950. *Phosphorescence and Fluorescence of Some Aromatic Nitro-amines.*

By R. Foster, D. Ll. Hammick, G. M. Hood, and A. C. E. Sanders.

Hitherto undetermined phosphorescence bands of a number of aromatic nitro-amines have been measured in the region 400—800 mμ. The effects of methyl and ethyl groups as substituents on the phosphorescence and fluorescence have been noted and discussed particularly in the light of their possible steric effects.

The phenomenon of phosphorescence of organic compounds in rigid media was observed as early as 1896 by Schmidt,[1] but it is only recently that a satisfactory explanation of it has been given. Molecules in their ground state (*N*) on absorption of light of sufficient energy, exist for a short time, about 10^{-9} sec., in the first excited state (*F*) from which they normally return to the ground state either by a radiationless, thermal process or by the emission of light, *i.e.*, fluorescence. Jablonski[2] postulated the existence of another, metastable, state (*P*) of lower energy than the state *F* and suggested that instead of going directly to the ground state some of the molecules in the state *F* might pass into a *P* state. Phosphorescence is the emission of radiation when molecules return to the ground state from this *P* state. Lewis and Kasha[3] produced experimental evidence that the *P* state is the first triplet level of a molecule whose ground state is a singlet. This has been confirmed by direct observation of paramagnetism in molecules which have been excited to this state[4] and also during phosphorescence.[5] The fact that the transitions between triplet and singlet levels are formally forbidden results in the relatively long period required for the complete emission of such radiation, which is the characteristic of phosphorescence. If the substance is held in a rigid medium at a low temperature, the likelihood of the energy of the *P* state being lost by thermal collisions, rather than by phosphorescence emission, is reduced.

p-Nitroaniline has been reported by Lewis and Kasha[3] to show strong phosphorescence when cooled in a rigid medium to −180°. We have now investigated the phosphorescence and incidently the fluorescence of a number of methyl- and ethyl-substituted *p*-nitroanilines under such conditions.

Experimental

We are indebted to Dr. E. J. Bowen, F.R.S., for the loan of apparatus for the examination of phosphorescence and fluorescence spectra.[6] The light source is supplied by an alternating current of 50 cycles/sec. The amplifier responds only to multiples of 50 cycles/sec. Because of the short lifetime of the fluorescent state, any fluorescence emission of the material under examination will alternate in intensity with the same frequency as the intensity of the incident light which, being supplied with 50 cycles/sec. A.C., will alternate 100 times a second. Thus the light from the spectrometer will cause a varying current in the photomultiplier tube, and because its frequency will be a multiple of 50 cycles/sec., the signal will be accepted by the amplifier. The same will be true of phosphorescence provided that its lifetime is shorter than, or of the same order as, the time of alternation of the light source. But with phosphorescence of longer lifetime, *viz.*, 10^{-1} sec. or longer, the current produced in the photomultiplier tube will be steady and will be rejected by the amplifier. Consequently, when the spectrum is scanned, only fluorescence and short-lifetime phosphorescence is measured. We have modified the system by inserting a rotating shutter in the path of the light just before it enters the spectrometer, arranged so that the light emitted from the material under examination is chopped at a rate which is a multiple of 50 cycles/sec. (actually a shutter of 4 sectors rotating at 1500 r.p.m. is used) so that the sum of the fluorescence and phosphorescence emissions is measured because

---

[1] Schmidt, *Ann. Physik*, 1896, **58**, 103.
[2] Jablonski, *Nature*, 1933, **131**, 839; *Z. Physik*, 1935, **94**, 38.
[3] Lewis and Kasha, *J. Amer. Chem. Soc.*, 1944, **66**, 2100.
[4] Lewis, Calvin, and Kasha, *J. Chem. Phys.*, 1949, **17**, 804.
[5] Evans, *Nature*, 1955, **176**, 777.
[6] Bowen and Brocklehurst, *J.*, 1954, 3875.

all the emitted light is varying in intensity with a frequency which is a multiple of 50 cycles/sec. By scaling up the intensities obtained in the determination in which the rotating shutter is used, to compensate for the masking effect of the shutter, and subtracting the resultant curve from that obtained in a determination in which no shutter is used, a phosphorescence spectrum is obtained (provided its lifetime is greater than 10^{-1} sec.).

Solutions.—The solvent used in all the measurements of emission spectra was a mixture of ethanol and methanol (5 : 1 v/v). The alcohols were purified by fractionation through a 40 cm. column of glass helices. The concentrations of all the solutions were 10^{-2}—10^{-3}M.

Accuracy.—In the spectra, some of the bands, particularly the fluorescence bands, flatten near the maximum, there presumably being unresolved vibration structure in the bands. The maximum recorded is the intersection of the line joining the mid-points of the tie lines with the envelope of the absorption curve. In successive determinations a reproducibility of ±50 cm.$^{-1}$ was obtained in the case of the fluorescence spectra, and ±25 cm.$^{-1}$ in that of the phosphorescence spectra.

Preparation of Materials.—Most of the compounds were prepared by standard procedures and recrystallised to constant m. p. In particular, 2 : 6-dimethyl-4-nitroaniline was prepared by Wepster's method.[7] *N* : *N* : 2 : 6-*Tetramethyl-4-nitroaniline* appears not to have been made before. It was prepared by heating 2 : 6-dimethyl-4-nitroaniline (4 g.) and methyl iodide (5 ml.) with methanol (12 ml.) in a sealed tube at 130° for 12 hr. The product was extracted with acid, precipitated by addition of ammonia solution, and recrystallised from aqueous ethanol (1 : 1 v/v). The colour was removed by elution from activated alumina by light petroleum (b. p. 60—80°); m. p. 68° (yield 30%) (Found: C, 62·2; H, 7·2; N, 14·2. $C_{10}H_{14}O_2N_2$ requires C, 61·8; H, 7·2; N, 14·4%).

	Emission		Absorption [a]	
	ν (phos.) (cm.$^{-1}$)	ν (fluor.) (cm.$^{-1}$)	ν (cm.$^{-1}$)	ε × 10^{-3}
4-Nitroaniline	19,400 [b]	—	27,010 [c]	16·2 [c]
2-Methyl-4-nitroaniline	19,150	—	26,390 [d]	17·4 [d]
N-Methyl-4-nitroaniline	19,025	—	25,600 [e]	18·4 [e]
NN-Dimethyl-4-nitroaniline	18,975	21,450	25,600 [e]	19·0 [e]
2 : 6-Dimethyl-4-nitroaniline	18,950	—	26,700	14·2
N : 2-Dimethyl-4-nitroaniline	18,925	—	25,840	15·3
N : *N* : 2-Trimethyl-4-nitroaniline	18,800	20,950	27,100	10·1
N : *N* : 2 : 6-Tetramethyl-4-nitroaniline	18,650	19,625	26,800	5·6
3-Methyl-4-nitroaniline	—	—	27,030	12·8
3 : 5-Dimethyl-4-nitroaniline	—	—	25,890	5·0
2 : 3 : 5 : 6-Tetramethyl-4-nitroaniline	—	—	25,580	1·5
N-Ethyl-4-nitroaniline	19,025	—	—	—
NN-Diethyl-4-nitroaniline	18,875	20,775	—	—
3-Nitroaniline	—	19,100	—	—
6-Methyl-3-nitroaniline	—	19,150	—	—
2-Methyl-3-nitroaniline	—	19,025	—	—
NN-Dimethyl-3-nitroaniline	—	18,875	—	—
2-Nitroaniline	—	19,725	—	—
4-Methyl-2-nitroaniline	—	19,225	—	—
4-Nitro-1-naphthylamine	17,300	—	—	—
6-Nitro-2-naphthylamine	—	19,900	—	—
4-Amino-4′-nitrodiphenyl	—	19,150	—	—
4 : 4′-Dinitrodiphenyl	20,125 [f]	—	—	—

[a] In ethanol. [b] Lewis and Kasha [3] give 19,300 cm.$^{-1}$. [c] Glotz, *Bull. Soc. chim. France*, 1934, **1**, 1148. [d] Morton and McGookin, *J.*, 1934, 904. [e] Kumler, *J. Amer. Chem. Soc.*, 1946, **68**, 1185. [f] Lewis and Kasha [3] give 20,200 cm.$^{-1}$

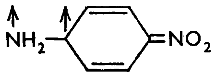
DISCUSSION

In Lewis and Kasha's [3] triplet state a pair of electrons has become uncoupled and have parallel spins. We may attempt to deduce structures for such states. In *p*-nitroaniline it seems likely that the uncoupled electrons will be disposed in such a way that there is a general accession of negative charge to the nitro-group and away from the amino-group. Of the more obvious structures (I)—(IV) we select tentatively (IV) as complying with this requirement and also giving the best interpretation of our results. The stability of such a structure could be modified by substituents which alter the electron density within the benzene ring or which by steric interference with the nitro-group increase its energy by disturbing the planarity requirements for resonance of the nitro-group with the ring. The

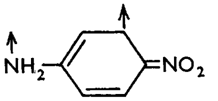
---

[7] Wepster, *Rec. Trav. chim.*, 1954, **73**, 809.

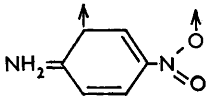
steric interference of the methyl groups *ortho* to the nitro-group is apparently sufficient to disallow phosphorescence of longer than 10^{-1} sec. life; for example, 3-methyl-4-nitroaniline and 3 : 5-dimethyl-4-nitroaniline do not phosphoresce under our conditions. Other evidence of steric interference between these groups may be found in the relatively low extinction coefficients of certain absorption bands of these compounds (see col. 5 of Table). This conclusion is also reached by Remington [8] and is supported by the work of Stewart [9] who measured the heat of combustion of *o*-nitrotoluene and deduced that an energy of 7·6 kcal. would be required to force the methyl and nitro-groups into the plane of the benzene ring. Similar steric prevention of planarity of a dimethylamino-group with the benzene ring should result from *ortho*-methyl groups. Klevens and Platt [10] deduced that the dimethylamino-group in *N* : *N* : 2 : 6-tetramethylaniline is twisted 90° out of the plane of the benzene ring. From the absorption spectra (see Table), the extinction coefficients of *N* : *N* : 2-trimethyl- and *N* : *N* : 2 : 6-tetramethyl-4-nitroaniline are small compared with the extinction coefficient of *NN*-dimethyl-4-nitroanilne itself, giving a further indication of the steric effect. From the Table it will be seen that substitution *ortho* to the amino-group does not inhibit phosphorescence; this is to be expected, because in structure (IV) the amino-group is not conjugated with the ring, and interference with its rotation does not affect the planar resonance structure.



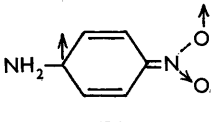
(I)



(II)



(III)



(IV)

The symbol ↑ represents an uncoupled electron.

Apart from the steric effects, the alkyl groups substituted in any position will modify the energy of the structure by their inductive effects. The magnitude of the inductive effect may be expected to vary with the position of the group. Our results, however, show little more than that the phosphorescence frequencies and hence energies fall as more alkyl groups are introduced. Thus the phosphorescence energies decrease in the series : *p*-nitroaniline, and 2-methyl-, *N*-methyl-, *NN*-dimethyl-, 2 : 6-dimethyl-, *N* : 2-dimethyl-, *N* : *N* : 2-trimethyl-, and *N* : *N* : 2 : 6-tetramethyl-4-nitroaniline.

No phosphorescence was observed with the *o*- or *m*-nitroanilines. In the case of *m*-nitroaniline no structure corresponding to (IV) can be drawn and in that of *o*-nitroaniline some *ortho*-effect may be operating. It is possible, of course, that the phosphorescence is too short-lived to be measured on our instrument, or alternatively, that there is 100% fluorescence so that the *P* state is not occupied.

4-Nitro-1-naphthylamine phosphoresces strongly. This compound may be regarded as 4-nitro-2 : 3-benzoaniline and it might be expected that the energy of the phosphorescent state would be lower than that of *p*-nitroaniline because of the increased conjugation. This agrees with the experimentally determined value (17,300 cm.$^{-1}$) compared with that of *p*-nitroaniline (19,400 cm.$^{-1}$), which is close to that obtained by Lewis and Kasha [3] for 5-nitro-1-naphthylamine (17,900 cm.$^{-1}$). It is difficult to see why neither 6-nitro-2-naphthylamine nor 4-amino-4′-nitrodiphenyl phosphoresces, though it may be that all the energy of excitation is lost as fluorescence. It is interesting that 4 : 4′-dinitrodiphenyl, which does not fluoresce, has a phosphorescence band at 20,125 cm.$^{-1}$, which is close to that obtained by Lewis and Kasha for nitrobenzene (21,100 cm.$^{-1}$).

Fluorescence.—In the *p*-nitroaniline series of compounds, only the *NN*-disubstituted compounds fluoresce. Lippert [11] has suggested that a decrease in the electron-repelling power of the amino-group in going from NMe$_2$ to NH$_2$ has the effect of increasing the frequency of the fluorescence emission band. He concludes that, for all the primary and

---

[8] Remington, *J. Amer. Chem. Soc.*, 1945, **67**, 1838.
[9] Stewart, *Phys. Rev.*, 1931, **38**, 1372.
[10] Klevens and Platt, *J. Amer. Chem. Soc.*, 1949, **71**, 1714.
[11] Lippert, *Z. phys. Chem. (Frankfurt)*, 1954, **2**, 328.

secondary *p*-nitroanilines, the energy of excitation will be greater than the bond energy, so that dissociation of the carbon–nitrogen bond occurs; hence there is no fluorescence. For solutions in dimethylformamide, this dissociation would appear to occur at about 20,000 cm.$^{-1}$. In the mixed alcohol solvent used in the present work a rather higher limit would be indicated, as compounds with a fluorescence band at 21,450 cm.$^{-1}$ have been measured. An alternative explanation, which appears to be less satisfactory, is that the primary and secondary amines may associate by hydrogen bonding. It is known that hydrogen bonding can facilitate the degradation of electronic energy and so quench fluorescence. Furthermore, there is evidence that in the solid state there is hydrogen bonding in the case of *p*-nitroaniline,[12] and in polar solvents between an amino-nitrogen atom and the solvent.[13] Such effects are, of course, not possible with the tertiary amines. However, it is difficult to see how this explanation could be applied to the fluorescence of 6-nitro-2-naphthylamine, 4-amino-4′-nitrodiphenyl, or the primary *o*- and *m*-nitroanilines.

The authors are most grateful to Dr. E. J. Bowen, F.R.S., for the use of the apparatus referred to above, and for his helpful discussions.

DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, July 6th,* 1956.]

[12] Abrahams and Robertson, *Acta Cryst.*, 1948, **1**, 252.
[13] Kumler and Strait, *J. Amer. Chem. Soc.*, 1943, **65**, 2349.