtedly have been detected.

Measurements with fogged photographic plates of known spectral characteristics showed that the deflection of the recorder-pen was strictly proportional to the incident light intensity at any wave-length. If, when the sample was irradiated, triplet–triplet absorption occurred, then the intensity at wave-length λ fell from $I_0(\lambda)$ to $I_t(\lambda)$, say, although this measured intensity would sometimes include a contribution $I_s(\lambda)$ due to luminescence of the solution and scattered exciting light. The apparent optical density (2.2) at wave-length λ was then

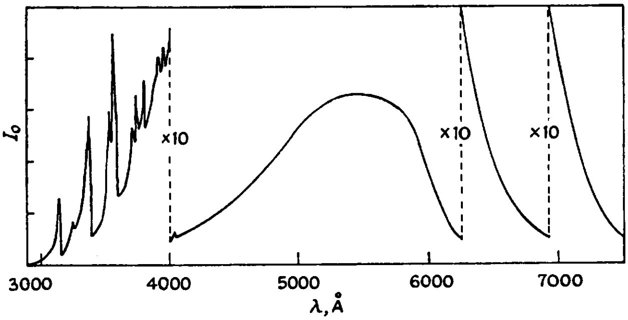

FIG. 8. Spectrum of Pointolite source, as measured by the Cary spectrophotometer.

$$\rho_A(\lambda) = \log\{I_0(\lambda)/[I_t(\lambda) - I_s(\lambda)]\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The measurement of triplet–triplet absorption thus required three traces: $I_0(\lambda)$ obtained with the source S alone; $I_s(\lambda)$ obtained with the exciting lamps only, and $I_t(\lambda)$ obtained with both source and excitation. A typical set of three such curves is shown in Fig. 9. From these an optical density curve is obtained by applying eqn. (1) at sufficient points. The relation between the optical-density curve so obtained and *T–T* extinction coefficients is discussed in (2.3). One further source of possible error must be mentioned. The different relative triplet concentrations used in each region had to be determined from the ratios of the optical densities observed in regions where the spectra overlap: they were not, as in conventional spectrometric practice, known precisely. Errors thus introduced are naturally cumulative as one moves along a series of spectral regions.

(5.4) *Preparation of Rigid Solutions, and Purification of Materials.*—The solvent EPA consisted of ether, *iso*pentane, and ethanol (4 : 4 : 1 by vol.); the composition was altered from that introduced by Lewis and Kasha (*J. Amer. Chem. Soc.*, 1944, **66**, 2100) in order to reduce the tendency of this glass to shatter at the top of the frozen column, where the strain must be considerable even with careful freezing. The solvent PMh contained *iso*pentane and methyl*cyclo*hexane in the proportions 5 : 1; no trouble with cracking was experienced with this glass. In either case, however, the freezing of the solutions was always performed very carefully, over a period of at least 45 min., to produce a glass as free as possible from strain and lens effects (there is a contraction of over 20% on cooling these solvents to liquid nitrogen temperature).

The considerations which influence the choice of solvent are the necessity to avoid the photoreactions which may occur in EPA [cf. (3.2)], and the relative ease of handling; EPA is the more convenient, since no especial precautions are needed, when preparing the solutions, to avoid the ingress of atmospheric moisture. However, with PMh, unless such precautions are taken (see below), the rigid glass appears milky by reflected light, and yellow by transmitted light; this is probably due to short-wave-length light scattering by microscopic ice crystals (Potts, *J. Chem. Phys.*, 1952, **20**, 809; Passerini and Ross, *J. Sci. Instr.*, 1953, **30**, 274). With EPA such scattering sets in rather sharply near 2800 Å (in 10-cm. path length), and for the most part this wave-length lay beyond the spectral range searched for *T*–*T* absorption.

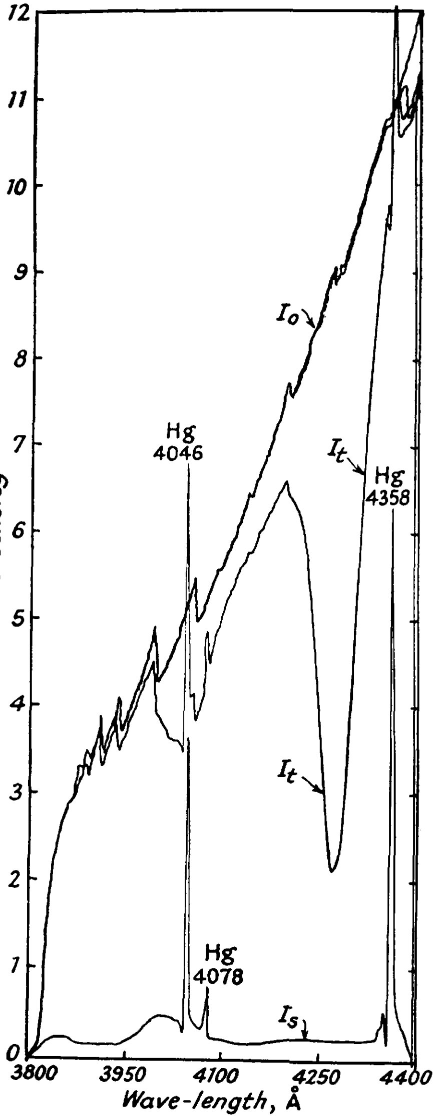

FIG. 9. Typical set of three curves, showing the triplet–triplet absorption bands of anthracene. The two upper traces each consist of two superimposed traces, measured in the order I_0, I_t, I_0 (repeat), I_t (repeat), and illustrate the satisfactory reproducibility obtainable under favourable conditions. The comparative unimportance of interference by scattered mercury lines and the intense anthracene fluorescence (trace I_s) is apparent. The record terminates at 3800 Å, owing to the ordinary absorption of the solute.

To avoid this loss in transmission at short-wave-length, PMh solutions were made up entirely in an atmosphere of dry nitrogen, and were refluxed in the process to achieve some measure of degassing (Potts, *loc. cit.*). The solvents were premixed and kept over phosphoric oxide for 24 hr. before use; the solution, once prepared, was introduced into the assembled cell through a capilliary tube pushed down between the evacuated tube and the Neoprene diaphragm (Fig. 2). To avoid contamination by lubricating greases, the place of stopcocks in this apparatus was taken by Neoprene tubing provided with screw-clips.

Solvents. Ether and alcohol were purified by appropriate drying and distillation (cf. Sinsheimer, Scott, and Loofbourow, *J. Biol. Chem.*, 1950, **187**, 299); B.D.H. *iso*pentane and methyl*cyclo*hexane were purified by treatment with sulphuric acid, and subsequent passage through silica gel (cf. Potts, *loc. cit.*) or else through activated charcoal, previously heated under vacuum to remove the large water content.

Solutes. Benzene was a highly purified sample, prepared from " AnalaR " benzene by chemical pre-treatment, followed by repeated recrystallization; hexamethylbenzene, naphthalene, fluorene, diphenyl, diphenylamine, and acridine were reagent-grade samples purified by several recrystallizations from alcohol. Resublimed and chromatographed anthracene of high purity was provided by Dr. P. C. Hobbins. The four- and five-ring hydrocarbons were synthetic samples given us by Dr. E. M. F. Roe and chromatographed by Prof. R. Curti. Pyridine, quinoline, and *iso*quinoline were fractionally vacuum-distilled in an efficient column, and had refractive indices in agreement with the literature values. Small samples of the larger heterocyclics were given to us by Prof. A. Albert and were once recrystallized.

The authors are indebted to Dr. Roe, Prof. Albert, and Dr. Hobbins for gifts of chemicals, and wish especially to thank Prof. Renato Curti, of the University of Pavia, for carrying out the chromatographic purifications. They have benefited, too, from discussions with Prof. M. Kasha. This work was largely carried out during the tenure of an Australian National University Scholarship by one of them (I. G. R.).

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