The Fluorescence Spectra of Coronene and 1 : 12-*Benzoperylene at Low Temperatures.*

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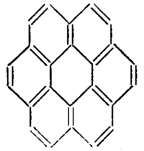
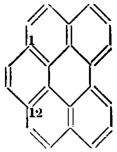
[Reprint Order No. 5517.]

The fluorescence spectra of coronene and 1 : 12-benzoperylene in hydrocarbon glasses at about −180° are reported. In light petroleum the spectra consist of series of sharp bands in the violet and blue. In hexane and heptane, further splitting of some of the bands occurs. Specific solvent effects seem to be involved.

The fluorescence spectrum of coronene (I) has been studied by Shpol'skii, Il'ina, and Klimova (*Doklady Akad. Nauk S.S.S.R.*, 1952, **87**, 935). They reported that, in organic solvents, it consists of a series of narrow bands in the violet and blue. When the solutions are cooled with liquid air, the bands become very narrow—much more so than those of most other aromatic hydrocarbons. In particular, in frozen hexane and heptane, there is further splitting of the bands into very fine " lines," of which more than eighty were detected by photography.

(I)





(II)

The present work confirms these results in general, but it is shown that the coronene used by the Russian workers must have contained an impurity, and that the spectrum studied was that of two substances. The coronene used by us had been separated from the by-products of the hydrogenation of coal, by repeated fractional crystallisation. Even after further purification by chromatography on alumina, it was found that the fluorescence spectrum varied with the wave-length of the exciting light; there were also small differences in the absorption spectrum in the range 3500—4000 Å. The impurity responsible for this effect can be partly removed and concentrated by repeated vacuum-distillations, and appears from its absorption spectrum to be 1 : 12-benzoperylene (II) (Clar, " Aromatische Kohlenwasserstoffe," Springer, Berlin, 1941). Absorption measurements show that the original coronene contained about 6% of benzoperylene, and fractions were finally obtained containing less than 1% and about 40%. Further purification of the benzoperylene was not attempted for this work as the two substances absorb selectively at different wave-lengths. The molar extinction coefficients at 3650 and 3135 Å are: coronene, 320 and 32,000; benzoperylene, 23,000 and 7500. Although the coronene used by the Russian workers contained very little benzoperylene, their excitation by 3650 Å light exaggerated the benzoperylene fluorescence from the material. Our results are for our purest coronene excited at 3135 Å, and for the specimen containing 40% of benzoperylene excited at 3650 Å. In each case there was no detectable fluorescence from the other substance. The two separate spectra, taken together, include nearly all the peaks obtained by the Russians.

Experimental

A high-pressure mercury lamp with a clear glass envelope was used with a Chance OX 1 glass filter as a source of 3650 Å light. Light of wave-length 3135 Å was obtained from a similar lamp from which the envelope had been removed; Chance OX 7 glass and a solution of nickel, cobalt, and copper sulphates were used as filters. The optical arrangements are shown in Fig. 1: the light from the lamp (*A*), focused by a lens (*L*), was reflected by a front surface-aluminised mirror (*M*) on to the specimen in a recessed copper disc (*D*); the latter was attached to a copper rod, the lower end of which was immersed in liquid oxygen. Thermal insulation of the specimen was provided by a vacuum-jacket connected to the rod by a copper–glass seal (*C*). The incident and the fluorescent light passed through a silica disc immediately above the specimen. A copper–constantan thermocouple (*T*) soldered to the side of the copper disc, showed that a temperature of about −180° was reached.

The fluorescent light was reflected by a prism into the slit (*S*) of a Hilger constant-deviation spectrometer with a glass prism. Light from the exit-slit fell on the cathode of a photomultiplier (R.C.A. 931A), the output of which was measured after amplification. The instrument was calibrated with a standard tungsten lamp to enable the results to be plotted as intensities on a quantum basis.

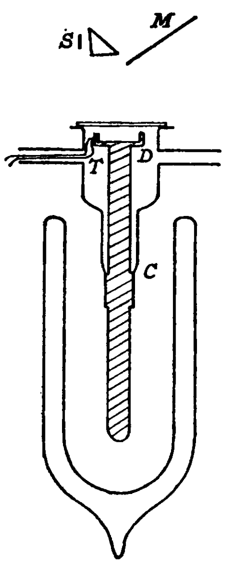


FIG. 1. *Apparatus for the measurement of fluorescence spectra at low temperatures.*

RESULTS AND DISCUSSION

Measurements were made on the fluorescence spectra of coronene in *n*-hexane, *n*-heptane, light petroleum (b. p. 80—100°), liquid paraffin, and ethanol, and of benzoperylene in the first three solvents. In light petroleum the coronene spectrum has twelve sharp peaks; in heptane, five of these split into doublets, the peaks of which are separated by 60—70 cm.$^{-1}$, and two new weak peaks appear. The spectrum in hexane is similar, but the doublets are less sharply resolved. The wave-lengths of the peaks in hexane and heptane are identical within the experimental error, but both are shifted to the red relative to the light petroleum solution, by about 40 cm.$^{-1}$. In alcohol, the spectrum is practically identical, in position and structure, with that in light petroleum. Liquid paraffin gives similar results, but the spectrum is somewhat more diffuse.

1 : 12-Benzoperylene in light petroleum has a relatively diffuse fluorescence spectrum. This becomes sharper in heptane, and, unlike the coronene spectrum, sharper still in hexane. The peaks do not shift appreciably on change of solvent. The peak at 4450 Å coincides with the main peak of coronene, but its relative intensity is the same in mixtures containing more coronene so it is very probably due to the benzoperylene.

Coronene, in solution at low temperatures, has a strong yellow phosphorescence which has a lifetime of several seconds. The low sensitivity of the photomultiplier to yellow light prevented us from obtaining significant measurements. The phosphorescence spectrum has been recorded by Shopl'skii and his co-workers (*loc. cit.*); it has a very sharp structure, and there are distinct differences between hexane and heptane solutions. Benzoperylene has no detectable afterglow, and its presence as an impurity does not therefore interfere with their results in this wave-length region.

The first singlet–singlet transition of coronene is probably forbidden by symmetry (Brocklehurst, *J.*, 1953, 3318), but becomes weakly allowed by coupling with unsymmetrical vibrations, as in the case of benzene (see, *e.g.*, Sponer, Nordheim, Sklar, and Teller, *J. Chem. Phys.*, 1939, **7**, 207). There is then the possibility of further combination with symmetrical vibrations, as in the case of allowed transitions (Franck–Condon principle). At liquid-oxygen temperature, only vibrations of the ground state need be considered. In the spectrum obtained from light petroleum solution, there are four series of three bands, *i.e.*, four different unsymmetrical vibrations must be involved. The magnitudes of these quanta cannot be measured as the position of the 0–0 line is uncertain. The symmetrical vibration is the same in all four series, as they all show inter-peak distances of approximately 1330 cm.$^{-1}$. The spectra in hexane and heptane can be interpreted similarly, doublets only occurring in two of the four series. The spectrum of benzoperylene is more complicated : this is surprising as the transition is not forbidden (as is shown, for example, by the strength of the first absorption band).

The doublets in the spectrum of coronene in hexane and heptane, and the shift of the spectrum relative to light petroleum, are very remarkable. The bands in light petroleum

FIG. 2. *Fluorescence spectrum of coronene in heptane at* −180°. *Peak wave-lengths given in* Å.

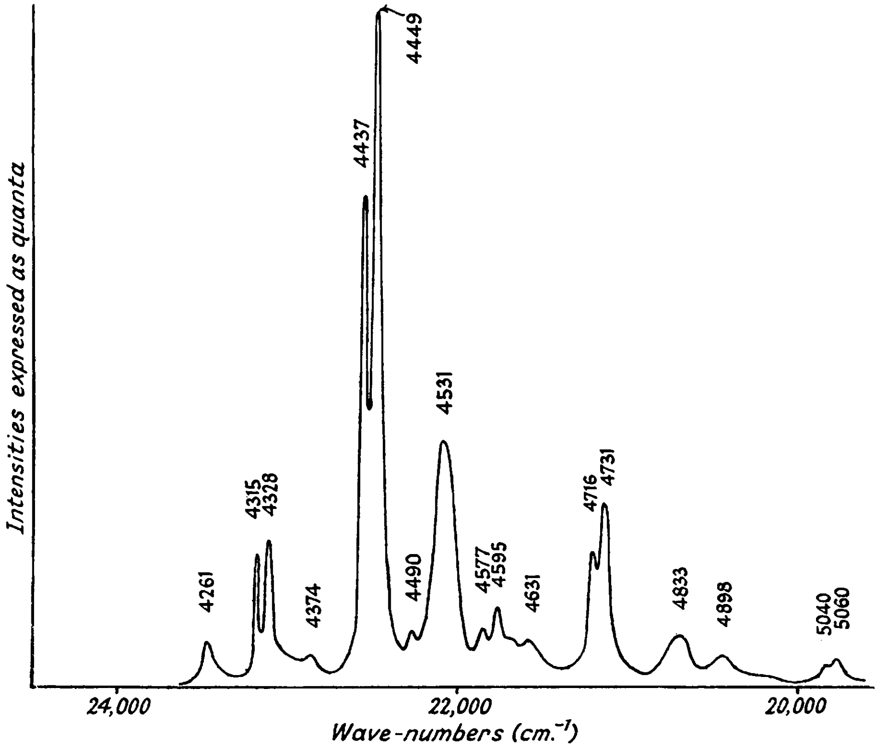
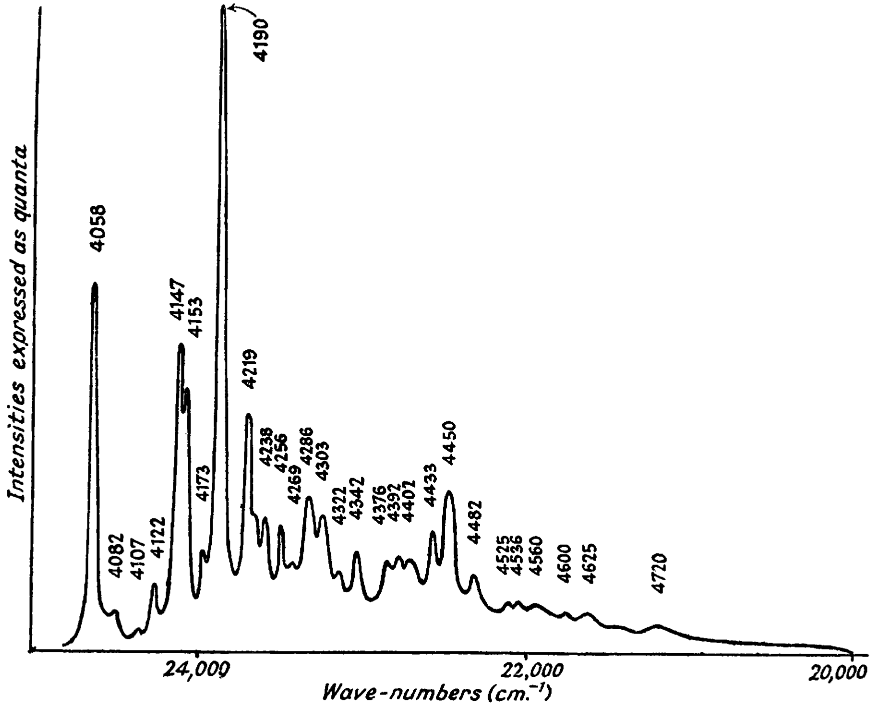


FIG. 3. *Fluorescence spectrum of* 1 : 12-*benzoperylene in hexane at* −180°. *Peak wave-lengths given in* Å.



are as sharp as those in hexane or heptane, and it seems that the lack of doublet structure is not due to a general broadening of the bands by this solvent. The hexane and heptane used are not chemically pure but are petroleum fractions (B.D.H.), free from fluorescent impurities. They are mixtures of the same nature as the light petroleum, though boiling at lower temperatures and over a narrower range. The doublet effect appears to depend on the solvent in a way not attributable to impurities. The different effects of hexane and heptane on coronene and benzoperylene indicate that specific solvent effects of a peculiar type are involved.

The condition of the frozen solvents is uncertain. The Russian workers considered that their hexane and heptane were crystalline, but it seems probable that our solvents formed glasses. The solutions were cooled very rapidly to prevent crystallisation of the solute, and the chemically mixed nature of the solvents facilitates glass formation. The specimens were always transparent and showed many cracks. It is certain that the solutes remain in true solution, since the spectrum of solid coronene is very diffuse, showing little sign of structure.

The fluorescence spectra of solid aromatic hydrocarbons have fine structure at the temperature of liquid hydrogen (*e.g.*, solid benzene; see Sponer *et al.*, *loc. cit.*). This is believed to result from coupling of the transition with vibrations of the whole lattice. It seems unlikely, however, that similar interaction between an excited molecule and the surrounding solvent lattice would be strong enough to produce the effects found here. In any case, by analogy with the case of solid benzene, the sub-bands would be expected to occur on the long-wave side of the main bands. Their occurrence on the short-wave side only seems to indicate a specific effect on the upper state.

One of us (B. B.) wishes to thank the D.S.I.R. for a maintenance grant.

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[*Received, July 2nd,* 1954.]