The Emission Spectra of Aromatic Hydrocarbons in Crystalline Paraffins at −180°.

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The fluorescence and phosphorescence spectra of coronene, 1 : 12-benzoperylene, perylene, triphenylene, and 9 : 10-dichloroanthracene in crystalline paraffins at −180° are reported. The solvents were *n*-paraffins—pentane, hexane, heptane, octane, and nonane. The splitting of the coronene bands previously reported (Bowen and Brocklehurst, *J.*, 1954, 3875), the intensity of its 0–0 band, and the sharpness and position of the spectra of the other compounds vary markedly with solvent. These effects are due to specific interactions of the solute molecules with the crystal lattice of the solvent, which appear to depend on the relative sizes of the molecules involved.

The absorption and emission spectra of organic compounds become sharper on cooling. In nearly all spectroscopic work at low temperatures, glass-forming solvents (*e.g.*, ether–pentane–alcohol) have been used, but the spectra of solid solutions in crystalline solvents appear to be sharper still (*e.g.*, triphenylmethyl in triphenylamine, Weissman, *J. Chem. Phys.*, 1954, **22**, 155; naphthalene in durene, McClure, *ibid.*, 1954, **22**, 1668).

In a previous paper (Bowen and Brocklehurst, *J.*, 1954, 3875), the fluorescence spectra of coronene and 1 : 12-benzoperylene in several solvents at −180° were described. In light petroleum and alcohol, which form glasses on freezing, both substances have quite sharp fluorescence spectra. In frozen hexane and heptane, the spectrum of benzoperylene becomes still sharper while most of the coronene bands split into doublets separated by about 70 cm.$^{-1}$, as earlier observed by Shpol'skii, Il'ina, and Klimova (*Doklady Akad. Nauk S.S.S.R.*, 1952, **87**, 935). The hexane and heptane used were B.D.H. "aromatic free" petroleum fractions and were thought to form glasses because of the non-homogeneous nature of their molecular constituents, but later work shows that they do in fact crystallise.

Coronene, in frozen mixtures of hexane and heptane containing 30—70% (vol.) of heptane, has a fluorescence spectrum identical with that from light petroleum solution. Outside this composition range, the results can be interpreted in terms of two spectra superimposed, one of doublets and one of singlets. Presumably, two phases are formed—one glassy as given by light petroleum and containing both hexane and heptane, the other crystalline and consisting of hexane or heptane only. That the individual solvents crystallise has been confirmed by the use of purer specimens. When the latter are cooled, white, needle-like crystals are formed (the B.D.H. specimens freeze to transparent blocks) and the spectrum of coronene in them is similar to that from the B.D.H. specimens. Mixtures of hexane and heptane, and light petroleum, also form white masses, because the glass cracks, but no crystals are visible.

In this work, the solvents used were *n*-pentane, -hexane, and -heptane (99% pure) and *n*-octane and -nonane (99·9% pure). These will be called "pure" to distinguish them from the B.D.H. specimens, though the latter merely contain more of similar impurities. A mixture of equal volumes of hexane and heptane (B.D.H.) was used as a convenient glass-forming solvent for comparative purposes. Because supplies of the pure solvents were limited, most of the measurements on hexane, heptane, and octane solutions were made with the B.D.H. specimens; no difference was found except for coronene, as described below. More detailed measurements have been made on the solvent effects on the fluorescence spectra of coronene and benzoperylene; the fluorescence spectra of perylene and some anthracene derivatives, and the phosphorescence spectra of coronene and triphenylene, have also been studied in the same way.

EXPERIMENTAL

The apparatus was identical with that described previously (Bowen and Brocklehurst, *loc. cit.*). Fluorescent light from the frozen specimen passed through a Hilger constant-deviation glass-prism spectrometer and its intensity was measured by a photomultiplier. Some of the spectra were also recorded photographically with the same apparatus, the photomultiplier being replaced by a camera; this was more convenient for the study of phosphorescence, and wavelengths could be measured more accurately. An iron arc was used for wavelength calibrations. It is estimated that, for narrow bands, wavelengths could be determined to ±1 Å or better in the blue, and to ±5 Å in the yellow, the chief limitation being the width of the bands. Further work at lower temperatures would be required for greater precision. Relative intensities on the plates were measured with a microphotometer. The photomultiplier had been calibrated and was used for measurements of the fluorescence in relative quantum units of intensity.

Fluorescence spectra at room temperature were also measured with the spectrometer and photomultiplier. Absorption spectra at room temperature were measured with a Unicam S.P. 500 spectrophotometer; because of the low solubility of coronene, 3-cm. cells were used. The emission of coronene and of triphenylene was excited by the mercury 3135 Å line, and that of the other substances by the mercury 3650 Å line. Concentrations used were approximately 10^{-4}M; more dilute solutions of perylene and the anthracene derivatives (about 10^{-5}M) were used to avoid reabsorption of fluorescence; this was unnecessary for the other compounds.

The specimens of coronene and benzoperylene were prepared as described previously (*idem, loc. cit.*). Anthracene derivatives were synthesised in this laboratory and purified by chromatography. We are grateful to Professor J. W. Cook for the specimen of perylene, to Dr. D. F. Evans for the triphenylene, and to Professor Sir Cyril Hinshelwood and Dr. R. E. Richards for gifts of the paraffin hydrocarbons.

RESULTS AND DISCUSSION

Coronene.—The fluorescence spectrum of coronene in B.D.H. heptane has already been published (*idem, loc. cit.*). More peaks have been detected photographically. All the

TABLE 1. *Fluorescence spectrum of coronene in pure heptane at* −180°.

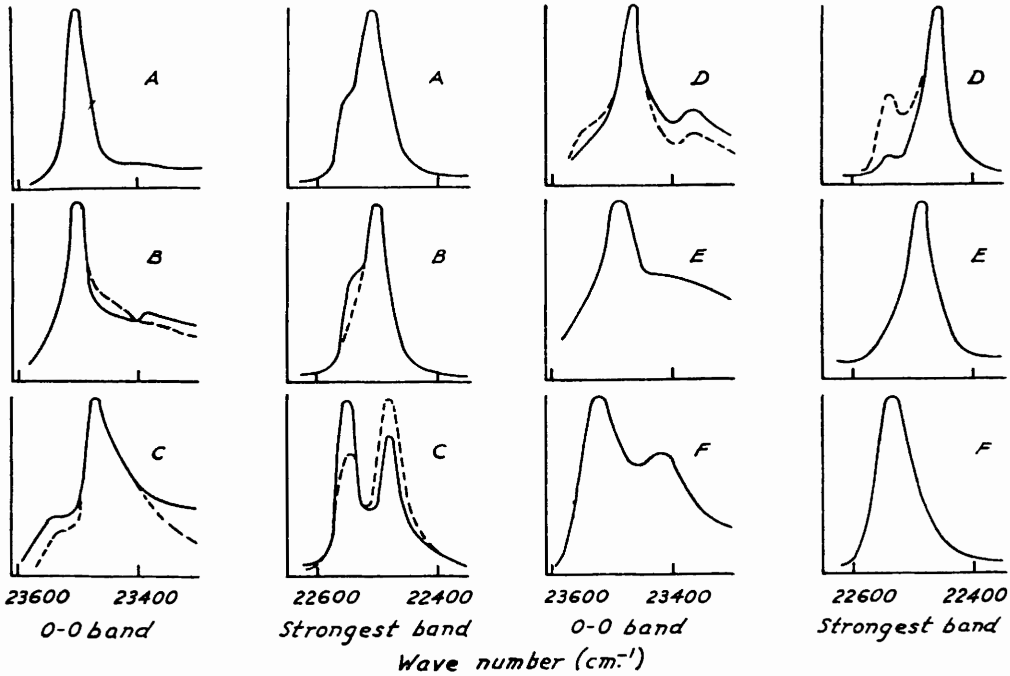
Intensity (*a*)	Intensity (*b*)	λ (Å)	ν' (cm.$^{-1}$)	$\Delta\nu'$ (cm.$^{-1}$)	Assignment (cm.$^{-1}$)
VW	2·1	4249	23,535	−65	−70 ?
W	6·2	4261	23,470	0	0–0 band
S	19·7	4315	23,175	295	365 − 70
S	15·7	4328	23,105	365	365
M	—	4338	23,050	420	?
W	—	4350	22,990	480	550 − 70
W	—	4365	22,910	560	550
W	5·0	4375	22,855	615	685 − 70 ?
W	—	4402	22,715	755	825 − 70
W	5·1	4407	22,690	780	850 − 70
W	—	4416	22,645	825	825
M	—	4425	22,600	870	850
VS	100·0	4436	22,545	925	995 − 70
VS	79·6	4449	22,475	995	995
W	—	4468	22,380	1090	1155 − 70
W	—	4481	22,315	1155	1155
M	10·8	4494	22,250	1220	1290 − 70
M	—	4509	22,180	1290	1290
S	29·3	4518	22,135	1335	1405 − 70
S		4524	22,105	1365	1435 − 70
S		4528	22,085	1385	1455 − 70
S		4532	22,065	1405	1405
W	—	4558	21,940	1530	?
W	—	4563	21,915	1555	?
M	10·2	4581	21,830	1640	365 − 70 + 1350
M	10·9	4597	21,755	1715	365 + 1350
W	7·7	4621	21,640	1830	550 − 70 + 1350
W	7·0	4636	21,570	1900	550 + 1350
W	—	4649	21,510	1960	685 − 70 + 1350
VW	—	4662	21,450	2020	685 + 1350
W	—	4685	21,345	2125	850 − 70 + 1350
W	—	4705	21,255	2215	850 + 1350
S	25·7	4718	21,195	2275	955 − 70 + 1350
S	21·8	4734	21,125	2345	995 + 1350
VW	—	4774	20,945	2525	1155 + 1350 ?
W	3·3	4789	20,880	2590	1290 − 70 + 1350 ?
M	7·8	4824	20,730	2740	1455 − 70 + 1350
M	7·4	4840	20,660	2810	1455 + 1350
VW	—	4872	20,525	2945	?
M	5·3	4883	20,480	2990	365 − 70 + 2 × 1350
M	4·9	4902	20,400	3070	365 + 2 × 1350
W	—	4929	20,290	3180	550 − 70 + 2 × 1350
W		4946	20,220	3250	550 + 2 × 1350
M	5·4	5042	19,835	3635	995 − 70 + 2 × 1350
M	4·9	5064	19,750	3720	995 + 2 × 1350

(*a*) Approximate intensities from photographic plate: S, strong; M, medium; W, weak; V, very.
(*b*) Accurate intensities measured with the photomultiplier and expressed as relative quanta.

peaks, except perhaps the first (4261 Å), occur in pairs. The strong band at 4530 Å consists of three such doublets superimposed. In Table 1, the wavelengths and approximate intensities of the bands emitted by coronene in pure heptane are listed; these values correct and supplement those of Fig. 2 of the reference given.

The transition to the first excited state of coronene is forbidden by symmetry but becomes weakly allowed by coupling with unsymmetrical vibrations (Brocklehurst, *J.*, 1953, 3318) as in the case of benzene (see, *e.g.*, Sponer, Nordheim, Sklar, and Teller, *J. Chem. Phys.*, 1939, 7, 207). The peculiar behaviour of the first fluorescence band (4261 Å), discussed below, shows that it is the 0–0 band of the transition. All the other bands behave like the strongest band (4436, 4449 Å). Fig. 1 shows the effect of solvent on the first and strongest bands at −180°. These measurements were made with the photomultiplier; photographic measurements resolved the bands in octane and nonane into narrow doublets, and Fig. 2 shows the amount of splitting as a function of solvent chain lengths; negative values correspond to a red shift. The peak positions (at both temperatures) are given relative to the position of the single peak in a mixture of hexane and heptane at −180°. The doublet splitting in a given solvent was the same for all the bands, within the experimental error, and was independent of the purity of the solvent. The room-temperature results are necessarily much less accurate, but the direction of the shift between each pair of solvents is certain from intensity measurements on the sides of the peaks. (The position of the spectrum in a mixture of hexane and heptane at room temperature lies between the positions in the individual solvents.)

FIG. 1. *Effect of solvent on the structure of the coronene fluorescence spectrum in solution at* −180°.



—— Pure solvents; ‐ ‐ ‐ ‐ B.D.H. solvents. *A*, Nonane; *B*, octane; *C*, heptane; *D*, hexane; *E*, pentane; *F*, hexane + heptane.

At −180° the bands are sharper in crystalline solvents than in the glassy mixture of hexane and heptane. However, the doublet splitting is clearly not due to a mere sharpening of the spectra. The breadth of the bands (apart from the splitting) increases in the order: hexane, heptane, octane, nonane, pentane, glassy solvents. Coronene thus resembles the other substances investigated, but the effect is small.

Fig. 1 shows that the relative intensities of the two components of the doublets are very sensitive to the purity of the solvent. The ordinary B.D.H. " aromatic free " hexane gives an even stronger short-wave component than the special " spectroscopic " grade normally used. The differences are not consistent with an explanation based on partial glass formation by the B.D.H. solvents. Attempts to produce similar effects were made by adding small quantities of paraffinic " impurities " but the results could always be explained in terms of glass formation.

In rigid solvents coronene has a long-lived yellow phosphorescence. Its spectrum in the same series of solvents has been photographed. Results for octane are given in Table 2 (in heptane, doublet splitting leads to considerable overlapping of bands). The vibrational structure is different from the fluorescence, but doublet splitting and solvent " impurity effects " occur in precisely the same way in hexane and heptane, the doublet splitting being somewhat smaller (Fig. 2). The apparent lack of splitting in octane and nonane may be due to the lower resolving power of the spectrograph in this region. The spectrum in pentane shows no splitting and appears to be distorted relative to that from other solvents (this also occurs in the fluorescence). No splitting of the 0–0 band could be detected in any solvent but the weak bands on the long-wave side of it vary with solvent as in the fluorescence spectrum.

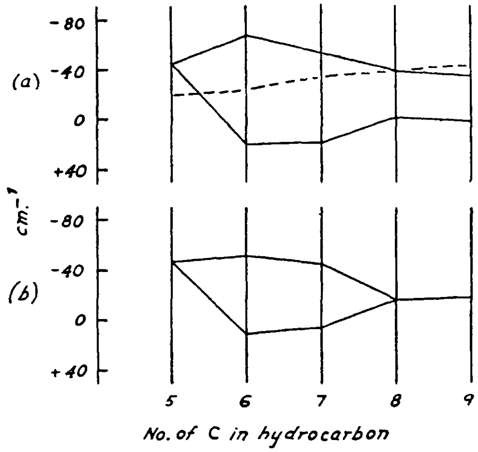


FIG. 2. *Effect of solvent on position of coronene spectra relative to the position in hexane–heptane glass.*

——— at −180°.
– – – – at room temperature.

(*a*) Fluorescence.
(*b*) Phosphorescence.

TABLE 2. *Phosphorescence spectrum of coronene in octane at* −180°.

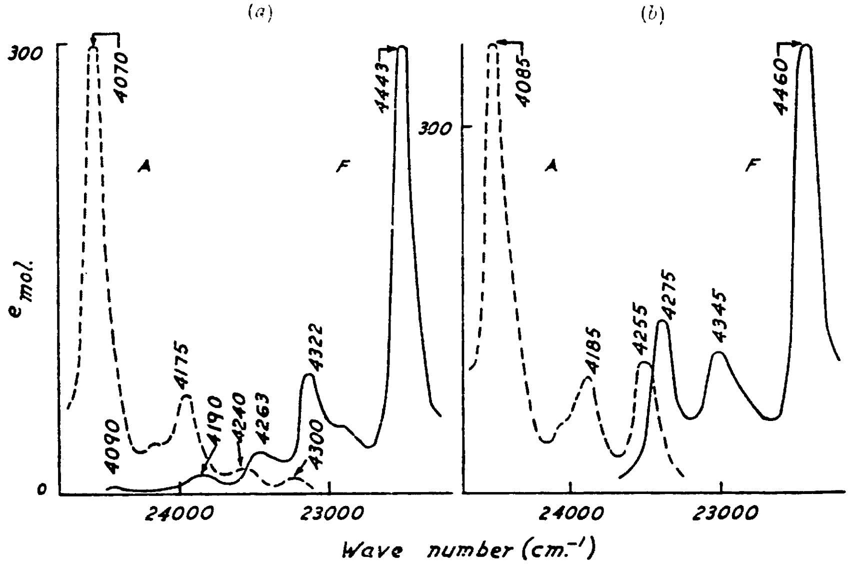
I *	λ (Å)	ν' ($cm.^{-1}$)	$\Delta\nu'$ ($cm.^{-1}$)	Assignment ($cm.^{-1}$)	I *	λ (Å)	ν' ($cm.^{-1}$)	$\Delta\nu'$ ($cm.^{-1}$)	Assignment ($cm.^{-1}$)
W	5154	19,400	0	0–0 band	W	5822	17,175	2225	—
M	5253	19,035	365	365	W	5883	17,000	2400	—
M	5287	18,915	485	—	S	5925	16,880	2520	1160 + 1350
VW	5341	18,720	680	—	S	5946	16,820	2580	1230 + 1350
VW	5366	18,635	765	—	S	6014	16,630	2770	1450 (& 1405) + 1350
W	5389	18,555	845	—	S	6091	16,420	2980	1630 + 1350
W	5425	18,435	965	—	VW	6157	16,240	3160	—
S	5483	18,240	1160	1160	M	6180	16,180	3220	—
S	5503	18,170	1230	1230	M	6277	15,930	3470	—
S	5557	17,995	1405	1405	W	6341	15,770	3630	—
S	5571	17,950	1450	1450	W	6386	15,660	3740	—
VS	5628	17,770	1630	1630	M	6449	15,505	3895	1160 + 2 × 1350
S	5663	17,660	1740	1740	M	6472	15,450	3950	1230 + 2 × 1350
VW	5699	17,545	1855	—	M	6501	15,380	4020	?
VW	5720	17,480	1920	—	M	6546	15,275	4125	1450 (& 1405) + 2 × 1350
S	5783	17.290	2110	—	S	6637	15,070	4330	1630 + 2 × 1350

* Here and in Tables 3 and 4. I = intensity.

Because of these very specific solvent effects, it seems certain that the coronene is in true solid solution in the frozen solvents. No separation of solid coronene (which has a diffuse fluorescence spectrum in the green) was observed. It is surprising that the large coronene molecules fit into the crystal lattices of the paraffins while some smaller aromatic hydrocarbons, *e.g.*, anthracene and naphthalene, will not do so. Formation of associated pairs of coronene molecules seems unlikely; the concentration was very small and the spectrum in heptane was independent of concentration in the range 10^{-4}—10^{-6}M. Associated pairs of pyrene molecules can fluoresce (Förster and Kasper, *Z. phys. Chem., Frankfurt*, **1954**, **1**, 275) but their spectrum is a structureless band far removed from the normal fluorescence spectrum. No photochemical changes on prolonged exposure were detected.

An interpretation of the coronene fluorescence spectrum has been given by Sidman (*J. Chem. Phys.*, in the press). He has identified the 4261 Å band as the 0–0 transition; this is confirmed by the effect of solvent on its intensity. Fig. 3 shows parts of the absorption and fluorescence spectra of coronene in hexane and benzene at room temperature. Wavelengths are approximate; the 4263, 4322, and 4443 Å bands in hexane at room temperature correspond to the 4261, 4328, and 4449 Å bands in heptane at −180°. The intensity of the 0–0 band depends on solvent perturbations, while the other bands are little affected by solvent. In carbon disulphide the 0–0 absorption band is actually weaker than in benzene. The feeble 1–0 bands detected in hexane (4090, 4190 Å in fluorescence, 4300 Å in absorption) complete the mirror-image relationship of the absorption and fluorescence spectra; a feeble 1–0 absorption band ($e_{\text{mol.}}$ about 2) can be detected in saturated solution in carbon disulphide. These bands should be temperature-dependent and do not appear in fluorescence at −180°. The previous assignment of the room-temperature bands (Brocklehurst, *loc. cit.*) is clearly incorrect.

FIG. 3. *Spectra of coronene at room temperature in* (*a*) *hexane and* (*b*) *benzene.*



A, Absorption; *F*, fluorescence. (Peak wavelengths given at Å.)

The doublet splitting is explained (Sidman, *loc. cit.*) as the removal of the double degeneracy of the unsymmetrical vibrations permitting the transition, by unsymmetrical force fields in the crystalline solvents. The 0–0 band should therefore not split at all. As shown in Fig. 1, in frozen hexane and heptane a weak shoulder (4249 Å) appears on the short-wave side of the 0–0 band and shows the "impurity effect" to some extent, as if this band were also a doublet. This effect is small but it is confirmed by the photographic measurements. The wavelength of the main 0–0 band varies with solvent in just the same way as the long-wave component of the doublets. If the 0–0 band is really a doublet like the other bands, then the splitting is better explained in terms of two possible environments for the solute within the crystal lattice; *e.g.*, the coronene molecules might lie parallel to or perpendicular to the solvent molecules, if the latter are arranged in parallel rows. If the 0–0 band were much weaker in one environment than in the other, its partial splitting would be accounted for. As would be expected, the stronger 0–0 band is associated with the long-wave component of the doublets. However, it is difficult to see why only two such distinct environments should exist and why the effect is peculiar to coronene. The shoulder on the 0–0 band may be a purely coincidental result of coupling with lattice vibrations.

If the doublet splitting is associated with unsymmetrical vibrations, then all the fluorescence and phosphorescence bands (except the 0–0 bands) are due to coupling with one quantum of any unsymmetrical vibration and 0, 1, or 2 quanta of the symmetrical breathing frequency (1350 cm.$^{-1}$). The other frequencies may be composed of smaller unsymmetrical vibration frequencies plus other symmetrical vibrations; no attempt at further assignment has been made since the infrared and Raman spectra of coronene are not known. The assignments have been given, however, because the intensity changes of the " impurity effect " make it possible to assign frequencies even when only one doublet component could be resolved (*e.g.*, in the 4530 Å group). They also show the interesting comparison between the two spectra. The main symmetrical vibration (1350 cm.$^{-1}$), the first 0–1 band (365 cm.$^{-1}$), and possibly some other bands occur in both spectra; apart from this the two spectra are quite different and the frequency of the strongest fluorescence band (995 cm.$^{-1}$) cannot be detected at all in the phosphorescence. These differences are not peculiar to coronene (see, *e.g.*, benzene; Shull, *J. Chem. Phys.*, 1949, **17**, 295) and are presumably due to differences in the size and shape of the molecule in the triplet state. Despite these differences, the occurrence of unsymmetrical vibration frequencies in the phosphorescence spectrum shows that the transition to the first triplet level is forbidden by symmetry as well as by spin considerations. This is almost certain in any case from the long lifetime of the phosphorescence (McClure, *ibid.*, p. 905); the same has been found to be true for benzene (Shull, *loc. cit.*).

If Sidman's explanation is correct, the extent of the doublet splitting (Fig. 2) must depend on the asymmetry of the force field round the coronene molecule. It is not a simple function of the dispersion forces between solute and solvent which increase, with the increasing polarisability, in the series pentane to nonane (compare the shifting of the spectrum at room temperature). The crystal structures of these paraffins are not known, but the molecules probably lie parallel to their neighbours in two directions and at an angle to those displaced from them along their long axis. A large flat molecule like coronene can easily fit into such a lattice, replacing a few solvent molecules, provided it is not longer than the solvent molecules. Hexane and heptane are about the same length as coronene, octane and nonane are longer, and pentane is shorter. From the marked differences between pentane and hexane, it seems probable that the coronene can fit easily into the lattices of hexane and the larger paraffins but produces considerable distortion of the pentane lattice. Another possibility is that the coronene may be forced to fit into the pentane lattice in a different way.

In the other solvents, if the paraffin molecules lie centrally over the coronene molecule, the terminal methyl groups will be associated with one axis of the coronene molecule. This will provide the asymmetry in the environment which is responsible for splitting the degeneracy of the unsymmetrical vibrations. This asymmetry will decrease as the solvent molecules become longer than the coronene molecule.

The remarkable changes of intensity distribution produced by impurities in a solvent and the differences between different solvents in this respect are not easily explained. The effect of impurities may be to produce changes in the crystal structure of the solvent. Both effects are more easily understood in terms of doublet splitting due to two different possible environments of the coronene molecule. On the other hand, Sidman's explanation gives a more satisfactory picture of the changes in the extent of splitting with solvent; to explain these on the other hypothesis, it would be necessary to postulate that the position of the spectrum of the molecules in one environment showed shifts with change of solvent in the opposite direction to the position of the spectrum of those in the other environment. This is not impossible, however, since some substances show such shifts in one direction, some in the other (see Fig. 7).

The 0–0 *Band.*—The effect of solvents in the pentane–nonane series on the intensity of the 0–0 fluorescence band is shown in Fig. 4. At room temperature, there is no significant difference except between pentane and hexane. In pentane, the peak intensity of the 0–0 band is 30% greater than in hexane and the band is also broader (the other bands are not affected). The values for room temperature refer to B.D.H. solvents: the value for the peak intensity ratio for heptane at −180° refers to the stronger doublet peak; it becomes 25% larger if referred to the long-wave peak. At −180° there is a remarkable difference between nonane and octane. In nonane the 0–0 band is very strong and sharp (Fig. 1); in octane the band is much weaker, and thereafter the intensity rises again to pentane. At the same time the breadth of the band becomes greater so that the area of the band is the same in pentane as in nonane. This broadening of the band and the extra peaks on the long-wave side of the band are probably due to coupling with the acoustic vibrations of the solvent lattice (Gross and Vuks, *J. Phys. Radium*, 1935, **6**, 457; 1936, **7**, 113; Sponer *et al.*, *loc. cit.*; McClure, *J. Chem. Phys.*, 1954, **22**, 1668). For this reason, the peak intensity ratios are perhaps more significant in assessing the solvent's part in permitting the 0—0 band.

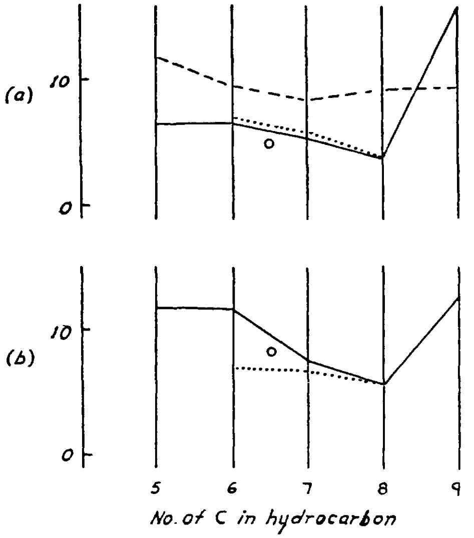


FIG. 4. *Effect of solvent on intensity of the coronene fluorescence* 0–0 *band.*

(*a*) Peak intensity.
(*b*) band area, relative to main peak (= 100):
——— at −180°, pure solvents.
. . . . at −180°, B.D.H. solvents.
– – – – at room temperature.
O hexane + heptane at −180°.

The 0–0 band is forbidden by symmetry but becomes weakly allowed if the molecular symmetry is altered by solvent perturbations. However, this asymmetric solvent effect shows no correlation with that responsible for the doublet splitting; nor is there a good correlation with the strength of the ordinary dispersion forces between solute and solvent. The differences between solvents at −180° are clearly associated in some way with their crystal structures. No accurate measurements were made on the intensity of the phosphorescence 0–0 band, but its intensity does not appear to vary much even between octane and nonane. Its structure does vary with solvent—again probably because of coupling with lattice vibrations.

The exceptional behaviour of pentane at room temperature is presumably another result of its being smaller than coronene, but this is surprising since, in the liquid state, paraffins can take on a greater variety of configurations and all would be expected to behave similarly. The intensity of the 0–0 band in hexane is greater at room temperature than at −180° (the relative band areas are 15·3 and 11·4, respectively) and it is greater in fluorescence than in absorption (band area 6·5). The latter effect is due to the greater interaction of the solvent with the more polarisable excited state. Benzene interacts much more strongly with coronene (band areas: 26·4 in absorption, 42·0 in fluorescence); here, however, some effect of molecular shape or size must be involved since the 0–0 band is weaker in carbon disulphide (21·2 in absorption) despite the larger solvent interaction (shown by the red shift of the spectrum).

Triphenylene.—Since the fluorescence spectrum of this substance was situated in an unfavourable region for the glass spectrograph, measurements were confined to photography of the phosphorescence, which lies in the blue and green. Transitions between the ground state and the lowest excited state (and presumably the first triplet state) are forbidden by symmetry (compare 1 : 3 : 5-trichlorobenzene, Sponer and Hall, Vol. commem. V. Henri, 1947/8, 211, which also belongs to the D_{3h} symmetry group). Coupling with unsymmetrical vibrations must therefore occur, but no doublet splitting was observed. However, this does not invalidate the above interpretation of the splitting of the coronene bands, in view of the highly specific nature of the effect.

The vibrational structure resembles that of the coronene phosphorescence spectrum but is more complicated. There are a larger number of progressions due to coupling with unsymmetrical vibrations, but apparently only one breathing frequency (1350 cm.$^{-1}$). This increased complexity is comparable with that of 1 : 3 : 5-trichlorobenzene (*idem, loc. cit.*). The peaks are grouped in progressions in Table 3. The first six bands are much weaker than the remainder of the spectrum, but they have been tentatively classified with the stronger bands. The position of the 0–0 band is not certain.

TABLE 3. *Phosphorescence spectrum of triphenylene in hexane at* −180° (λ, wavelength in Å).

I	λ	*I*	λ	*I*	λ	*I*	λ	*I*	λ
(W)	(4236)	(W)	(4253)	—	—	(W)	(4283)	—	—
VS	4492	WM	4513	S	4525	VS	4541	VS	4552
M	4780	WM	4808	W	4820	MS	4837	S	4848
		W	5125	VW	5152	VW	5174		
		VW	5506						
x		*y*		*x*		*x*		*x*	
(M)	(4297)	—	—	(M)	(4323)	—	—	(M)	(4347)
S	4561	M	4578	M	4587	S	4594	VVS	4618
S	4858	M	4876			M	4896	VS	4923
M	5194	W	5219			M	5241	MS	5270
						VW	5639		
y		*y*		*x*		*y*		*x*	
VS	4373	M	4398	S	4405	MS	4415	(W)	(4431)
S	4647	M	4672			W	4691	S	4709
S	4950	M	4988					M	5026
MS	5301	M	5336					M	5382
y		*y*		*x*		*x*		*y*	
VW	4440	VW	4446	M	4455	S	4463	S	4484
				W	4739	W	4747	S	4771
				W	5059			M	5096
				W	5427			WM	5463
x		*x*		*y*		*x*		*y*	

One remarkable feature of the spectrum appears to be peculiar to triphenylene; in some progressions the intensity falls off very rapidly, only one, two, or at most, three members of the progression being detectable; in other cases, the intensity falls off slowly in the progression. Accurate measurements of the relative intensities could not be made, but the distinction between the two types of progression is very clear-cut; they are marked x and y respectively in Table 3. Relative intensities in such progressions are governed by the Franck–Condon principle and depend on the relative sizes of the upper and lower states. The existence of two types of progression may result from the peculiar shape of the triphenylene molecule; one type of unsymmetrical vibration may be associated with a direction in the molecule along which little expansion occurs in the transition to the triplet state, and will then give rise to an x-type progression; if, however, an unsymmetrical vibration is associated with a direction where the triplet state is considerably larger than the ground state, more quanta of the 1350 cm.$^{-1}$ breathing vibration will be excited (y-type progression).

Other Substances.—The spectra of the other substances studied are somewhat sharper in rigid glasses at −180° than at room temperature. In crystalline hexane, however, they are very much sharper, and much fine structure can be resolved. The sharpness falls off rapidly in the approximate order: hexane, heptane, octane, nonane, glassy solvents, pentane (except for benzoperylene). In so far as it can be distinguished from the sharpening effect, no splitting of the bands was observed (with the possible exception of some of the perylene bands); spectra from B.D.H. solvents were identical with those from pure solvents.

The fluorescence spectrum of 1 : 12-benzoperylene in hexane at −180°, measured with the photomultiplier, has been reported previously (Bowen and Brocklehurst, *loc. cit.*). Many more bands can be detected photographically; 74 bands were measured in the spectrum from hexane, but there is more fine structure than can be resolved by our apparatus at this temperature. Therefore only the more prominent bands are given in Table 4. The spectrum is much more complicated than those of the other substances studied; as in the case of chlorobenzene (Sponer and Wollman, *J. Chem. Phys.*, 1941, **9**, 816), which has the same low symmetry (C_{2v}), this is due to the large number of the possible vibrations of an unsymmetrical molecule. It differs from chlorobenzene in that the transition is fully allowed (as is shown by the strength of the first absorption band).

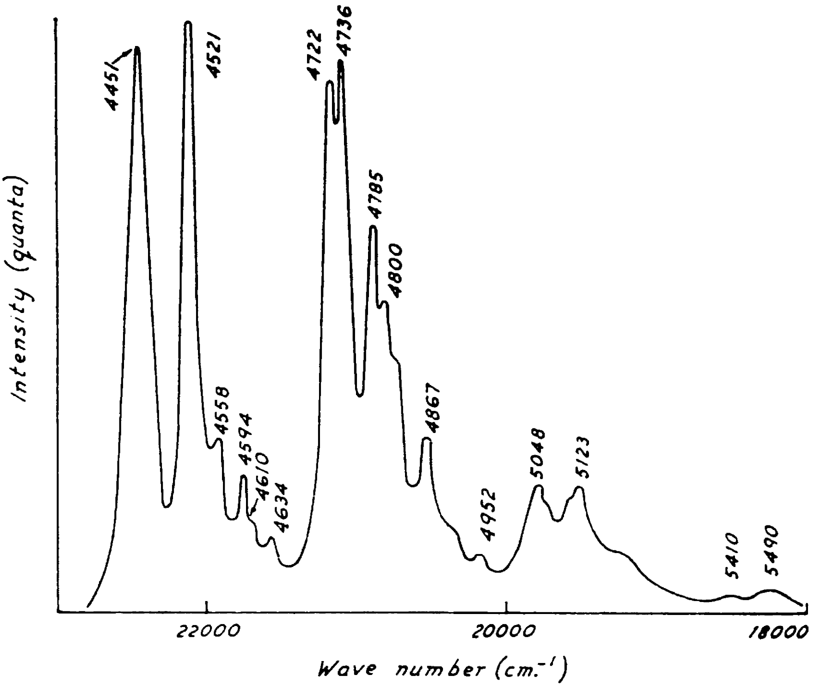
TABLE 4. *Fluorescence spectrum of* 1 : 12-*benzoperylene in hexane and pentane at* −180°.

Hexane				Pentane			
I	λ (Å)	ν′ (cm.$^{-1}$)	Δν′ (cm.$^{-1}$)	I	λ (Å)	ν′ (cm.$^{-1}$)	Δν′ (cm.$^{-1}$)
S	4060	24,630	0	S	4049	24,700	0
				W	4054	24,655	35
W	4083	24,490	140	W	4071	24,560	140
				W	4099	24,395	305
M	4121	24,265	365	W	4111	24,325	375
M	4125	24,245	385	W	4114	24,310	390
				W	4119	24,280	420
W	4136	24,175	455				
W	4140	24,155	475	W	4130	24,215	485
				M	4135	24,180	520
S	4149	24,100	530	S	4137	24,170	530
S	4155	24,070	560	M	4144	24,130	570
				S	4146	24,120	580
				M	4151	24,090	610
M	4175	23,950	680	M	4164	24,015	685
VS	4191	23,860	770	VS	4180	23,925	775
S	4198	23,820	810	S	4187	23,885	815
W	4204	23,790	840	W	4192	23,855	845
W	4219	23,700	930	W	4208	23,765	935
M	4222	23,685	945	M	4211	23,745	955
M	4230	23,640	990	M	4218	23,710	990
M	4241	23,580	1050	M	4228	23,650	1050
	25 M and W bands						
				M	4413	22,660	2040
M	4434	22,555	2075	M	4421	22,620	2080
				VW	4429	22,580	2120
M	4451	22,465	2165	M	4439	22,530	2170
				M	4447	22,485	2215
	20 W bands						
W	4715	21,210	3420	VW	4701	21,270	3430
W	4727	21,155	3475	W	4711	21,225	3475
W	4736	21,115	3515				
W	4746	21,070	3560	W	4730	21,140	3560

Unlike all the other substances studied, benzoperylene has an even sharper spectrum in pentane than in hexane; also some new bands appear and others are shifted (Table 4); fewer bands could be resolved than for hexane because of the complexity of the spectrum.

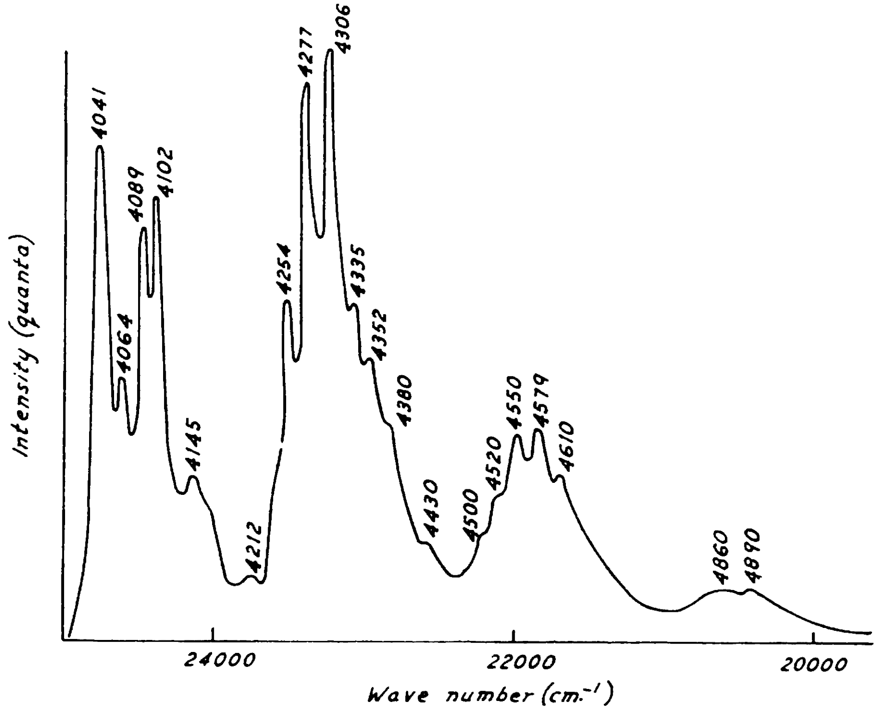
The fluorescence spectrum of perylene in frozen hexane (Fig. 5) is relatively simple (as is to be expected for an allowed transition in a symmetrical molecule). It is also less sharp than those of the larger hydrocarbons. The spectrum indicates coupling with two

FIG. 5. *Fluorescence spectrum of perylene in hexane at* −180°.



(Peak wavelengths given in Å.)

FIG. 6. *Fluorescence spectrum of* 9 : 10-*dichloroanthracene in hexane at* −180°.



(Peak wavelengths given in Å.)

main frequencies; it resembles the absorption spectrum measured in an alcohol glass at −180° (Clar, *Spectrochim. Acta*, 1950, **4**, 116) but it is sharper and more complicated. In heptane, there are additional weak bands at 4410 Å (*i.e.*, 180 cm.$^{-1}$ to the blue of the first strong band) and about 4685 Å; these are stronger in B.D.H. heptane and very weak in octane.

The fluorescence spectrum of 9 : 10-dichloroanthracene in frozen hexane is shown in Fig. 6. The main splitting of the first band is observed even in glassy solvents; most of the small peaks become shoulders in heptane and cannot be detected in the other solvents—perylene behaves very similarly. 9-Cyanoanthracene has a similar sharp spectrum in frozen hexane; 9 : 10-diphenylanthracene shows no fine structure in these solvents, its spectrum remaining very broad. Solutions of anthracene in hexane, when frozen, show a broad structureless band between 4000 and 5000 Å when excited by the mercury 3650 Å line. The spectrum of solid anthracene lies in the same region but consists of discrete bands; the diffuse band resembles that obtained by preparing a glassy solution of anthracene in the presence of excess of solid (Moodie and Reid, *J. Chem. Phys.*, 1952, **20**, 1510; 1954, **22**, 1126); it is presumably due to finely divided solid anthracene. Some anthracene does remain in solution and is preferentially excited by the mercury 2537 Å line—a sharp spectrum, like that of 9 : 10-dichloroanthracene, is obtained.

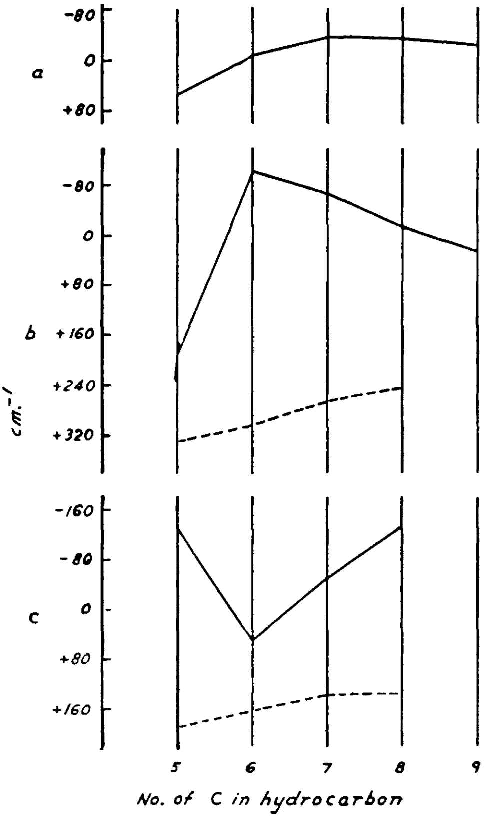


FIG. 7. *Effect of solvent on the position of spectra, relative to the position in hexane–heptane glass at* −180°.

——— at −180°.
– – – – at room temperature.

(*a*) 1 : 12-Benzoperylene.
(*b*) Perylene.
(*c*) 9 : 10-Dichloroanthracene.

Fig. 7 shows the effect of solvent on the positions of the fluorescence spectra (compare Fig. 2); values relative to spectra from a mixture of hexane and heptane are given. There is an excellent correlation between band sharpness and magnitude of the spectral shift, although for perylene the maximum sharpness is associated with a red shift and for all the other substances with a blue shift; the phosphorescence of triphenylene behaves like 9 : 10-dichloroanthracene in this respect.

Discussion.—Although the effects of non-polar solvents and temperature on fluorescence spectra of substances in liquid solutions and glasses can be explained in terms of dispersion forces, yet more specific effects must be invoked for the crystalline solutions considered here. The solvent shift at room temperature is small and no corresponding changes in sharpness could be detected (the spectra are, of course, much more diffuse than at —180°); measurable spectral blurring is only produced by solvents which interact much more strongly with the solute than do the paraffins. Spectra in glasses at low temperatures are sharper than at room temperature; presumably there is less variation in the environment of the solute molecules. In the crystalline solvents, if the solute molecule can fit into the lattice in only one way, then its spectra will be very sharp since all the molecules have exactly the same environment. If then, as suggested above, hexane molecules are nearest in lattice size to the solute molecule, the appearance of maximum sharpness in hexane can be explained. When the solvent molecules are larger than hexane, the position of the solute molecule in the lattice will be more variable and the spectrum therefore less sharp. Since the spectra of all the substances studied (except benzoperylene) are sharpest in hexane, it must be assumed that all the solutes have their long axes parallel to the solvent molecules. This is to be expected since in this configuration the number of solvent molecules displaced will be a minimum.

The effect of pentane on the spectra is very striking and it must again be supposed that the solute molecules cannot readily fit into its lattice because they are longer than the pentane molecule. This is supported by the fact that some substances tend to be precipitated from pentane on cooling. Also, it appeared that fluorescence and phosphorescence efficiencies are lower in pentane than in the other solvents. The behaviour of benzoperylene is very peculiar; its spectrum in pentane seems to be modified as well as sharpened (Table **4**).

The correlation of spectral shifts with sharpening (Fig. 7) suggests that in hexane the interaction between solvent and solute is a minimum; in pentane, the interaction increases because of the distortion of the crystal lattice; in the larger paraffins the dispersion forces will be stronger than in hexane. However, the shift between hexane and nonane is larger than at room temperature, so the latter effect is perhaps enhanced by distortion of the crystal lattice by the solute molecules; this effect will be smallest in hexane, where the the best fit of solute and solvent occurs. The effect of this distortion on the solute molecule apparently varies considerably: the sharpening and shifting of the spectra of perylene and 9 : 10-dichloroanthracene are particularly large; the same effect occurs in coronene but is much smaller, perhaps because coronene is more rigid than the other molecules and therefore is much less affected by the solvent in this respect; for example, it has a much smaller spectral shift with solvent at room temperature.

Spectral blurring is normally accompanied by a red shift of the spectra (because of greater interaction with the more polarisable excited state); this occurs here except in the case of perylene. It must be assumed that the solvent interacts more strongly with the perylene in the ground state than in the excited state. Alternatively, it is possible that solvent interaction is a maximum in hexane (blurring of spectra depends on variations in the interaction with different solute molecules rather than the total interaction). Then perylene behaves normally and the other substances interact more strongly with solvent in the ground state than in the excited state. This might be explicable in terms of the exact arrangement of the solvent molecules around the solute molecule which will depend on its size and shape in the ground state; however, the change of size on excitation is probably very small—it is only 2·5% (linearly) for benzene (Garforth, Ingold, and Poole, *J.*, 1948, 508). It therefore seems more probable that interaction is a minimum in hexane; the anomalous behaviour of perylene may be the result of a marked change of shape on excitation; this seems possible since there is probably much greater conjugation between the two naphthalene nuclei in the excited state.

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