552. *Magnetic Perturbation of Singlet–Triplet Transitions. Part III.*[1] *Benzene Derivatives and Heterocyclic Compounds.*

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The singlet–triplet absorption bands of various monosubstituted benzene derivatives and monoaza-aromatic hydrocarbons have been measured, use being made of the perturbing effect of oxygen under pressure. The shifts of the benzene triplet level caused by different substituents are compared with those of the lowest singlet level. The spectra of the monoaza-aromatic hydrocarbons are very similar to those of the unsubstituted parent hydrocarbons, although characteristic small blue shifts are observed.

The very weak bands of pyrazine recently studied by Goodman and Kasha are considerably intensified by dissolved oxygen under pressure, confirming their assignment as singlet–triplet absorption bands.

Previous studies of the perturbing effect of oxygen under pressure have been extended to two main classes of organic compound, namely monosubstituted benzene derivatives and the monoaza-analogues of certain aromatic hydrocarbons.

Experimental

Measurements were made on a Unicam SP. 500 spectrophotometer as already described.[1,2] The compounds were purified by chromatography or fractional distillation. 1- and 2-Aza-anthracenes were prepared as directed by Etienne.[3] Phenylcyclopropane was obtained by gentle refluxing of 5-phenyl-3-pyrazoline for *ca.* 1 hr., followed by slow distillation through a short column packed with glass helices. The distillate was shaken with ice-cold aqueous 1% potassium permanganate to remove methylstyrenes,[4] excess of sodium hydrogen sulphite solution was added, and the phenylcyclopropane washed, dried, and fractionally distilled (yield, *ca.* 50%; b. p. 173°). This modification of the usual method [5] is simpler and gives a better yield. The ultraviolet absorption spectrum in solution was in good agreement with that recorded by Robertson, Music, and Matsen.[6]

Results and Discussion

Benzene Derivatives.—The triplet levels obtained are given in Table 1, together with other results, and some of the spectra are illustrated in Fig. 1. The data are unfortunately not as extensive as could be desired, since in several cases (especially with compounds containing a group such as –OH which donates electrons to the benzene ring), the triplet bands are completely obscured by strong charge-transfer absorption.[1,7] Conversely, with compounds containing groups such as $-CF_3$ or –CN which withdraw electrons from the benzene ring and reduce its donor properties, the background charge-transfer absorption is less than that in benzene itself, although the triplet bands lie at longer wavelengths.

The triplet level of benzonitrile (26,880 cm.$^{-1}$) is in good agreement with that obtained from the phosphorescence spectrum (27,000 cm.$^{-1}$).[8] It is therefore clear that the extremely weak absorption bands at about 32,000 cm.$^{-1}$ observed by Hirt and King [9] for liquid benzonitrile and tentatively assigned as singlet–triplet bands, cannot in fact be due to transitions to the lowest triplet level of the benzonitrile molecule. Although it is possible that a higher triplet level is involved, it seems most likely that they are due to an impurity present in very small amount.

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[1] Part II, Evans, *J.*, 1957, 3885.
[2] Evans, *J.*, 1957, 1351.
[3] Etienne, *Ann. Chim. France*, 1946, **1**, 1.
[4] Case, *J. Amer. Chem. Soc.*, 1934, **56**, 715.
[5] Hammond and Todd, *J. Amer. Chem. Soc.*, 1954, **76**, 4081.
[6] Robertson, Music, and Matsen, *J. Amer. Chem. Soc.*, 1950, **72**, 5260.
[7] Evans, *J.*, 1953, 345.
[8] Lewis and Kasha, *J. Amer. Chem. Soc.*, 1944, **66**, 2100.
[9] Hirt and King, *J. Chem. Phys.*, 1952, **20**, 1821.

The triplet level of nitrobenzene, as determined from its phosphorescence, has been reported to lie at 21,110 cm.$^{-1}$.[8] However, no absorption in this region was observed in the presence of oxygen under pressure. The perturbing effect of the oxygen may be inhibited by the strongly electron-attracting nitro-group, but it seems more likely that the observed phosphorescence is due to a triplet level in which the electron unpairing is essentially located in the nitro-group (n–π^* transition), or possibly to impurities.

TABLE 1. *Triplet levels (cm.$^{-1}$) of benzene derivatives by oxygen perturbation. (Chloroform solutions unless otherwise stated.)*

(Benzene	liquid	29,440 [a]	Phenylcyclopropane	~28,300
	vapour	29,510 [b])	Benzonitrile	26,880 (phosphorescence 27,000) [e]
Fluorobenzene		29,500 [a]		
	vapour	29,530 [b]	Benzoyl chloride	26,280
Benzotri-fluoride	solution	29,150 *	Acetophenone	25,950 (phosphorescence 26,000 [d], 25,850 [f])
	vapour	29,150 *		
Toluene	solution	29,000 * (phosphorescence 28,889 [c], 28,900 [d])	Phenylacetylene	25,190
			Styrene	21,600 [a]
Methyl phenyl sulphone		28,700		
Chlorobenzene	vapour	28,570		

* 2,2,4-Trimethylpentane solution.

[a] Evans, *J.*, 1957, 1351. [b] Evans, *J.*, 1957, 3885. [c] Kanda and Sponer, *J. Chem. Phys.*, 1958, **28**, 798. [d] Dikun and Sveshnikov, *Zhur. eksp. teor. Fiz.*, 1949, **19**, 1000. [e] Lewis and Kasha, *J. Amer. Chem. Soc.*, 1944, **66**, 2100. [f] Terenin and Ermolaev, *Trans. Faraday Soc.*, 1956, **52**, 1042.

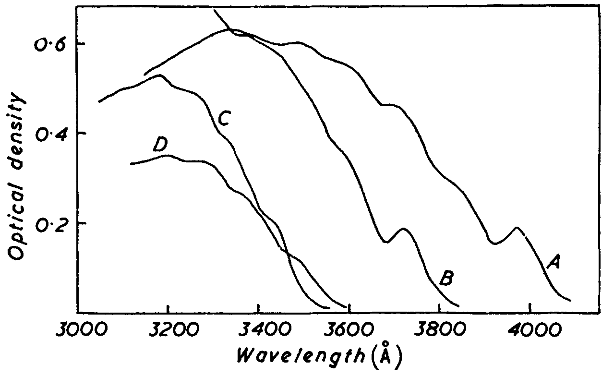

FIG. 1. *Light absorption of oxygen at* ca. 130 *atm. dissolved in solutions of benzene derivatives.* (5·2 *cm. cell.*)

A, 0·5M-Phenylacetylene in chloroform.
B, 1M-Benzonitrile in chloroform.
C, 0·4M-Benzotrifluoride in 2,2,4-trimethylpentane.
D, 0·5M-Methyl phenyl sulphone in chloroform.

TABLE 2. *Shifts (cm.$^{-1}$) of the lowest singlet and triplet levels of benzene to lower frequencies caused by various substituents.*

Substituent	Singlet *	Triplet	Substituent	Singlet *	Triplet	Substituent	Singlet *	Triplet
$-F$	270	50	$-Cl$	1037	940	$-NH_2$	4060	2670
$-CF_3$	270	350	$-OH$	1740	970	$-CHO$	1895	4270
$-CH_3$	616	580	cyclo-C_3H_5 ...	1228	~1240	$-C{\equiv}CH$	1719	4250
$-SO_2CH_3$ ...	850	740	$-CN$	1573	2560	$-CH{=}CH_2$ ...	3327	7840

* Except for $-SO_2CH_3$, vapour data from the literature were used.

In Table 2, the shifts (to higher frequencies) of the lowest benzene triplet level caused by different substituent groups are given (based partly on the present data and partly on phosphorescence spectra), together with the shifts of the lowest singlet level. This comparison is of interest since the effect of substituents on the lowest singlet level of benzene has been extensively studied[10] by using simple molecular-orbital theory. Recently Goodman and Shull[11] have applied an improved molecular-orbital theory with considerable success to both the singlet and triplet levels of certain monosubstituted benzene derivatives. Table 2 shows that if the substituent group does not contain a multiple bond conjugated

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[10] Matsen, *J. Amer. Chem. Soc.*, 1950, **72**, 5243.

[11] Goodman and Shull, *J. Chem. Phys.*, 1957, **27**, 1388.

with the benzene ring, the shift of the triplet level is rather less than that of the singlet level, in agreement with Goodman and Shull's calculations. If, however, a multiple bond is present, the reverse is normally true. The $-SO_2{\cdot}CH_3$ group represents a special case. Although the S–O bonds probably possess considerable double-bond character, there is evidence that they do not conjugate appreciably with the benzene ring.[12]

FIG. 2.

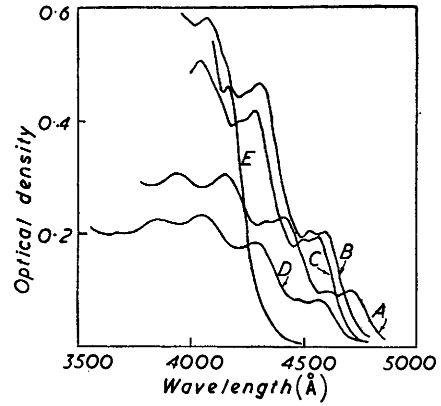

FIG. 3.

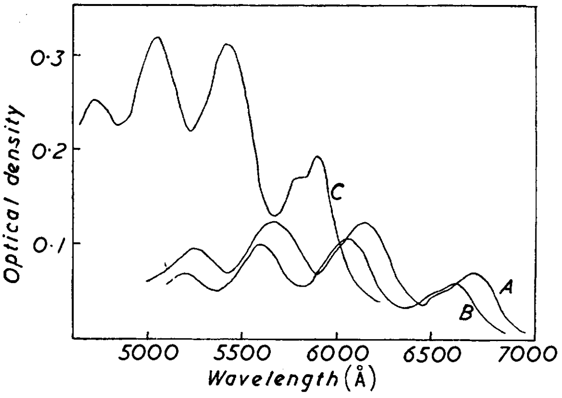

FIG. 2. *Light absorption of oxygen at* ca. 130 *atm. dissolved in* 0·5M-*chloroform solutions of heterocyclic compounds.* (5·2 *cm. cell.*)

A, Isoquinoline; max. at 21,210, 21,740, 22,650, 23,000, 24,040, 25,380 cm.$^{-1}$.
B, 7,8-Benzoquinoline; max. at 21,740, 22,000, 23,200, 24,540 cm.$^{-1}$.
C, 5,6-Benzoquinoline; max. at 21,880, 22,230, 23,340, *ca.* 23,700, 24,720 cm.$^{-1}$.
D, Quinoline; max. at 21,850, 22,350, 23,300, 23,750, 24,660, 25,900 cm.$^{-1}$.
E, Thionaphthen; max. at 23,970 cm.$^{-1}$.

FIG. 3. *Light absorption of oxygen at* ca. 130 *atm. dissolved in chloroform solutions of heterocyclic compounds.*

A, 0·92M-2-Aza-anthracene; max. at 14,870, 16,260, 17,650, 19,100 cm.$^{-1}$.
B, 0·37M-1-Aza-anthracene; max. at 15,070, 16,480, 17,860, 19,250 cm.$^{-1}$.
C, 0·5M-1-Azapyrene; max. at 16,930, 17,300, 18,450, 19,830, 21,170 cm.$^{-1}$.

Heterocyclic Compounds.—Results for monoaza-aromatic hydrocarbons are given in Figs. 2 and 3 and Table 3. The singlet–triplet absorption spectrum of a particular heterocyclic compound closely resembles that of the parent hydrocarbon as regards both the position of the 0,0 band and also the vibrational structure. By an appropriate shift of the frequency scale in each case, the main bands in the spectrum of an aromatic hydrocarbon can be made to coincide almost exactly with those of its monoaza-derivative. (The average deviation for 32 bands from 8 aza-compounds is only ±20 cm.$^{-1}$.) This very close similarity in vibrational structure is not surprising, since the (ground-state) ring vibrational

TABLE 3. *Triplet levels* (*cm.*$^{-1}$) *of heterocyclic compounds in chloroform solution.* (*Accuracy about* ±50 *cm.*$^{-1}$.)

Pyridine	29,650 ± 100 cm.$^{-1}$ [a]	Phenanthridine	~22,200
Quinoline	21,850 (P 21,700 [b])	Acridine	15,840 [c]
	21,840 (T)	2-Aza-anthracene	14,870
4-Methylquinoline	21,780	1-Aza-anthracene	15,070
Isoquinoline	21,210	1-Azapyrene *	16,930
5,6-Benzoquinoline	21,880	Thionaphthen	23,970 (P 24,010 [d],
7,8-Benzoquinoline	21,740		SP 23,917 ± 60 [e])

* Richter numbering.

[a] Evans, *J.*, 1957, 3885. [b] Lewis and Kasha, *J. Amer. Chem. Soc.*, 1944, **66**, 2100. [c] Evans, *J.*, 1957, 1351. [d] Heckman, *J. Mol. Spectroscopy*, 1958, **2**, 27. [e] Padhye and Patel, *J. Sci. Ind. Res., India*, 1956, **15**, *B*, 206.

P, phosphorescence at. SP, solvent perturbation at. T, in 2,2,4-trimethylpentane.

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[12] Barnard, Fabian, and Koch, *J.*, 1949, 2442.

frequencies of an aromatic hydrocarbon are little altered by substitution of a nitrogen atom.[13]

A rather similar situation is found with the normal (singlet–singlet) absorption spectra,[14] although since the bands are usually more diffuse the comparison is less accurate in this case.

The substitution of –N= for –CH= in various positions of an aromatic hydrocarbon does cause slight blue shifts of the triplet level, and values for these shifts (based on oxygen perturbation data obtained under similar conditions) are given in Table 4. They follow the same pattern as the (red) shifts of the singlet levels of the aromatic hydrocarbons caused by substituents such as $-CH_3$.[15] Thus, the largest effect is caused by substitution at the 9-position of anthracene, while in naphthalene and anthracene the effect is much greater for the 1- than the 2-derivative. There is a rough correlation between the triplet shifts and theoretical parameters for the aromatic hydrocarbons such as the free valency at the position substituted. However, a more precise interpretation would probably involve the *change* in the theoretical parameter in going from the ground state to the triplet level (cf. Pullman and Pullman [16]).

TABLE 4. *Shifts (cm.$^{-1}$) to higher frequencies of the triplet levels of aromatic hydrocarbons caused by substitution of –N= for –CH=. Accuracy about* ± 70 *cm.$^{-1}$* (± 130 *cm.$^{-1}$ for pyridine*).

Posn. subst.	Shift	Posn. subst.	Shift	Posn. subst.	Shift
Benzene		Anthracene		Phenanthrene	
—	200	1	200	1	280
		2	0	4	140
Naphthalene		9	970	9	~600
1	670				
2	30			Pyrene	
				1 *	0

* Richter numbering.

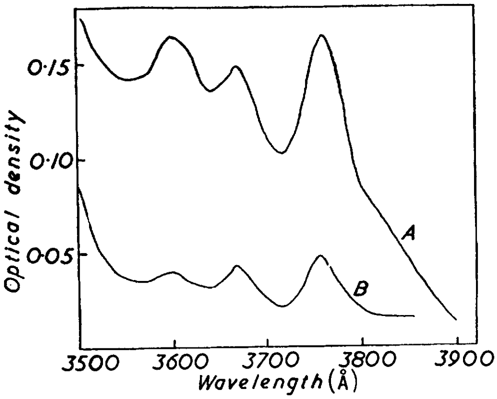

FIG. 4. *Light absorption of* 0·234M-*pyrazine in* 2,2,4-*trimethylpentane.* (5·2 *cm. cell.*)
A, Saturated with oxygen at *ca.* 130 atm.
B, In absence of oxygen. Max. at 26,600, 27,240 27,780 cm.$^{-1}$.

The intensities of the induced singlet–triplet bands (corrected for differences in concentration [2]) are appreciably smaller for the monoaza-compounds than for the parent hydrocarbons. The ratio of the intensities varies with the particular hydrocarbon studied, but is of the order of one half. In addition, except for pyridine, the short-wavelength charge-transfer absorption is less evident with the heterocyclic compounds. Both these

[13] Jones and Sandorfy, " Technique of Organic Chemistry," Vol. IX, Interscience, New York, 1956, p. 533.
[14] Badger, Pearce, and Pettit, *J.*, 1951, 3199.
[15] Peters, *J.*, 1957, 1993.
[16] Pullman and Pullman, " Progress in Organic Chemistry," Butterworths, London, 1958, Vol. 4, p. 31.

effects may be connected with the reduction of the π-donor characteristics of the aromatic hydrocarbon caused by the replacement of $-CH=$ by $-N=$.[2]

Goodman and Kasha[17] observed three very weak bands around 3700 Å in the absorption spectrum of pyrazine, which were interpreted as arising from an n–π^* transition to the lowest triplet level of the pyrazine molecule. [The longest-wavelength band is at 26,553 cm.$^{-1}$, and the first phosphorescence band of pyrazine in EPA (ether–isopentane–alcohol) glass is at 25,991 cm.$^{-1}$.] The correctness of this assignment is shown by the results in Fig. 4. The spectrum in the absence of oxygen is in good agreement with that given by Goodman and Kasha, and subsequently by Hirt,[18] whilst the presence of oxygen at high pressure considerably increases the intensity of the absorption bands but does not affect their position. In this particular example, the *unperturbed* singlet–triplet absorption is of unusually high intensity (an explanation of this has been given [19]), and hence two characteristic features of oxygen perturbation are well illustrated. First, no appreciable shift of the singlet–triplet bands is caused by the dissolved oxygen; secondly the extent of the perturbation does not bear any relationship to the intensity of the unperturbed singlet–triplet absorption.

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[17] Goodman and Kasha, *J. Mol. Spectroscopy*, 1958, **2**, 58.
[18] Hirt, *Spectrochim. Acta*, 1958, **12**, 114.
[19] Sidman, *J. Mol. Spectroscopy*, 1958, **2**, 333.