several portions of ethanol, then ether, and dried to give 5.8 g. (58%) of recovered III, m.p. 201.9–203° with gas evolution. Additional small quantities of III separated from the mother liquor; however, no crystalline 2-aminoethanethiol hydrochloride was isolated.

2-Aminoethylbenzyl dithiocarbonate hydrochloride (V). A solution of 2-benzylthio-2-thiazoline[8] (41.9 g., 0.2 mole) in 500 ml. of 6N hydrochloric acid was heated under reflux for 2 hr. After storage at 0° for 1 hr., the crystalline product was removed by suction filtration and dried in a vacuum desiccator. The yield of V, m.p. 172.2–175.2° (lit.,[4] m.p. 175°), was 43.6 g. (82.8%). A sample recrystallized from hot glacial acetic acid melted at 177.9–178.7°.

Acknowledgment. The authors wish to express their thanks to Mr. Norman Colthup for assistance in interpreting the infrared data and to Dr. Julius Kuck and the staff of the Microanalytical Laboratory for the microanalyses.

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[8] A. H. Goddin, U. S. Patent 2,516,313.

Absorption Spectra of the 4-Dimethylamino Derivatives of Azobenzene and Stilbene

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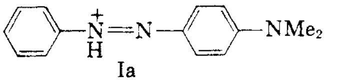
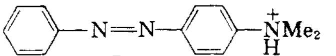
In neutral solution 4-dimethylaminoazobenzene displays a strong absorption band at 420 mμ which in acidic solution is replaced by one band at 520 mμ and another at 320 mμ.[1] Absorption in the 520 mμ region has been associated with the azonium cation (Ia) to which can be attributed a high degree of stabilization by charge-resonance[2] while the 320 mμ peak is considered to be due to the ammonium cation (Ib) essentially because azobenzene in neutral solution also absorbs strongly at 320 mμ.[1,3]

Further, it has been postulated[1,3] that both cations exist together in solution as a tautomeric equilibrium mixture (Ia⇄Ib); support for these interpretations has come from several sources.[4,5,6]



Ia



Ib

Klotz, Fiess, Chen Ho, and Mellody,[7] however, have questioned the validity of attributing the absorption at 520 mμ to the ion (Ia) and have attempted to reconcile addition of a proton solely at the dimethylamino- group (Ib) with an absorption shift to longer wave lengths. Criticisms of this view have already been raised by some authors.[4,8,9]

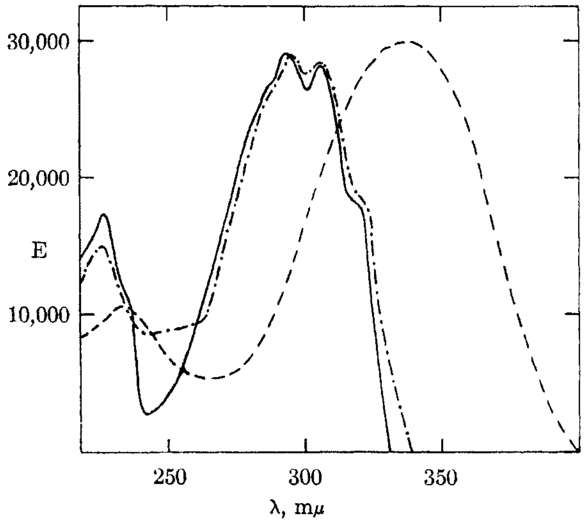
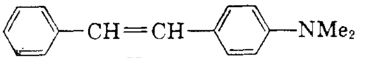


Fig. 1. Absorption spectra: Stilbene in neutral aqueous-ethanol (——); 4-Dimethylaminostilbene in neutral (- - -) and acidic (2N sulfuric acid) aqueous-ethanol (-·-·-)

In an attempt to bring fresh evidence to bear on this question the ultraviolet absorption spectrum of 4-dimethylaminostilbene (II) has been examined in 50% aqueous-ethanol under acidic (2N sulfuric acid) and neutral conditions and the separate curves have been compared with that of stilbene in neutral solution. (See Fig. 1.) 4-Dimethylaminostilbene is isosteric with 4-dimethylaminoazobenzene but unlike the azo-compound possesses only one basic center and should therefore add a proton only at the dimethylamino- group.



II

The spectrum of 4-dimethylaminostilbene, as shown, in acidic solution is very nearly identical with that of stilbene in neutral solution and definitely reveals no absorption at wave lengths higher than the main band of the parent free base. These observations fail to lend support to the spectral interpretations suggested by Klotz *et al.*[7] On the other hand the assignment of the 320 mμ band, shown by 4-dimethylaminoazobenzene in acidic solution, to the ammonium cation (Ib) is clearly reinforced.

EXPERIMENTAL

Absorption spectra. A Hilger Uvispek Spectrophotometer was used to determine the spectra. The appropriate solvent

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[1] G. M. Badger, R. G. Buttery, and G. E. Lewis, *J. Chem. Soc.*, 1888 (1954).

[2] C. R. Bury, *J. Am. Chem. Soc.*, **57**, 2115 (1935).

[3] A. Hantzsch and A. Burawoy, *Ber.*, **63**, 1760 (1930).

[4] G. Cilento, E. C. Miller, and J. A. Miller, *J. Am. Chem. Soc.*, **78**, 1718 (1956).

[5] E. Sawicki, *J. Org. Chem.*, **21**, 605 (1956).

[6] H. H. Jaffe and Si-Jung Yeh, *J. Org. Chem.*, **22**, 1281 (1957).

[7] I. M. Klotz, H. A. Fiess, J. Y. Chen Ho, and M. Mellody, *J. Am. Chem. Soc.*, **76**, 5136 (1954).

[8] E. Sawicki, *J. Org. Chem.*, **22**, 365 (1957).

[9] I. N. Zhmurova, *J. Gen. Chem.* (*U.S.S.R.*), **27**, 2745 (1957).

in each case was prepared from equal volumes of absolute ethanol and either distilled water or 4*N* sulfuric acid. Immediately prior to use the samples of stilbene and 4-dimethylaminostilbene were purified by chromatography on alumina followed by recrystallization from ethanol thereby, ensuring that any traces of the *cis* isomers were removed.

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Liquid Scintillators. XII. Absorption and Fluorescence Spectra of 2,5-Diaryl-1,3,4-oxadiazoles[1]

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The importance of spectral properties of scintillators has been outlined,[2,3] at which time the absorption and emission spectra of a variety of aryl-substituted oxazoles were reported. Similar data have been obtained for another important class of liquid scintillator solutes, the 1,3,4-oxadizaoles. The synthesis[4] of these compounds and evaluation as liquid scintillator solutes[5] have been reported previously. Two new pyridyl derivatives are described in the Experimental.

The absorption and fluorescence data are presented in Table I; the mean wave length, $\bar{\lambda}$, is that wave length which bisects the area under the fluorescence spectrum.

The effect of an oxadiazole nucleus on the spectrum of an aromatic system is very similar to that of a *p*-phenylene group. *p*-Terphenyl (λ_{max} 280, ϵ 2.5 × 10^4), *p*-quaterphenyl (λ_{max} 300, ϵ 3.9 × 10^4), and *p*-quinquephenyl (λ_{max} 310, ϵ 6.3 × 10^4)[6] may be compared with the five analogous oxadiazoles having the equivalent number of rings.

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] D. G. Ott, F. N. Hayes, E. Hansbury, and V. N. Kerr, *J. Am. Chem. Soc.*, **79,** 5448 (1957).

[3] R. K. Swank, W. L. Buck, F. N. Hayes, and D. G. Ott, *Rev. Sci. Instr.*, **29,** 279 (1958).

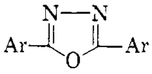
[4] F. N. Hayes, B. S. Rogers, and D. G. Ott, *J. Am. Chem. Soc.*, **77,** 1850 (1955).

[5] F. N. Hayes, D. G. Ott, and V. N. Kerr, *Nucleonics*, **13,** No. 12, 38 (1955).

[6] A. E. Gillam and D. H. Hey, *J. Chem. Soc.*, **1939,** 1170.

TABLE I

Absorption and Fluorescence Spectral Data[a]



Ar	Ar′	Absorption		Fluorescence		
		λ^{abs}_{max}	$\epsilon \times 10^{-4}$	λ^{fl}_{max1}	λ^{fl}_{max2}	$\bar{\lambda}$
C_6H_5	C_6H_5	282	2.6	336	350	360
C_6H_5	4-$C_6H_5C_6H_4$	300[b]	4.5	364	380	388
C_6H_5	1-$C_{10}H_7$	313	1.8	372	392	392
C_6H_5	2-$C_{10}H_7$	310	2.7	364	—	380
C_6H_5	2-Furyl	292	3.3	364	—	372
C_6H_5	2-Thienyl	298	2.4	373	—	388
C_6H_5	3-Pyridyl	285	2.3	355	—	362
C_6H_5	4-Pyridyl	284	2.5	335	353	360
p-$CH_3OC_6H_4$	4-$C_6H_5C_6H_4$	308	4.0	372	390	394
p-$CH_3OC_6H_4$	1-$C_{10}H_7$	317	2.3	380	396	402
p-$CH_3OC_6H_4$	2-$C_{10}H_7$	308	3.2	366	382	386
p-$CH_3C_6H_4$	*p*-$CH_3C_6H_4$	289	3.1	342	354	366
p-$CH_3OC_6H_4$	*p*-$CH_3OC_6H_4$	301	3.3	356	370	380
p-FC_6H_4	*p*-FC_6H_4	283	2.4	335	350	358
p-ClC_6H_4	*p*-ClC_6H_4	294	3.2	344	362	370
p-BrC_6H_4	*p*-BrC_6H_4	297	3.6	347	360	374
p-IC_6H_4	*p*-IC_6H_4	303	3.7	344	—	382
4-$C_6H_5C_6H_4$	4-$C_6H_5C_6H_4$	313[b]	6.1	378	396	396
$C_6H_5CH{=}CH$	$C_6H_5CH{=}CH$	331	3.6	406	422	442
2-Furyl	2-Furyl	297	2.6	355	370	378
2-Thienyl	2-Thienyl	313	2.4	377	390	420
1-$C_{10}H_7$	1-$C_{10}H_7$	335	2.3	392	408	412
2-$C_{10}H_7$	2-$C_{10}H_7$	332	3.3	370	388	388
5,5-Diphenyl-2,2′-bi-1,3,4-oxadiazole		298[b]	4.0	354	370	378
2,2′-*p*-Phenylenebis(5-phenyl-1,3,4-oxadiazole)		315[c]	4.8	373	390	392

[a] Wave lengths are in m*u*; the solvent was cyclohexane for absorption and toluene for fluorescence unless otherwise indicated. [b] Solvent was 2% chloroform in cyclohexane. [c] Solvent was chloroform; a band at 325 m*u*, ϵ 4.8 × 10^4, is also present.