589. *Low-temperature Absorption and Phosphorescence Spectra of Some Iodo-compounds.*

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Iodine-substituted single-ring compounds sometimes show diffuseness in their spectra and only feeble phosphorescence (triplet–singlet emission), because of the importance of the $N \rightarrow Q$ absorption (Mulliken) characteristic of the alkyl iodides. Low-temperature absorption spectra and phosphorescence of a number of these iodo-compounds have been measured, and the significance of this phenomenon emphasised, except in the case of the iodobenzoic acids, where phosphorescence is relatively strong.

Methyl Iodide.—In the spectra of all alkyl halides, the longest wave-length electronic absorption is a continuum. Mulliken treated these continua theoretically (*J. Chem. Phys.*, 1940, **8**, 382) and interpreted them as similar to the $N-Q$ type spectra of the halogen halides. He found a discrepancy, however, between the theoretical and the observed intensity for methyl iodide. Although at the time the extent of the long wave-length region was not kown for certain, Porret and Goodeve's work (*Trans. Faraday Soc.*, 1937, **33**, 690) suggested to Mulliken that at least a small fraction of molecules dissociate to give a $^2P_{3/2}$ iodine atom.

We have examined methyl iodide in light petroleum solution and also the pure liquid with the aid of the Beckman spectrophotometer, the absorption curve obtained being shown in Fig. 1. Reproduced with it is the curve obtained by Porret and Goodeve (*loc. cit.*) for the vapour. Our curve corroborates Mulliken's conclusions that in methyl iodide the majority of the intensity lies in the $N-Q_0$ transition, the $N-^3Q_1$ appearing weakly (limit about 5000 Å), and it must be assumed that the weak $N-^1Q$ is well concealed under that of the $N-Q_0$.

Porret and Goodeve's work (*loc. cit.*) led them to believe in the existence of two maxima in the extinction curve, one at 38,800 and the other at 34,600 cm.$^{-1}$. After examination of the spectrum of methyl iodide in glassy solution at $-180°$, however, we find no evidence to support this supposition. We found only one maximum, corresponding to the one at 38,800 cm.$^{-1}$ in the vapour.

Iodobenzene.—It has been reported (Dunn and Iredale, *J.*, 1952, 1592) that the anomalous absorption intensity of iodobenzene in the 2600 Å region lies in a contribution from the $N-Q$ type transition present. The red shift of the *O,O* band of iodobenzene in the vapour relative to that of benzene was given as about 1330 cm.$^{-1}$ as compared with 271, 1037, and 1093 cm.$^{-1}$ for fluoro-, chloro-, and bromo-benzene, respectively. A discussion of the "reversed" order of red shift and intensification is relevant. An explanation of this has been given by Matsen and Robertson (*J. Amer. Chem. Soc.*, 1950, **72**, 5252) but they had to resort to use of the inductive effect, the validity of which is open to question.

If we wish to discuss red shift and intensification along the lines suggested by Herzfeld (*Chem. Reviews*, 1947, **41**, 233) it is important to know the order of mesomeric electron

release in the ground state of the molecules under consideration. This order has been a matter of considerable dispute. The methods of determining it are of two types: (1) calculation of a mesomeric moment from dipole-moment measurements, and (2) the effect of nuclear attached halogen on the reactivities of aromatic side chains.

The first method involves treating the observed dipole moment as the vector sum of three moments, namely m_{ind}, the moment induced in the rest of the molecule by the polar carbon–halogen bond, m_{prim}, the moment of the carbon–halogen bond, and m_e the moment due to the mesomeric migration of electrons into or out of the aromatic ring. The main causes of error in this method are (1) the difficulty of allowing for induction, *i.e.*, in evaluating m_{ind}, and (2) doubt as to how far it is correct to assume that the primary moments are equal in saturated and unsaturated compounds.

These intrinsic errors being disregarded, all the work published using this method (Sutton, *Proc. Roy. Soc.*, 1931, *A*, **133**, 668; Hugill, Coop, and Sutton, *Trans. Faraday Soc.*, 1938, **34**, 1534; Groves and Sugden, *J.*, 1937, 1992; Audsley and Goss, *J.*, 1942, 497), with the exception of that of Sutton who used solution measurements entirely, suffers from the lack of dipole-moment measurements on the vapours of the iodo-compounds involved.

FIG. 1.   *Methyl iodide.*   FIG. 2.   *Iodobenzene.*
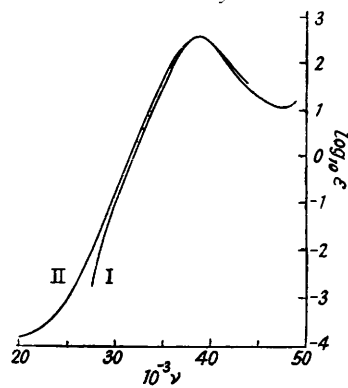
I. Porret and Goodeve's curve.
II. Liquid and solution measurements.
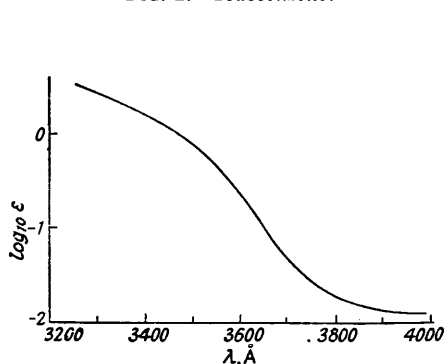
These values have been obtained by the use of various solvent effect factors from solution measurements and prove completely inadequate.

However, the results of the second method are consistent and show that the mesomeric electron release decreases in the order $F > Cl > Br > I$. The evidence for this order was first obtained in 1926 (Shoesmith and Slater, *J.*, 1926, 216; Ingold, *Ann. Reports*, 1927, 156). The chemical evidence has been collated by Bennett and Baddeley (*J.*, 1933, 261; see also Bennett, *ibid.*, p. 1112) and recently it has been summarised and augmented by Baker and Hopkins (*J.*, 1949, 1089).

If, then, it is assumed that this order is the same in the excited state but that the decrease is much faster, we would expect the shift to be in the order found, *i.e.*, $I > Br > Cl > F$, if Herzfeld's ideas are valid. The justification for the much faster decrease for iodine over the other halogens for the excited state would come from the size of the p orbitals of iodine which would produce severe limitations upon mesomeric electron release.

The intensity of absorption will depend on the perturbation of both the ground and the excited states. It should be noted that mesomerism will tend to increase the charge distribution on the *ortho*-positions; this will then favour the transition under consideration, as the transition moment lies in the plane of the molecule perpendicular to the carbon–halogen bond. That the perturbation is relatively stronger for fluorine than for chlorine, etc., accounts for the high intensity of the spectrum of fluorobenzene and the fact that the allowed transition is many times stronger than the forbidden one, while for iodo-benzene the intensity is low and the forbidden transition is much stronger than the allowed.

Although the appearance of the spectrum of iodobenzene would suggest that it has the least intensity of the halogenobenzenes, $\varepsilon_{max.}$ is 670 in solution. The reason for this has been discussed by Dunn and Iredale (*loc. cit.*).

We have also examined the spectrum of iodobenzene in solutions of high concentrations in order to determine the long wave-length limit as shown in Fig. 2. As can be seen, the limit is at about 4000 Å, thus showing that the Q complex depends on the $N-Q_0$ transition for its intensity. It can then be said that the continuous spectra of methyl iodide and iodobenzene differ in that the transitions $N-^3Q_1$ and $N-Q_1$ play no part in determining the intensity of the absorption in iodobenzene, although their effect is quite noticeable in methyl iodide. The Q_0 state must then be responsible for the predissociation.

Phosphorescence of Iodobenzene.—Singlet–triplet absorption analogous to that in benzene should occur in the region 3500 Å. This transition can be seen in Fig. 2, though it is overlapped by the $N-Q$-type transition and appears only as a slight hump in this region. Attempts to obtain triplet–singlet phosphorescence emission from this level have not been very successful. H. J. Tinson in this laboratory has after much trial and error obtained a spectrum of the emission under rather drastic conditions. A faint spectrum was obtained after 7 hr.' exposure with a 0·8-mm. slit, a small Hilger spectrograph of very good light-gathering power being used. The spectrum was at first ascribed to the presence of an impurity; but after subsequent work on other iodo-compounds we are convinced of its validity. Although the high-energy end of the spectrum is very faint, it is the right spectral region, *i.e.*, about 3500—3600 Å.

From the work presented so far, we are able to gather that weak coupling takes place between the Q_0 state and the B_1 level of the π system as a consequence of the close proximity and similar intensity of these two states. However, on further substitution, as shown below, the interaction between the two states is weakened mainly as a result of changes in position of the π level with respect to that of the Q_0 state.

Substituted Iodobenzenes.—Until recently, little was known about the spectra of substituted iodobenzenes except the scanty information obtainable from solution measurements. Purvis (*J.*, 1911, **99**, 2318) attempted vapour measurements but reported continua for *o*- and *m*-iodotoluene and *o*- and *m*-di-iodobenzene. More recently Henri (*J. Phys. Radium*, 1928, **9**, 205) obtained continuous absorption for the three isomeric di-iodo-benzenes in the vapour. Solution measurements have been very limited, Conrad–Billroth being the main contributor.

To gather further information, some new spectra have been investigated and some others repeated. The compounds were examined in light petroleum solution and some at $-180°$ in a glassy solvent. The phosphorescence emissions of some of them have been examined and recorded. The simple *ortho*- and *meta*-monosubstituted iodobenzenes have the point group symmetry C_s. This is reflected most noticeably in their spectra. The *ortho*- and *meta*-derivatives have similar spectra, whilst those of the *para*-derivatives (point group C_{2v}) show higher intensities and greater red shift of the first two electronic transitions.

o-, m-, and p-*Chloroiodobenzene.*—These compounds were examined with the Beckman spectrophotometer in light petroleum solution. They had been examined by Conrad-Billroth and Förster (*Z. physikal. Chem.*, 1936, *B*, **33**, 311). The absorption curves are shown in Fig. 3. In order to examine the structure of the first electronic transition (the one similar to the $^1A_{1g} - {}^1B_{2u}$ transition in benzene) the absorption spectra of the three isomers were examined in light petroleum solution at $-180°$. The positions of the bands are shown in the Table, measurements being taken on the centre of each band. The positions of the four broad diffuse bands of the *para*-isomer are somewhat uncertain.

o-Chloroiodobenzene				m-Chloroiodobenzene				p-Chloroiodobenzene	
Band	Å	Band	Å	Band	Å	Band	Å	Band	Å
1	2805·5	6	2626	1	2817	6	2567	1	2855
2	2760·5	7	2587	2	2792	7	2569	2	2756
3	2733·5	8	2551	3	2710			3	2667
4	2699	9	2525	4	2667			4	2587
5	2657			5	2641				

Because of the inherent diffuseness of these spectra it was not possible to carry out an accurate vibrational analysis.

The location of the *O,O* band in an electronic transition is facilitated by observing the spectrum at low temperature. As the temperature is lowered, thermal population of low vibrational states is very greatly decreased with subsequent intensification of transitions arising from the vibrationless ground state. By comparison of the spectrum at room with that at low temperature it is possible to determine which is the *O,O* transition, as the bands suffer only a very slight blue shift on lowering of temperature.

In accord with the symmetry of these compounds and the nature of the chlorine substituent, the first band observed in solution in each case proved to be the *O,O* transition.

The spectrum of the *ortho*-isomer when observed in the vapour has the same appearance as that at a low temperature with the exception that the bands are slightly less diffuse, this being most noticeable with the *O,O* transition. All the intense transitions in the vapour state therefore arise from the vibrationless ground state.

Phosphorescence.—The appearance of phosphorescence emission for these compounds was obtained by H. J. Tinson in this laboratory under rather drastic conditions (5 hr.' exposure with 0·5-mm. slit). The tracings from these plates are shown in Fig. 4. The
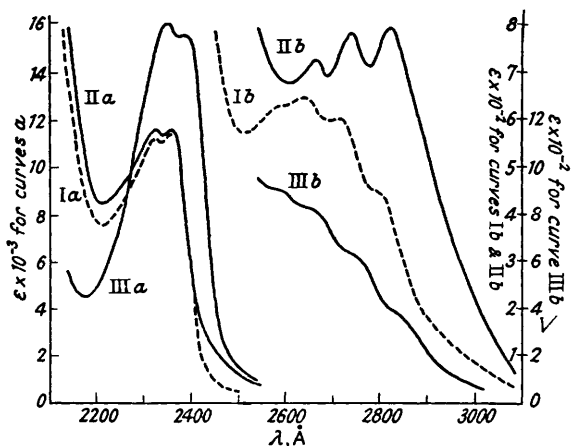

Fig. 3.
(I) o-, (II) m-, *and* (III)
p-*Chloroiodobenzene.*

relative intensities of the emissions are not necessarily in the order shown. The emissions are stronger than that recorded for iodobenzene and are very diffuse. The energy order of the emissions is interesting, being in the direction $p > m > o$.

o-, m-, *and* p-*Iodonitrobenzene.*—The spectra of these compounds (Fig. 5), which have not been previously recorded, show the appearance of three electronic transitions in the region 2200—3000 Å and are easily identified with the corresponding transitions in nitro-benzene as given by Platt (*J. Chem. Phys.*, 1951, **19**, 101); for nitrobenzene, he gives two other transitions lying to shorter wave-lengths, one of which, in the region 2000 Å, is hinted at by the curve for the *ortho*-isomer which is beginning to turn at 2200 Å.

Evidence for the longest wave-length, low-intensity transition in nitrobenzene was first obtained by Hastings and Matsen (*J. Amer. Chem. Soc.*, 1948, **70**, 3514) and can be seen in solution measurements in light petroleum as a series of slight shoulders overlapped by the transition at 2700 Å. This transition is visible in both the *ortho*- and the *meta*-isomer, which show close relationship. It cannot be seen, however, for the *para*-isomer in the curve shown in Fig. 5, but is visible as a succession of shoulders when examined closely.

The second transition of benzene undergoes a large red shift in the order $o < m < p$, this transition being particularly susceptible to substitution, as pointed out by Doub and Vanderbelt (*J. Amer. Chem. Soc.*, 1947, **69**, 2714). The perturbation of the second singlet level then is in the order o- $< m\text{-}C_6H_4I\cdot NO_2 < Ph\cdot NO_2 < p\text{-}C_6H_4I\cdot NO_2$. The third transition shows the peculiarity experienced with all these compounds in that it shifts progressively to the blue as the second transition moves to the red. It shows also a remarkable decrease of intensity in the same sequence.
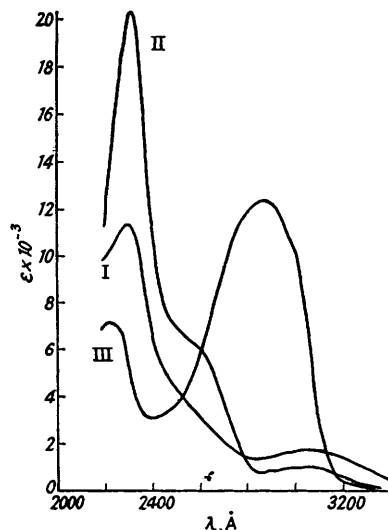
m- *and* p-*Bromoiodobenzene.*—The spectra of these two compounds in light petroleum are shown in Fig. 6. The same properties are observed as with the other compounds. In the *para*-isomer the second electronic transition has an extremely high extinction co-efficient and has nearly completely overlapped the weak first electronic transition. The first electronic transition of the *meta*-isomer has a relatively well-defined vibrational structure, and the *O,O* transition (2825 Å) is of lower intensity than that of the corre-

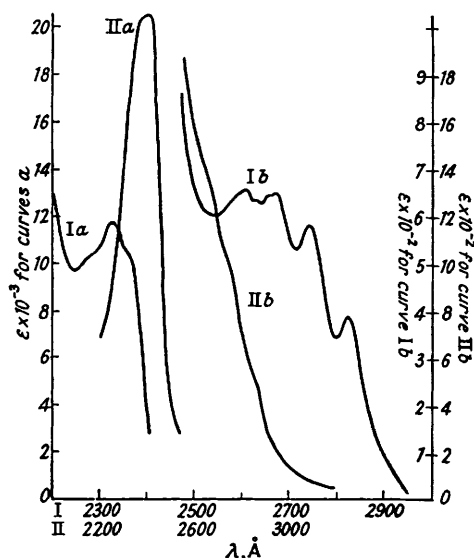FIG. 4. *Phosphorescence emission.*
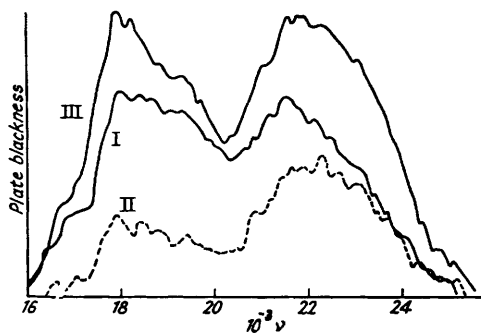
FIG. 5.

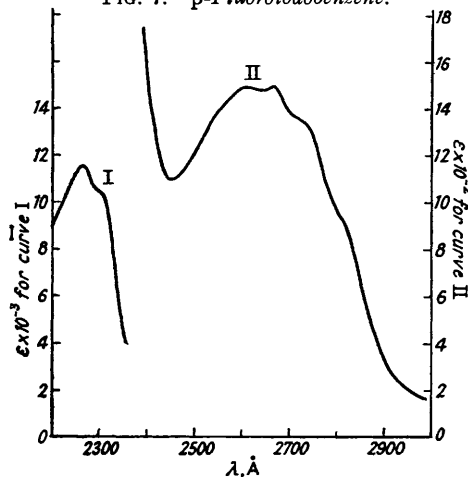(I) o-. (II) m-, *and* (III) p-*Chloroiodobenzene.*

(I) o-, (II) m-, *and* (III) p-*Iodonitrobenzene.*

FIG. 6.

(I) m- *and* (II) p-*Bromoiodobenzene.*

FIG. 7. p-*Fluoroiodobenzene.*

sponding chloro-compound, because of the reduced perturbation of the ring field by the bromine atom.

p-*Fluoroiodobenzene.*—The spectrum of this compound in light petroleum is shown in Fig. 7. It is different from that of the other *p*-halogenoiodobenzenes because of the reduced red shift brought about by the introduction of the fluorine atom in the nucleus. The second electronic transition has not overlapped the first transition which shows rather a high intensity. The spectrum has been reported by Conrad-Billroth and Förster (*loc. cit.*) but only in the region of the first electronic transition.

o-, m-, *and* p-*Iodobenzoic Acid.*—This series of compounds is perhaps the most interesting, as the parent compound, benzoic acid, has an easily measurable phos- phorescence emission so that the effect of introducing an iodine atom should be easily determined. The spectra of the three isomers are shown in Fig. 8. All the features noted with the other series are present here.

Phosphorescence. The effect of the iodine atom on the phosphorescence emission proved noteworthy. The tracings are shown in Fig. 9. On using the same experimental conditions, it was found that the emission could only be photographed when the concentration of iodobenzoic acid was above a value which varied in the order $p < m \ll o$. It was found for the *ortho*-isomer that below the concentration 2×10^{-4}M the emission would not affect the plate. The corresponding values for the *meta*- and the *para*-isomer were 5×10^{-5} and 3.6×10^{-5}M, respectively. As the three isomers are not very soluble in light petroleum, the concentration range for the work was very restricted. All con-
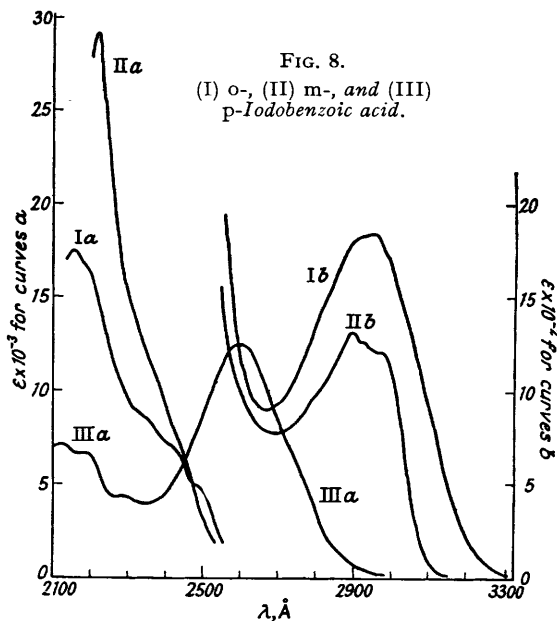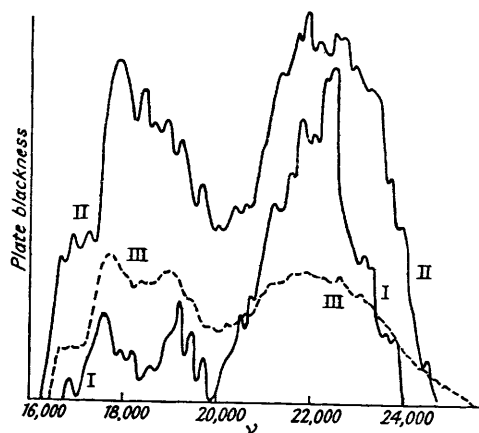

FIG. 8.
(I) o-, (II) m-, *and* (III)
p-*Iodobenzoic acid.*

FIG. 9.   *Phosphorescence emission.*
(I) o-, (II) m-, *and* (III) p-*Iodobenzoic acid.*

centrations refer to the value at room temperature, although under the experimental conditions contraction of the solvent takes place.

Successive exposures were taken in some cases on the same sample and the emission was found to weaken considerably upon irradiation. A red–purple Corex filter was also used to lessen the possibility of photodecomposition. The weakening of the emission on prolonged irradiation showed it to be due to the iodobenzoic acid and not to decomposition products. In all this work with iodo-compounds no formation of iodine takes place in the glass upon irradiation although it is instantaneous at room temperature.

The appearance and energy order of the three emissions are of interest. The spectrum of the *ortho*-isomer is relatively sharper than that of the *meta*, whilst that of the *para* is exceedingly diffuse.

The plates used are relatively insensitive in the green, which is responsible for the dip in all the tracing in this region, and cut off sharply at the red end so that all the tracings have similar long wave-length appearances.

Discussion.—From measurements in solution on substituted iodobenzenes we are able to observe the coarser features of the first three electronic transitions of these compounds. In every case the first electronic transition behaves as expected, *i.e.*, the order of red shift is from fluorine to iodine throughout a halogen sequence of one isomer, and for the three isomers of one compound the order of red shift is $o > m > p$. In halogen-substituted

benzenes, increase in atomic number of the substituent leads to great increase in intensity of the second transition and subsequent red shift. The absorption curves for *p*-fluoro- and *p*-bromo-iodobenzene show this effect admirably.

In a series of compounds, the position and intensity of the second transition in both the *ortho*- and the *meta*-isomer is very similar, whilst the *para*-compound exhibits larger intensification and red shift. In more complex compounds such as the iodonitrobenzenes and iodobenzoic acids, steric effects appear to affect the position and intensity of this transition in the *ortho*-isomer so that its energy lies above that of the parent compound. It is only in the *para*-compound that the transition lies at lower energies than in the parent compound.

The third transition could only be studied in the two series of more complex compounds (the iodonitrobenzenes and iodobenzoic acids) and exhibits peculiar characteristics. The energy order for the three isomers appears to lie in the direction $p > o > m$, whilst the intensity runs in the reverse order.

Platt (*J. Chem. Phys.*, 1951, **19**, 1418) has stated that opposed disubstitution inhibits g–g type transitions and intensifies g–u type. He cites this as an experimental test for the determination of the g–g or g–u nature of a transition. On applying these principles to the three transitions discussed above, we find that the first and second are of the g–u type whilst the third is g–g. As the second transition probably corresponds to the 2100 Å transition in benzene, this evidence would support the assignment $^1A_{1g} - {}^1B_{1u}$ and not $^1A_{1g} - {}^1E_{2g}$ as has recently been proposed by Craig (*Proc. Roy. Soc.*, 1950, **200**, 401) and Craig, Parr, and Ross (*J. Chem. Phys.*, 1950, **18**, 1561).

In absorption studies at $-180°$ attention was focused on the first electronic transition, as it has a sharp vibrational structure in benzene and irradiation in this region is responsible for the appearance of phosphorescence. The introduction of iodine into the ring pre-dissociates this level and gives the vibrational structure a diffuse appearance. The amount of predissociation appears to be determined by the energy difference between the N–Q continuum and the quantised level. Thus iodobenzene shows a more diffuse vibrational structure than *o*-chloroiodobenzene because coupling with the N–Q continuum is much stronger in the former compound. Decrease in energy leakage in the singlet state then leads to a greater probability of phosphorescence emission from the triplet state.

That the effect of iodine is chiefly noted on the levels in the immediate vicinity of the N–Q_0 transition is shown by the iodonaphthalenes (unpublished work). Here the first singlet level is not in the vicinity of the peak of the N–Q_0 transition and is not perturbed to any measurable extent by it with the subsequent appearance of intense phosphorescence emission and stability. The second singlet, however, is perturbed fairly appreciably by the N–Q_0 transition in the region 2600—2700 Å.

The effect of iodine on the phosphorescence emission of benzoic acid has been given and as yet only the following conclusions can be drawn : (1) the rate of non-radiative internal conversion from singlet into triplet state is in the order $p > m \gg o$, or (2) the rate of radiative transition from ground triplet to ground singlet is in the order $o \gg m > p$. The rates in (2) being assumed to be of the same order, the first alternative would account for the experimental observation that under similar conditions the intensity of phosphorescence appears to be strongest for the *para*-isomer. As, however, the phosphoroscope was of a fixed-speed type, the apparent intensity could be due to much stronger coupling between ground triplet and singlet states for the *ortho*-isomer, resulting in shorter lifetime and apparent loss in intensity.

<center>EXPERIMENTAL</center>

Apparatus.—Solution measurements were made with a Beckman DU Spectrophotometer. The apparatus used for the low-temperature work is of simple design, consisting of three units, the cell, cell holder, and outer container. The cell holder is filled with liquid oxygen or nitrogen, thus cooling the cell by conduction through a thin brass partition. The cell is of brass with silica end-pieces which are screwed into position. The light does not pass through the cooling agent, and condensation is prevented by evacuating the space between the cell holder and outer

container. The apparatus is then roughly a distorted Dewar flask with the cell inserted into a cavity in the inner wall.

A medium Hilger E III spectrograph was used for absorption measurements with the Beckman hydrogen lamp as a source of ultra-violet light.

The phosphoroscope has been described previously (Ferguson and Tinson, *J.*, 1952, 3083). The spectrograph used was a small Hilger E 420 F/4 instrument. A Baird Associates non-recording densitometer was used to examine the plates.

Solvent.—Light petroleum, b. p. 58—63°, was used as solvent in all the work, as it forms an excellent glass at low temperatures. Its purification has been described by Ferguson and Tinson (*loc. cit.*). The transparency of the glass thus formed to ultra-violet light is excellent.

Purity of Compounds.—All the compounds used were very carefully purified, the criterion of purity being constant spectroscopic properties. M. p. and b. p. data are not sufficient to specify the spectroscopic purity of a compound. It must possess constant absorption and emission properties. For the liquids, steam-distillation and subsequent vacuum-distillation at least twice were found sufficient to afford a pure liquid. The solids were recrystallised from an appropriate solvent and vacuum-sublimed at least three times.

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