into an open sample tube containing the same height of carbon disulfide as contained in the sealed sample tube. The corrections were 1.5 and 0.7° at -50 and $-100°$, respectively, when the temperature was measured by the second thermocouple at the height of the receiver coil. At the very bottom of the tube the temperature was 1° warmer than at the receiver coil. The temperature gradient along the axis of the tube near the receiver coil was less than 0.3°/cm. Samples spinning changed the temperature by less than 0.1°. The temperature was also unaffected by the presence of radiofrequency power used for deuterium decoupling. Temperature corrections were obtained for all the temperatures at which rates were measured.

All the spectra were obtained on a Varian HR60 spectrometer operating at 60 Mc/sec and modified by the addition of a second audio phase/detector[26] working at a variable frequency (ν_2) obtained from a General Radio interpolation oscillator, No. 1107A. The 60-Mc/sec transmitter frequency was frequency modulated at the frequency ν_2, and the output of the radiofrequency receiver was phase detected so as to obtain a dispersion mode signal. This signal was amplified by a Philbrick amplifier and applied in the correct sense to the pickup coils of the superstabilizer. The signal from the methylene chloride was used for locking the magnetic field to a frequency (60 Mc/sec $\pm$ ν_2) by the procedure just described. Thus a stabilized field sweep can be obtained by sweeping the frequency ν_2. For this purpose we used a 2-rpm synchronous motor fitted with gears ranging in reduction ratio from 1:1 to 50:1. Sweep rates as low as 4 cps/min were obtained by driving the main dial of the oscillator. Still lower sweep rates, down to 0.713 cps/min, were obtained over a sweep width of 20 cps, when the subsidiary dial was driven. Frequency measurements showed that the oscillator scale was linear with rotation.

Spectra were obtained *via* phase detection at a fixed frequency (ν_1) of about 2000 cps of the Varian integrator, which was used in the side-band mode. A variable attenuator was employed to control the intensity of the magnetic-field modulation at the frequency ν_1. For the double-resonance studies, a third frequency ν_3, was obtained from a Hewlett-Packard oscillator, Model 200AB, which had been modified by the attachment of several potentiometers to the RC circuit so as to allow precise settings of the frequency. This frequency was applied to the modulation input of the 60-Mc/sec transmitter, *via* a Hewlett-Packard 350D attenuator. In these experiments a notch filter, consisting of a series high-Q inductance–capacitor circuit tuned to ν_3, was connected across the output of the radiofrequency receiver.

Deuterium decoupling was accomplished with an NMR Specialties, Inc., Model HD60 spin decoupler. This instrument is essentially a single side-band suppressed-carrier radiofrequency generator which makes use of a 9.2-Mc/sec crystal-controlled oscillator. An audio oscillator was used to generate and adjust the side-band frequency. The radiofrequency power was increased until no further change was observed in the line being decoupled. Since the deuteron resonance spectrum in C_6HD_{11} was only a few cycles per second wide, even at low temperatures, very little power was required to obtain complete decoupling. At room temperature, the line width of the proton spectrum, with deuteron decoupling, of C_6HD_{11} was identical with that of TMS. The line width at half-height of TMS was in the range of 0.2 to 0.5 cps, depending on the care used in the adjustment of the field homogeneity

The frequency stability of the various audio oscillators was found to be excellent provided that these instruments had reached thermal equilibrium in a temperature-controlled environment.

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Investigation of Singlet–Triplet Transitions by the Phosphorescence Excitation Method. IV. The Singlet–Triplet Absorption Spectra of Aromatic Hydrocarbons

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Abstract: The phosphorescence excitation method is used to investigate the singlet–triplet absorption spectra of 45 representative aromatic hydrocarbons. From this preliminary study we have obtained singlet–triplet spectra which should be of general use. We have also obtained information regarding molecular vibrational frequencies of triplet-state molecules; energy transfer in halogenated benzene crystals; the triplet-state properties of iodo-substituted benzenes and evidence for uncertainty principle broadening of the S → T absorption spectra; external heavy-atom effects on S → T transitions of guest molecules in heavy-atom host crystals; detection of low-yield photochemical reactions; the assignment of the lowest triplet state in polyacenes; and substituent effects on S → T transitions.

Although it has been over 20 years since Lewis and Kasha first published their classic paper in which they identified the phosphorescent states of organic molecules as triplet states,[3] it has only been in recent years that many implications of their work have been fully appreciated. The current interest in the triplet state of organic molecules has been generated by recent developments in a number of fields, including photochemistry,[4–8] spectroscopy,[9–13] photobiology,[14–17] and

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theory of triplet states.[18-23] All of these developments have generated a need for more detailed information on the spectroscopic properties of triplet-state molecules. Until now most of our information regarding the properties of triplet-state molecules has been obtained from studies of triplet–singlet emission, but there are many important questions which cannot be answered by an investigation of the triplet → singlet emission.[24-27]

To obtain information about triplet states which lie above the lowest triplet state, vibrational frequencies of triplet-state molecules, exciton effects on S → T transitions, and oscillator strengths for S → T transitions, some type of absorption measurement is required. Direct measurement of singlet–triplet spectra by the usual absorption technique are difficult because the transitions are so weak (oscillator strengths typically range from $f = 10^{-9}$ to 10^{-6}). In order to obtain sufficient optical density, high sample concentrations and long path lengths are usually required, and with these conditions there are invariably problems due to impurity absorption. In spite of these difficulties, there have been, in favorable cases, some reasonably successful studies of S_0 → T absorption,[28-41] but the total number of molecules which have been studied by direct S → T absorption measurements remains rather small.

This scarcity of reliable and useful S_0 → T absorption spectra serves to emphasize the difficulties involved. We recently described a "new" method, the phosphorescence excitation (PE) method, which considerably simplifies the problem of measuring S → T absorption spectra.[42-48] In this method the action spectrum or the excitation spectrum of the phosphorescence of a sample is measured and, under appropriate conditions, this corresponds to the S_0 → T absorption spectrum of the sample. Excitation spectra techniques are, of course, not new.[49-51] What is surprising, however, is that it was only recently realized that this method is a particularly powerful and useful one for studying the very weak S_0 → T transitions in organic molecules.[42-48] Although the excitation technique is a very sensitive one for the detection of S_0 → T absorption, it is remarkably less susceptible to impurity effects than the direct absorption measurements. It is sufficiently simple to use that it reduces the determination of S_0 → T spectra to an almost routine measurement. The method should be of interest not only to spectroscopists who wish to carry out high-resolution studies, but also to organic chemists who would like a convenient method for obtaining S_0 → T spectra.

In earlier reports we discussed the use of the phosphorescence excitation method in the determination of S_0 → T spectra of aromatic molecules dissolved in nonheavy-atom- and heavy-atom-containing solvents[42,44,45,47] and of crystals of aromatic molecules.[43-46] With the crystalline samples we were able to observe the S_0 → T absorption spectra of molecules in the absence of any heavy-atom effect. More recently Hirota used this same technique with crystals doped with phenanthrene-d_{10} or naphthalene-d_8 to further enhance the sensitivity of the method.[52] In the present paper we wish to discuss some additional aspects of the method which were not adequately treated earlier. We illustrate the use of the method in the investigation of S_0 → T absorption spectra of some 40 atomatic hydrocarbons and give a preliminary discussion of some of our observations.

Results and Discussion

Naphthalene Derivatives. The S → T absorption spectrum of naphthalene has been studied by several different techniques. Kasha first obtained the direct S → T absorption spectrum of naphthalene by the use of ethyl iodide as a heavy-atom perturber.[32] Avakian, *et al.*, have used a delayed fluorescence excitation technique to study the S → T absorption spectrum of crystalline naphthalene.[40] Evans has used the O_2 perturbation technique to measure the S → T absorption spectra directly.[34] Very recently Hanson and Robinson have reported the positions of the S → T absorption bands of crystalline naphthalene.[53] The spectrum which we obtained by the PE method (shown in Figure 1) is found to agree well with the results previously reported.

The phosphorescence excitation spectra of various substituted naphthalenes are shown in Figures 1 and 2 along with their singlet–singlet absorption and phosphorescence emission spectra. The position of the 0–0 band of the S_0 → T absorption of the substituted

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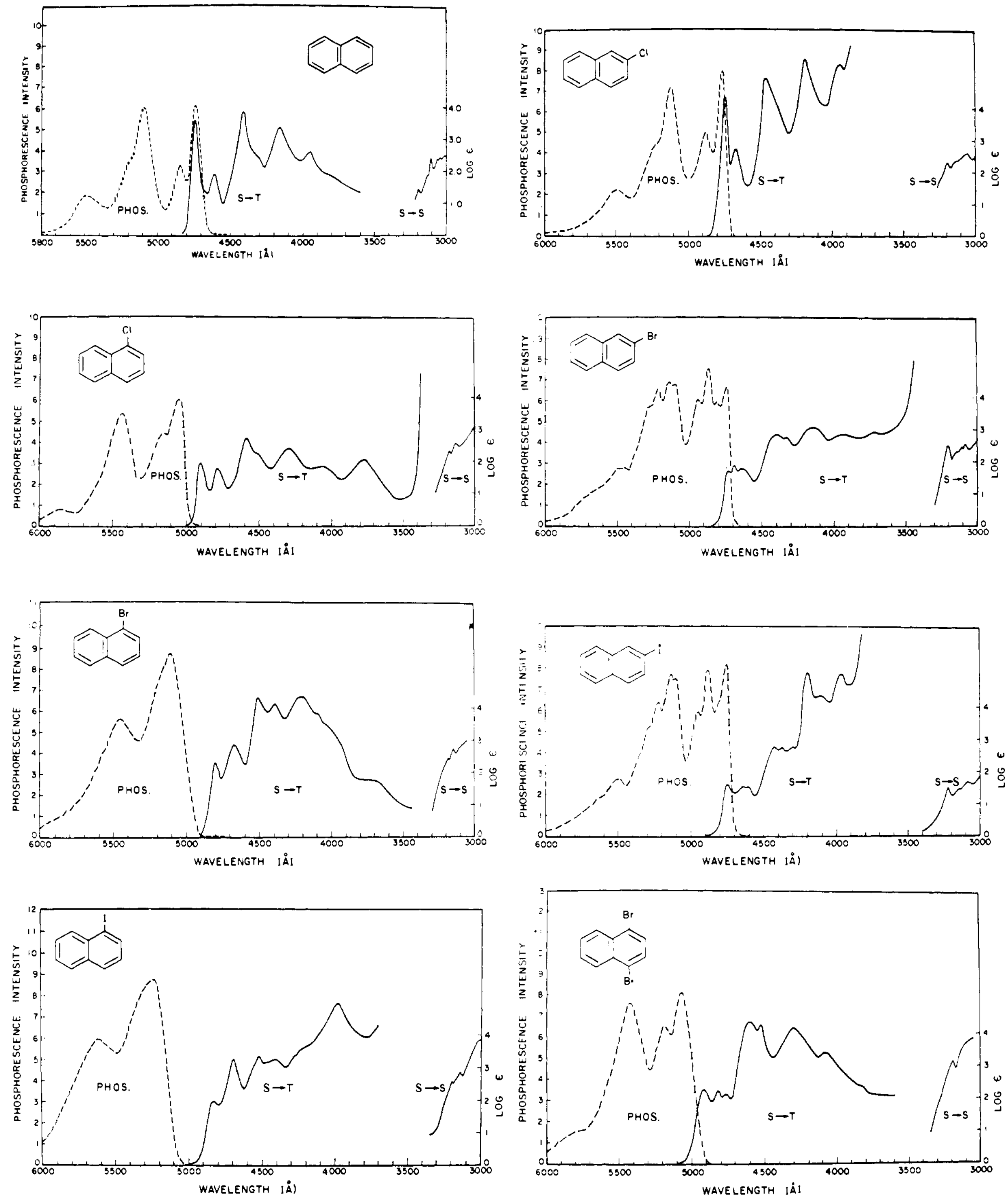

Figure 1. The S_0–T absorption and emission spectra and the $S_0 \rightarrow S$ absorption spectra of naphthalene and seven halogenated derivatives.

naphthalenes are summarized in Table I along with the same data for other compounds which we studied.

From the absorption and emission spectra we see that there is generally good overlap between the 0–0 band in absorption and emission, and with a few notable exceptions, the $S_0 \rightarrow T$ absorption spectra are roughly mirror image symmetric with respect to the phosphorescence spectra. This is fortunate since it is often assumed to be true in the analysis of the emission spectra. In every case the lowest triplet state was assigned as a $^3(\pi, \pi^*)$ state on the basis of (i) similarity with the $S_0 \rightarrow T$ absorption and emission of naphthalene, (ii) long lifetimes for the nonhalogenated compounds ($t \sim 1$ sec); and (iii) sensitivity of the $S_0 \rightarrow T$ absorption spectrum to an external heavy-atom effect.[24,32]

Definite evidence for a second triplet state was found only in the case of 2-naphthaldehyde (see Figure 2), and this state was assigned as an $^3(n, \pi)$ state. This assignment was based on a consideration of the intensity of the transition (no heavy-atom solvent was required to observe it) and its position with respect to the 0–0 band of the $S_0 \rightarrow S_{n,\pi}$ band ($S_{n,\pi} \leftrightarrow T_{n,\pi}$ splitting =

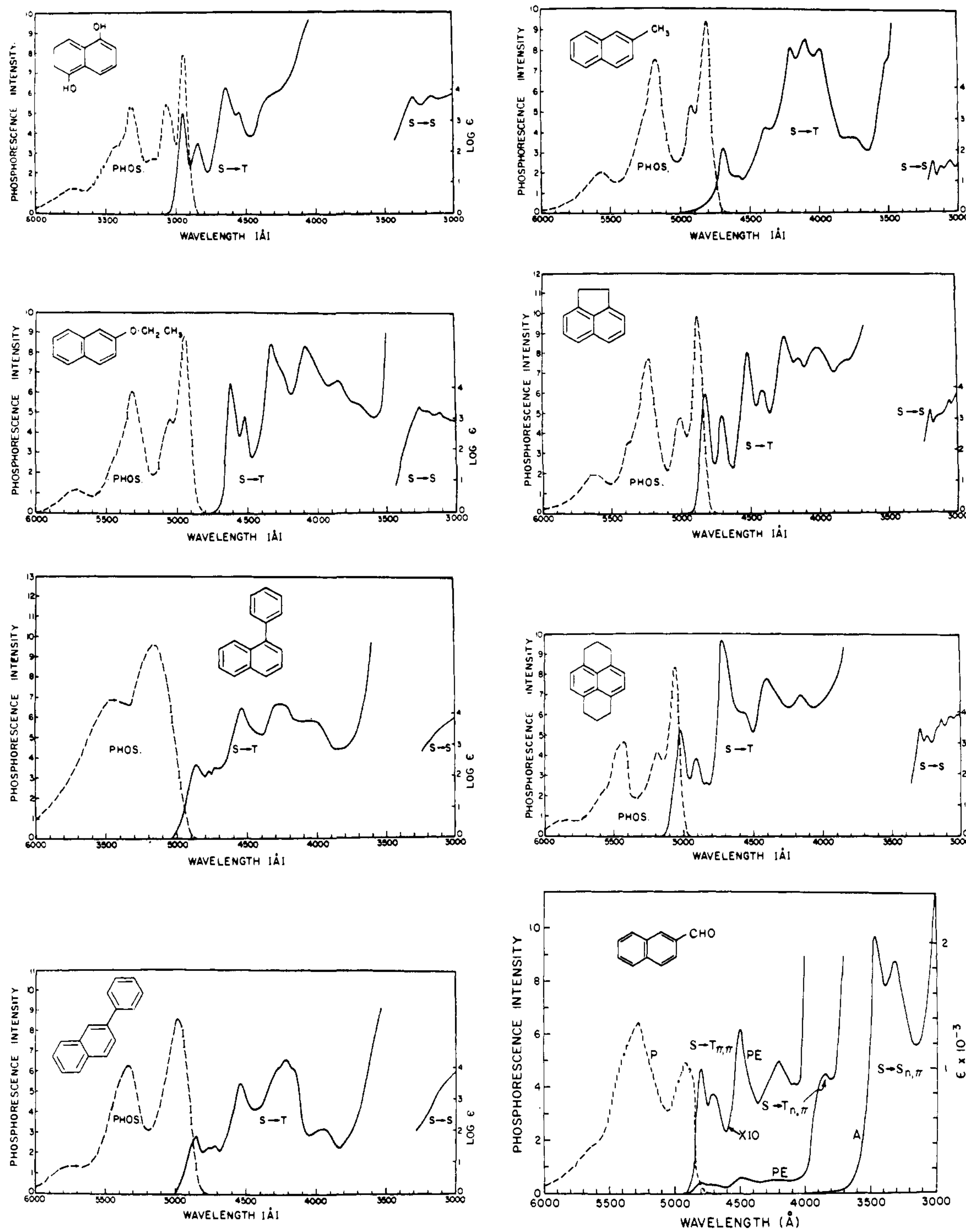

Figure 2. The S_0–T absorption and emission spectra and $S_0 \rightarrow S$ absorption spectra of eight naphthalene derivatives.

2400 cm^{-1} [48]). Several other naphthalene derivatives which contained substituents with nonbonding electrons gave diffuse $S_0 \rightarrow T$ spectra in the short-wavelength region. It is possible that this diffuseness was also due to transitions to low-lying (n, π) triplet states.

According to reliable theoretical calculations,[54,55] the lowest triplet state of naphthalene and presumably its derivatives, should be assigned as a ^3L_a state, and this prediction is supported both by a comparison of the calculated and observed zero-field splitting of the triplet state of naphthalene,[56,57] and by perimeter model calculations on the triplet-state energies of the polyacenes.[58] This assignment is further supported by the observation that the 0–0 band of the $S_0 \rightarrow T$ absorption and the second singlet state (^1L_a) are shifted in a parallel manner by the various substituents, whereas there is almost an anticorrelation between substituent effects on the lowest singlet state (^1L_b) and the lowest triplet state.

Phenanthrene Derivatives. The $S_0 \rightarrow T$ absorption spectra of some phenanthrene derivatives are presented in Figure 3. The vibrational structure of the $S_0 \rightarrow T$

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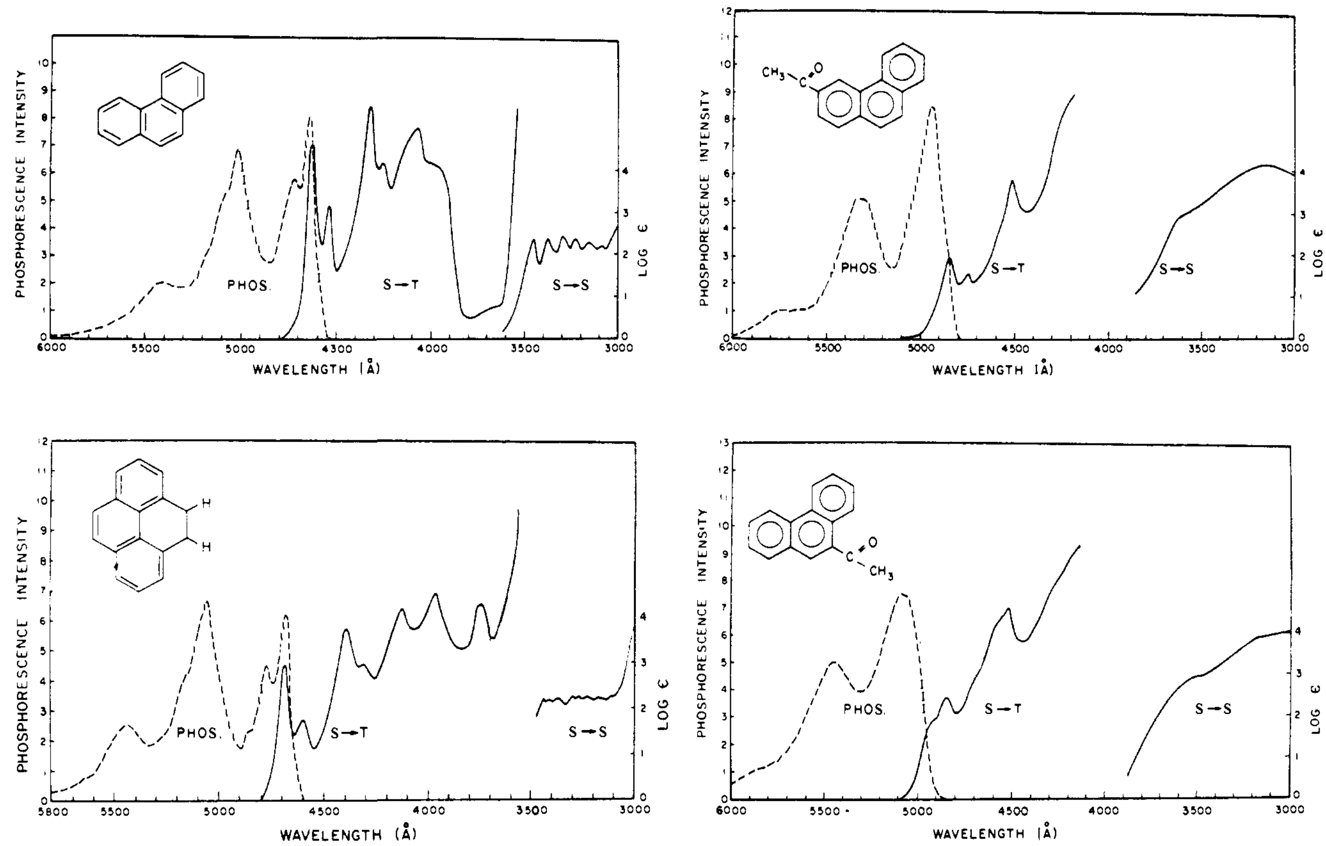

Figure 3. The S_0–T absorption and emission spectra and $S_0 \rightarrow S$ absorption spectra of four phenanthrenes.

absorption spectra of both phenanthrene and dihydropyrene are reasonably well resolved and a tentative vibrational analysis is given in Table II, along with corresponding data for the phosphorescence emission.

According to calculations by Ham and Ruedenberg[55] the second triplet state of phenanthrene is predicted to lie within 200 cm^{-1} of the lowest excited singlet state. Although we have been unable to locate this

Table I. Triplet-State Energies of Aromatic Hydrocarbons[a]

Naphthalenes	
Naphthalene	4720
1-Chloronaphthalene	4890
1-Bromonaphthalene	4800
1-Iodonaphthalene	4840
2-Chloronaphthalene	4750
2-Bromonaphthalene	4750
2-Iodonaphthalene	4750
1,4-Dibromonaphthalene	4920
2-Methylnaphthalene	4700
2-Ethoxynaphthalene	4620
1-Phenylnaphthalene	4860
2-Phenylnaphthalene	4870
1-Naphthoic acid	4970
2-Naphthoic acid	4810
2-Hydroxynaphthalene	4750
1,5-Dihydroxynaphthalene	4960
2,7-Dihydroxynaphthalene	4710
1,5-Dinitronaphthalene	5150
Acenaphthalene	4830
1,2,3,6,7,8-Hexahydropyrene	5020
2-Naphthaldehyde	4780
Phenanthrenes	
Phenanthrene	4630
4,5-Dihydropyrene	4690
3-Acetophenanthrene	4850
9-Acetophenanthrene	4900
Polyphenyls (taken from phosphorescence)	
Biphenyl	4370
2-Bromobiphenyl	4400
2-Iodobiphenyl	4550
4,4′-Dichlorobiphenyl	4550
o-Terphenyl	4640
m-Terphenyl	4440
1,3,5-Triphenylbenzene	4440
p-Terphenyl	4900
Polyphenyl Metal Compounds	
Diphenylmercury	3450
Tetraphenyltin	3420
Halogenated Benzenes	
1,4-Dichlorobenzene	3565
1-Bromo-4-chlorobenzene	3590
1,4-Dibromobenzene	3600
1,3,5-Trichlorobenzene	3615
1,3,5-Tribromobenzene	3620
1,2,4,5-Tetrachlorobenzene	3730
1,2,4,5-Tetrabromobenzene	3740
Hexachlorobenzene	3900

[a] Values given are the positions of the 0–0 band in angstrom units.

Table II. $S_0 \rightarrow T$ Transitions in Phenanthrene and 4,5-Dihydropyrene

Phenanthrene			4,5-Dihydropyrene
$S_0 \rightarrow T$ absorption, cm^{-1}	$T \rightarrow S_0$ phosphorescence[a] cm^{-1}	Analysis	$S_0 \rightarrow T$ absorption, cm^{-1}
0 (s)[b]	0 (s)	0, 0	0 (s)
400 (m)	410 (s)	0, 406	370 (m)
880 (sh)	820 (w)	0, 830	790 (sh)
	1220 (sh)	0, 830 + 406	
	1390 (sh)	0, 1347	
1480 (s)	1640 (s)	0, 1608	1410 (s)
1860 (w)	2030 (w)	0, 1608 + 406	1860 (w)
2390 (sh)	2430 (w)	0, 1603 + 880	
	2650 (sh)	0, 13,472	
	2810 (sh)	0, 1608 + 830 + 406	
2890 (m)	2990 (m)	0, 1608 + 1347	2870 (m)
	3220 (sh)	0, 1608 × 2	
	3390 (sh)	0, 1347 + 1608 + 406	
3660 (sh)	3590 (sh)	0,1608 × 2 + 406	3850 (m)

[a] T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, **37**, 2413 (1962).
[b] s, strong; m, medium; w, weak; sh, shoulder.

triplet state, the $S_0 \rightarrow T$ absorption spectrum presented in Figure 3 indicates that it must lie above 28,200 cm^{-1}, or within 800 cm^{-1} of the lowest singlet state. In the long-wavelength region (>3800 A) the $S_0 \rightarrow T$ absorption spectrum of dihydropyrene (see Figure 3) is quite similar to that of phenanthrene. In the 3800–3600-A region, however, a band appears in the dihydropyrene spectrum which does not occur in the phenanthrene spectrum. By application of the various tests of sample purity,[48] we demonstrated that this band was not due to some impurity. We have therefore tentatively assigned the 3700-A absorption band in dihydropyrene as a transition to the second triplet state.

Polyphenyls. The $S_0 \rightarrow T$ and $S_0 \rightarrow T$ absorption spectra and phosphorescence spectra of various polyphenyls are presented in Figure 4. An unfortunate feature which characterizes these compounds is the almost total lack of vibrational structure in the PE spectra. Although disappointing, this was not unexpected in view of the structureless $S_0 \rightarrow S$ absorption which these same compounds exhibit. In contrast to the structureless absorption, both the fluorescence and the phosphorescence spectra of the polyphenyls are usually structured,[59] so that with these compounds there is a breakdown in the usual mirror-image symmetry between absorption and emission spectra. Presumably this lack of mirror-image symmetry can be attributed to a difference between the geometry in the ground and excited states.[3,60] In the ground state there is a rotation about the essential single bond(s) linking the phenyl groups, whereas in the excited state there may be conjugation between the rings. Absorption probably involves excitation of molecules which have a number of different possible geometrical configurations, whereas emission occurs from molecules which all have the same planar geometry. These results serve to emphasize the need to study both the absorption and emission spectra in order to characterize excited-state properties of molecules.[61]

Evidence for excited-state double-bond character in the central C–C bond was, of course, obtained 22 years ago by Lewis and Kasha who found that *ortho* substituents which prevented the two rings of biphenyl from becoming coplanar also blue shifted the phosphorescence.[3] The fact that the phosphorescence of *o*-terphenyl occurs at higher energy than that of *p*-terphenyl (see Figure 4) can be attributed to steric interaction between the rings in the *ortho* derivative which prevents the rings from becoming coplanar.

There is a further parallel between the phosphorescence and fluorescence with respect to the variation in the energy of the emission for the various isomers. As has been pointed out elsewhere, all of the *m*-polyphenyls have substantially the same $S_0 \rightarrow S$ spectra.[60] As might have been anticipated, we find that the same is true for the phosphorescence. This invariance is taken to indicate that conjugation in these *meta* derivatives is only possible between two adjacent rings, whereas conjugation between more than two rings would involve structures with long bonds.[60] The large red shifts in both the fluorescence and phosphorescence spectra of the *p*-polyphenyls with increasing number of rings is, correspondingly, attributed to the fact that conjugation can extend through all phenyl rings.

Recently Hirota used the PE method to obtain the $S_0 \rightarrow T$ absorption spectrum of a biphenyl crystal doped with phenanthrene-d_{10}.[52] In contrast to the broad, structureless absorption bands which we obtained with the polyphenyls, the spectra which he reported for biphenyl was structured. As most of our measurements were made on samples dissolved in a rigid glass matrix, it is possible that the difference between our observations is related to some crystal effect. This is not the case in *p,p′*-dichlorobiphenyl, since the $S_0 \rightarrow T$ absorption spectra of both a crystalline and a solution sample were unstructured (see Figure 4). In view of this and the similarities between the $S_0 \rightarrow S$ and $S_0 \rightarrow T$ absorption and emission spectra, Hirota's observation of structured $S_0 \rightarrow T$ absorption in biphenyl is somewhat surprising.

In the course of our examination of *o*-terphenyl, we noted the appearance of several strong bands in the region of 3300–3500 A. By application of the various tests of sample purity discussed elsewhere,[48] we were able to show that these bands were due to an impurity which proved to be triphenylene. Although this complication could have been anticipated in view of Kharasch's earlier report of the photochemical formation of triphenylene from *o*-terphenyl in solution,[62] it is interesting to note that, through proper use of purity checks, the production of rather small quantities of a photochemical reaction product was easily detected.

Metal Polyphenyls. The $S_0 \rightarrow T$ spectra of crystalline samples of diphenylmercury and tetraphenyltin are shown in Figure 5. For comparison the $S_0 \rightarrow T$ spectra of tetraphenyltin in solution obtained by direct absorption is also shown in Figure 5,[63] and it is seen that the spectra obtained by the two different methods agree well. These spectra closely resemble the $S_0 \rightarrow T$ spectra of benzene which has its 0–0 band at 3388 A

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(61) J. B. Birks and D. J. Dyson, *Proc. Roy. Soc.* (London), **275**, 135 (1963).

(62) N. Kharasch, T. G. Alston, H. B. Lewis, and W. Wolf, *Chem. Commun.*, 242, (1965).

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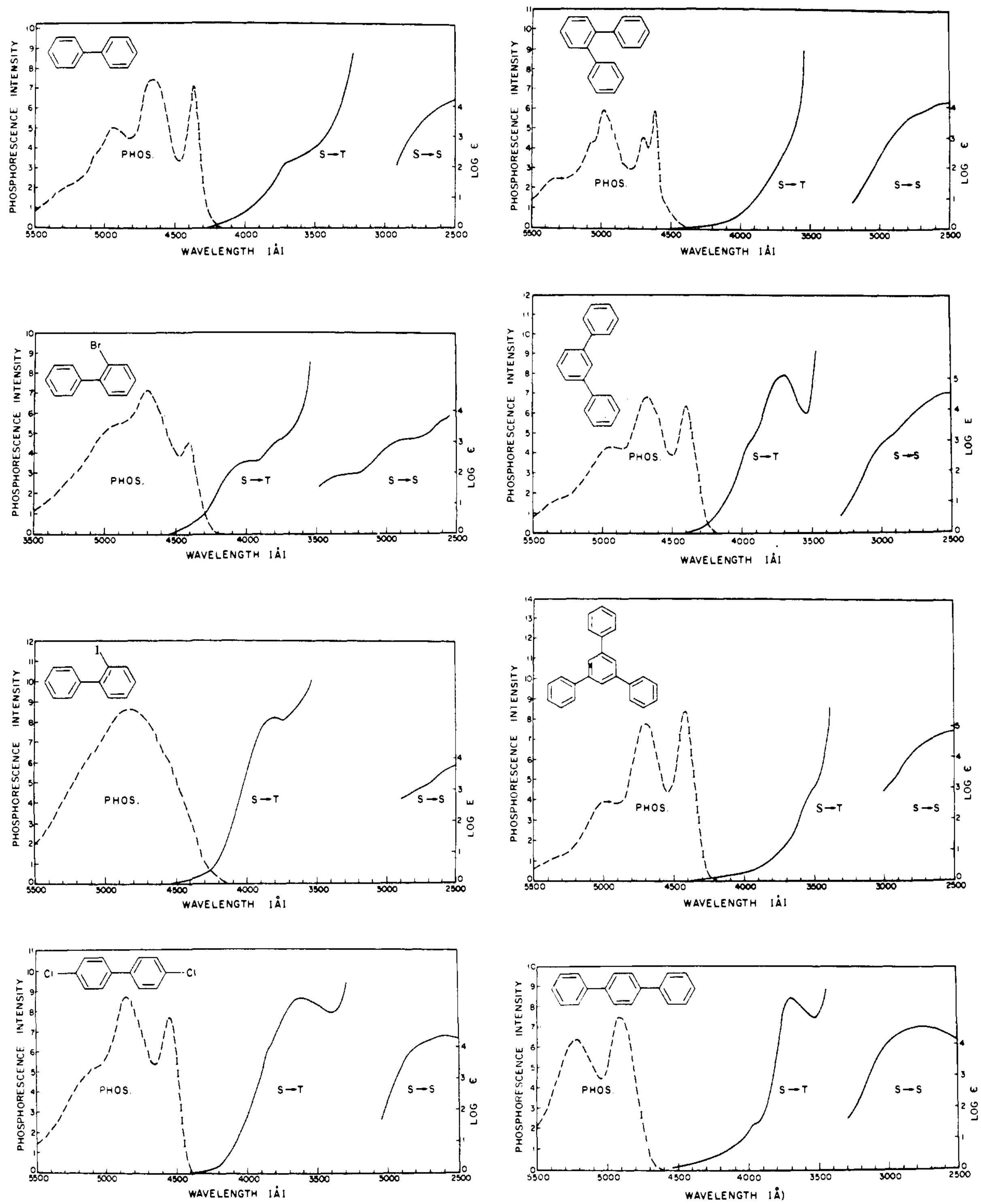

Figure 4. The S_0–T absorption and emission spectra and $S_0 \rightarrow S$ absorption spectra of eight polyphenyls.

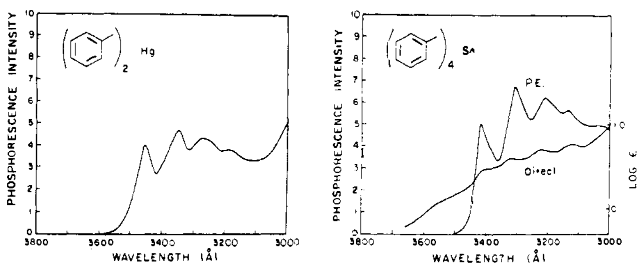

Figure 5. The S_0–T absorption spectra of two metal polyphenyls.

in solution and a prominent 900-cm^{-1} vibrational progression.[64] In diphenylmercury the 0–0 band is at 3450 A and the vibrational spacing is 910 cm^{-1}, while in tetraphenyltin the 0–0 band is at 3420 A, and the vibrational spacing is 930 cm^{-1}.

Halogenated Benzenes.[65] For our studies of the $S_0 \rightarrow T$ spectra of the substituted benzenes we used crystalline samples instead of solutions, because of

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(64) G. W. King and E. H. Pinnington, *J. Mol. Spectry.*, **15**, 394 (1965).

(65) In collaboration with J. J. Ewing.

complications caused by solvent impurities and because much higher sample concentrations could be obtained with crystals. The $S_0 \rightarrow T$ absorption spectra of eight naphthalene-doped halogenated benzene crystals are presented in Figure 6. Hirota has previously obtained the $S \rightarrow T$ spectrum of tetrachlorobenzene using the PE method, and our results are in accord with his.[52]

Because the assignment of the lowest triplet state in benzene is central to the assignment of the triplet states in other aromatic hydrocarbons, benzene and substituted benzenes have occupied a rather special status in triplet-state spectroscopy. In spite of the numerous efforts to identify the nature of the lowest triplet state in substituted benzenes, certain observations still remain puzzling. Hochstrasser, for example, has examined in detail the $S_0 \rightarrow T$ absorption spectra of both *p*-dibromobenzene and *p*-dichlorobenzene and concludes that either (i) our present understanding of the mechanism of spin–orbit coupling in halogenated aromatic hydrocarbons is incorrect, or (ii) that the preferred assignment of the lowest triplet state of benzene as a ${}^3L_a$ (${}^3B_{1u}$) state is incorrect.[66] The assignment of the lowest triplet state of hexachlorobenzene also seems to be in dispute.[67,68]

Even without a detailed vibrational analysis of our spectra, it is possible to derive some useful information regarding the assignment problem. In view of the relatively small effect of substituents on the energy of the $S_0 \rightarrow T$ transitions, we conclude that the lowest triplet of these substituted compounds should be given the same assignment as the lowest triplet state of benzene. A correct assignment of the triplet states in these substituted benzenes should give the correct benzene assignment.

Hexachlorobenzene. Olds has examined the polarization of the phosphorescence emission from single crystals of hexachlorobenzene and concluded that the lowest triplet state corresponds to a ${}^3B_{2u}$ (${}^3L_b$) in D_{6h} symmetry,[67] contrary to the usual ${}^3L_a$ assignment. Russell and Albrecht, on the other hand, have examined the polarization of the hexachlorobenzene phosphorescence emission in rigid glass solution and conclude that the lowest triplet state should be assigned as a ${}^3L_a$ state.[68] It should be noted, however, that the phosphorescence which they observed is displaced over 3000 cm^{-1} to the red of that observed by Olds, and over 4400 cm^{-1} from the 0–0 band which we observed in our $S_0 \rightarrow T$ excitation spectra. It is difficult to understand why there should be such a large displacement of the solution phosphorescence relative to the crystal absorption.

The lack of coincidence between our crystal absorption spectra and Olds' emission spectra is also surprising. For the reasons presented in the discussion of the PE method,[48] we believe that our crystal absorption measurements are more reliable than crystal emission studies. Furthermore, within the accuracy of our experiments (±5 A in this case), the same $S_0 \rightarrow T$ bands have been observed by Ron and Schnepp in direct absorption measurements on crystals of hexachlorobenzene.[69] Because of the lack of coincidence between the crystal absorption and emission spectra and because of the unusual phosphorescence which Albrecht observed in solution, a reexamination of hexachlorobenzene seems called for.

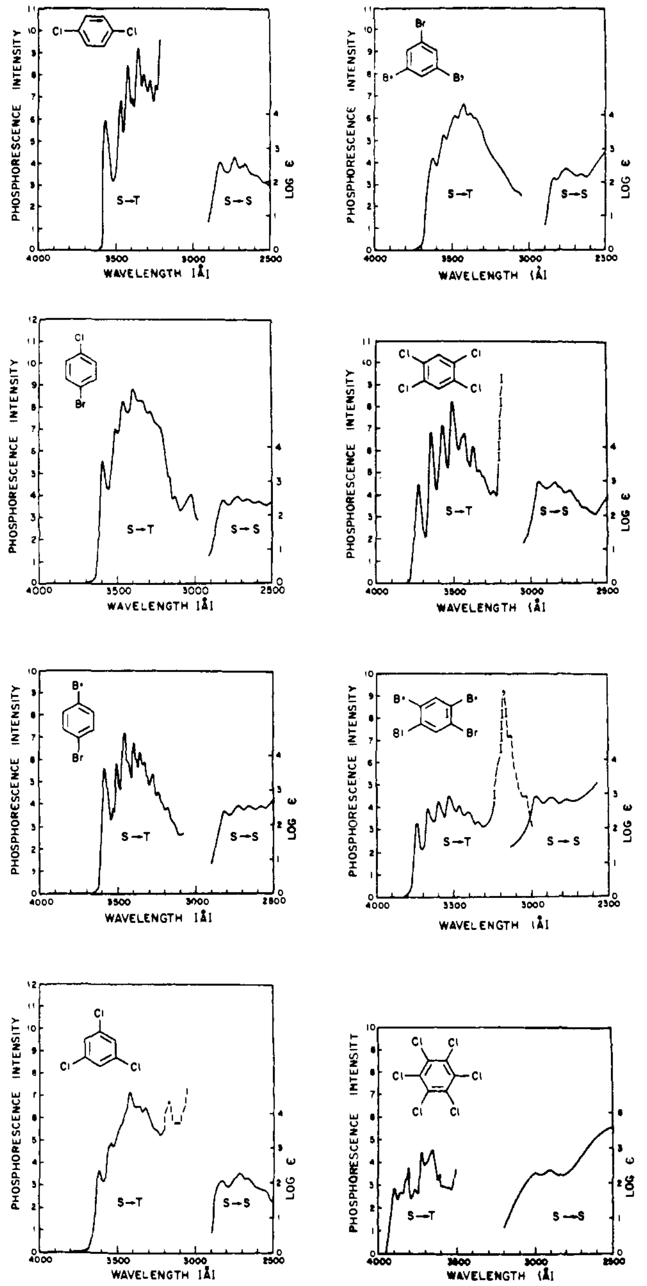

Figure 6. The S_0–T absorption spectra and the $S_0 \rightarrow S$ absorption spectra of eight halogenated benzene.

Iodobenzene Derivatives. Because of an internal heavy-atom effect, the $S_0 \rightarrow T$ transitions of *p*-iodotoluene and *p*-diiodobenzene are quite strong ($\epsilon \sim 0.5$), and some years ago McClure observed the $S_0 \rightarrow T$ absorption spectrum of *p*-diiodobenzene in direct absorption measurements.[28] More recently Castro and Hochstrasser obtained the $S_0 \rightarrow T$ absorption of single crystals of *p*-diiodobenzene at liquid helium temperatures.[41] In view of the intensity of the $S_0 \rightarrow T$ absorption in this compound, we were surprised to find that we were unable to obtain the singlet–triplet absorption spectra of naphthalene-doped crystals of *p*-iodotoluene or of *p*-diiodobenzene. At first we sus-

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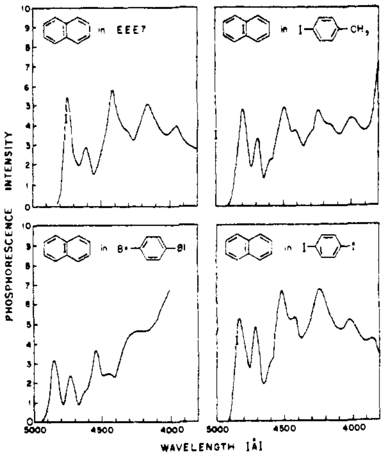

Figure 7. The $S_0 \rightarrow T$ absorption spectra of naphthalene in EEET and in several halogenated benzenes at 77°K.

pected that the naphthalene had not been incorporated in the crystals, but this was disproven by two observations. In the first place, strong naphthalene phosphorescence was observed when the samples were excited at 3200 A, the onset of the naphthalene $S_0 \rightarrow S$ absorption. Since pure naphthalene crystals are not phosphorescent, this proves that naphthalene was soluble to some extent in the iodobenzene crystals. Secondly, and more importantly, we were easily able to observe the $S_0 \rightarrow T$ absorption spectrum of the naphthalene which was present as a guest in the iodobenzene crystals (*p*-iodotoluene or *p*-diiodobenzene) by the PE method. These results are presented in Figure 7. Clearly, there was an external heavy-atom effect on naphthalene $S_0 \rightarrow T$ absorption, and this could have arisen only if some of the naphthalene was actually dissolved in the crystals. It is remarkable, therefore, that in the 3700–3200-A region (not shown in Figure 7), where the $S_0 \rightarrow T$ absorption of the host molecules is known to occur, there was a minimum in the PE spectrum, the depth of which depended upon the thickness of the crystal.

These experiments indicate that triplet-state iodobenzene molecules do not transfer their energy even to a naphthalene neighbor. Presumably there is some other radiationless deactivation process which occurs more rapidly (6×10^{13}/sec) than triplet–triplet energy transfer (10^{10}/sec).[70] Rupture of the C–I bond appears to be a likely process.[71,72] Such a large radiationless rate constant would lead to an uncertainty principle broadening of 100–300 cm^{-1}. Interestingly, the bands observed in the $S_0 \rightarrow T$ absorption spectra of the *p*-diiodobenzene at 4.2°K[41] are anomalously broad (~200 cm^{-1}), perhaps due to uncertainty principle broadening.

Singlet-Triplet Absorption Spectra of Guest Molecules in Heavy-Atom-Containing Crystals. In the course of our investigation of the singlet–triplet absorption spectra of naphthalene-doped crystals of the halogen-substituted benzenes, we found that it was also possible to observe the $S_0 \rightarrow T$ absorption spectrum of the naphthalene which was present substitutionally in low concentrations. These results are shown in Figure 7 along with the $S_0 \rightarrow T$ absorption spectrum of naphthalene in ethanol, ether, ethyl iodide, and toluene (EEET). As expected, the phosphorescence intensity produced by direct excitation of the naphthalene in the dibromobenzene crystal was some 10^3 times weaker than that produced by excitation of the host in its $S_0 \rightarrow T$ absorption band.

Although these spectra are not particularly well resolved, there do appear to be differences, depending upon the nature of the host. For example, in EEET the first $S_0 \rightarrow T$ band of the naphthalene is twice as strong as the second prominent vibronic band, whereas in the diiodobenzene crystal these two bands are of comparable intensity, and other bands which appeared only as weak shoulders in EEET now appear prominantly. El-Sayed has noticed similar effects on the naphthalene phosphorescence spectra due to heavy-atom substituents on the naphthalene and attributed it to the existence of two different spin–orbit coupling schemes within the molecule.[73] It appears from our very preliminary investigation of environmental effects on the naphthalene $S_0 \rightarrow T$ absorption spectra that there may be important similarities between the external and internal heavy-atom effects on $S_0 \rightarrow T$ transitions. If correct, this should facilitate our understanding of the mechanism of the external heavy-atom effect. The doped halogen crystals appear to provide a useful media for investigating external heavy-atom effects in a much more quantitative way than has been possible with the rigid glass systems, which have a random arrangement of heavy-atom molecules around the solute.

Experimental Section

Although we discussed the PE method in detail earlier,[42–48] there were some aspects which were not treated. For pure crystals which phosphoresce, impurity effects can usually be evaluated by the procedures used to check compounds dissolved in glassing solutions. If a crystal does not phosphoresce, it is necessary to dope it with some phosphorescent compound which has a triplet state below that of the host. With these doped crystals there are two types of impurities, which may be important.

(a) Unwanted impurities, which have a lower energy triplet state than the host molecules and which phosphoresce, are easily detected by checking the phosphorescence spectrum to see whether or not it is characteristic of the guest molecules.

(b) Impurities, which have a triplet state above that of the host, may absorb light in a $S_0 \rightarrow S$ transition, undergo intersystem crossing to a triplet state, and sensitize the guest phosphorescence by triplet–triplet energy transfer through the host. This type of impurity will probably not affect the spectra for at least 2000 cm^{-1} above the 0–0 band, because singlet–triplet splittings observed for organic molecules are usually greater than 2000 cm^{-1}.[74] Furthermore, the presence of this type of impurity can be detected by noting if there are changes in the excitation spectrum upon further purification of the guest and host compounds.

These simple experimental tests provide very useful criteria for establishing the authenticity of phosphorescence excitation spectra. Hot bands are another possible complication. Whether or not this is a problem depends on the Boltzman factor and the ratio of the extinction coefficient of nearby allowed $S_0 \rightarrow S$ transitions

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[70] The $S_0 \rightarrow T$ extinction coefficient for an aromatic hydrocarbon molecule perturbed by an iodine-containing neighbor molecule is estimated to be 2×10^{-3} (see ref 28) and the extinction coefficient of the $S_0 \rightarrow T$ transition in *p*-diiodobenzene is about 0.5. If we assume that there are six iodobenzenes which have the possibility of transferring triplet-state energy to naphthalene, then absorption of light by the iodobenzenes should be $\sim 1.5 \times 10^3$ ($= 6 \times 0.5/2 \times 10^{-3}$) times more effective in producing naphthalene triplet states than direct $S_0 \rightarrow T$ excitation of the naphthalene.

[71] T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworth & Co., Ltd., London, 1954.

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to the extinction coefficient of the $S_0 \rightarrow T$ transition. The Boltzman factor for a $\Delta E = 1000$ cm^{-1} is e^{-20} or 2×10^{-9} at 77°K. If the extinction coefficient ratio is less than 10^9, we may work to within 1000 cm^{-1} of a $S_0 \rightarrow S$ transition without problems due to hot bands. If the ratio of the extinction coefficients is smaller, then it is possible to work even closer to the 0–0 band of the $S_0 \rightarrow S$ transition.

Apparatus. The PE spectra and the phosphorescence spectra were obtained using a previously described phosphorescope.[48]

In our studies we have used two types of samples: (1) samples dissolved in a glassing solvent and (2) crystalline samples. To obtain the $S_0 \rightarrow T$ spectra of a dissolved sample, the following procedure was used. The sample was first dissolved in a suitable glassing mixture to which a heavy-atom component (methyl iodide, ethyl iodide, for bromoform) could be added.[48] For most of the measurements we used a 2:2:1:1 mixture of ethyl iodide–ether–ethanol–toluene (EEET). The solution was cooled in liquid nitrogen and then inserted in a precooled sample holder. The spectral distribution of the phosphorescence was obtained for several wavelengths of excitation. Finally, the excitation spectrum of the phosphorescence was obtained by monitoring the intensity of the phosphorescence as a function of the wavelength of the exciting light. For crystalline samples a similar procedure was used.

The resolution of the spectra for the benzene derivatives is better than 150 cm^{-1} while the resolution of the rest of the spectra is better than 200 cm^{-1}. The absolute wavelength is reproducible to better than ±10 A for spectra of the benzene derivatives and to better than ±20 A for the rest.

The spectral distribution of the photon output was determined for the various monochromators and gratings which we used by placing a fluorescent fluorescein solution at the sample position and monitoring the fluorescence intensity. The resulting photon distribution curves are presented in Figure 8. The photon distribution shown in Figure 8A was used for the substituted benzenes. The photon distribution shown in Figure 8B was used for all other compounds except 1- and 2-phenylnaphthalene, and acenaphthene and hexahydropyrene where the photon distribution shown in Figure 8C was used. The excitation spectra have not been corrected for the spectral distribution of the exciting light, as this was reasonably flat over the region of interest. In several cases, however, it was necessary to correct for the lines in xenon spectrum in the 4500–5000-A region. The phosphorescence spectra were not corrected for the response of the 1P28 photomultipler.

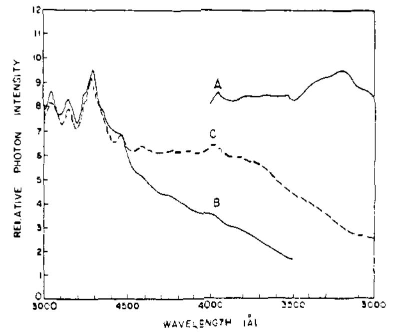

Figure 8. The relative photon intensities of the xenon source with different monochromators: (A) Bausch and Lomb ultraviolet monochromator (used for all halogenated benzenes); (B) Bausch and Lomb visible monochromator (used for all other molecules except four naphthalene derivatives); (C) Jarrell-Ash monochromator (used for 1- and 2-phenylnaphthalene, acenaphthene, and 1,2,3,6,7,8-hexahydropyrene).

Materials. A necessary criterion of purity in these experiments is the absence of any detectable extraneous emission not belonging to the compound of interest. The various methods for determining compound purity have been outlined elsewhere.[48] Because moderate purity was required, all compounds which were not purified more extensively by other means were routinely recrystallized several times from a suitable solvent. If a compound exhibited anomalous emission or indicated the presence of an impurity in any other way, it was subject to further purification until that impurity was eliminated. The following compounds were zone refined: *p*-dichlorobenzene; *p*-dibromobenzene; 1-bromo-4-chlorobenzene; 1,2,4,5-tetrachlorobenzene; hexachlorobenzene; biphenyl; *o*-, *m*-, and *p*-terphenyl; 1,3,5-triphenylbenzene; naphthalene; 2-bromonaphthalene; and phenanthrene. The following solvents were used without further purification: ethanol, U. S. Industries Chemical Co., reagent grade; ethyl ether, Mallinckrodt, analytical reagent; toluene, Matheson Coleman and Bell (MCB), spectroquality; 2-propanol, MCB, spectroquality; methyl iodide, MCB, White Label; and ethyl iodide, MCB, reagent. 2-Methyltetrahydrofuran was distilled from ketyl.

The bromoform which was used as a heavy-atom solvent for most of the polyphenyls was subject to the following purification: it was distilled at reduced pressure over copper wool in a nitrogen atmosphere, and then it was stored in a dark container over copper wool and had 2% 2-propanol added to increase stability.

The $S_0 \rightarrow S$ absorption spectra of the compounds were either measured in absolute ethanol or taken from the literature.[75–82]

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