different from all known disaccharide octa-acetates. The difference of their molecular rotations has the normal value for an α, β pair of sugar acetates, and they have been named in accordance with this fact. The structure of neolactose and the applicability of the new chlorinating method to other sugar derivatives will be investigated.

One of the authors (A. K.) expresses his thanks to the International Education Board for a grant which enabled him to take part in this research.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DYE LABORATORY OF THE CHEMISTRY DIVISION OF THE NATIONAL BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE]

THE ABSORPTION SPECTRA OF BENZENE-AZOBENZENE[1]

BY WALLACE R. BRODE

RECEIVED APRIL 17, 1926 PUBLISHED JULY 6, 1926

In the decade between 1905 and 1915 a number of workers[2] made rather extensive studies of the absorption spectra of benzene-azobenzene but during the past decade little or no work has been done on this remarkable colored compound. Benzene-azobenzene may well be considered the parent substance of all azo dyes and as such a more accurate determination of its absorption spectra should be welcome. With the development of more accurate apparatus and the general adoption of the method of relative transmission for the determination of absorption spectra, the curve for this compound can be determined with greater accuracy than was previously possible.

The results of this investigation show that the curve is not so simple as was previously thought, but that the principal band of this substance the simplest of azo dyes, is in reality composed of at least two overlapping bands. Repeated observations in various kinds of solvents have confirmed this fact beyond any doubt.

The apparatus used in making these measurements included a Hilger sector photometer and quartz spectrograph.[3] (For a detailed description of the apparatus see Ref. 4c.) A slit 0.1 mm. wide, which was the equivalent of 2.5 *f* units at a frequency of 750 *f* and 2.0 *f* at a frequency of 1200 *f*, was used in making these observations. The unit of frequency[4c] (*f*)

---

[1] Published by permission of the Director of the National Bureau of Standards of the U. S. Department of Commerce.

[2] (a) Hartley, *J. Chem. Soc.*, **51**, 152 (1887). (b) Baly and Tuck, *ibid.*, **89**, 982 (1906). (c) Tuck, *ibid.*, **91**, 449 (1907). (d) Hantzsch, *Ber.*, **42**, 2129 (1909). (e) Purvis and McCleland, *J. Chem. Soc.*, **101**, 1514 (1912). (f) Hantzsch, *Ber.*, **46**, 1537 (1913). (g) Purvis, *J. Chem. Soc.*, **105**, 590 (1914). (h) Baly and Hampson, *ibid.*, **107**, 248 (1915).

[3] Placed at the author's disposal by the Colorimetry Section of the Optics Division of the National Bureau of Standards, U. S. Department of Commerce.

used in this paper represents vibrations ÷ (seconds × 10^{12}). The data obtained in this investigation are plotted in the accepted form as described in previous papers by the author and others.[4] In plotting these curves the diameter of the dots indicating the observed points is given not smaller than twice the width of the spectral region covered by the energy of a given frequency passing through the slit.

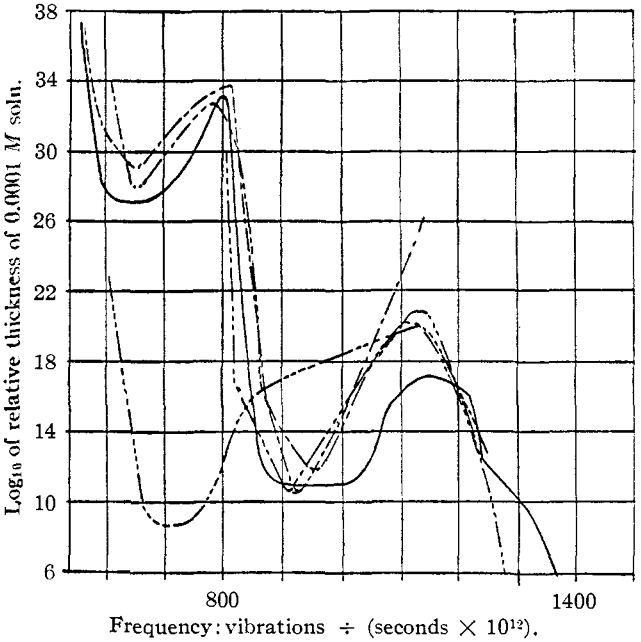

Fig. 1.—The absorption spectra of benzene-azobenzene as determined by Baly and Tuck[2b] (solid line); Baly and Hampson[2h] (one dot); Hantzsch[2d] (two dots); Purvis and McCleland[2c] (three dots) and in concd. hydrochloric acid by Tuck[2c] (four dots).

In Fig. 1 are given several of the previous determinations on benzene-azobenzene, all of which were determined by the thickness or concentration methods and not by the more accurate method of relative transmission. Since these data cannot be directly transformed into the relative transmission system it is impossible to compare these curves directly with those obtained in this work. The general shape, however, should be the same in all cases. It is to be noticed that none of these previous curves give any distinct indication of a hump on the side of the principal band (at 870 *f*) and from the straight line effects in many of them it may be assumed that the points of observation were too widely separated to show this effect.

---

[4] (a) Gibson and others, *J. Optical Soc. Am.*, **10**, 169 (1925). (b) Brode, *J. Phys. Chem.*, **30**, 56 (1926). (c) *Bur. Standards Sci. Paper*, **440** (1922).

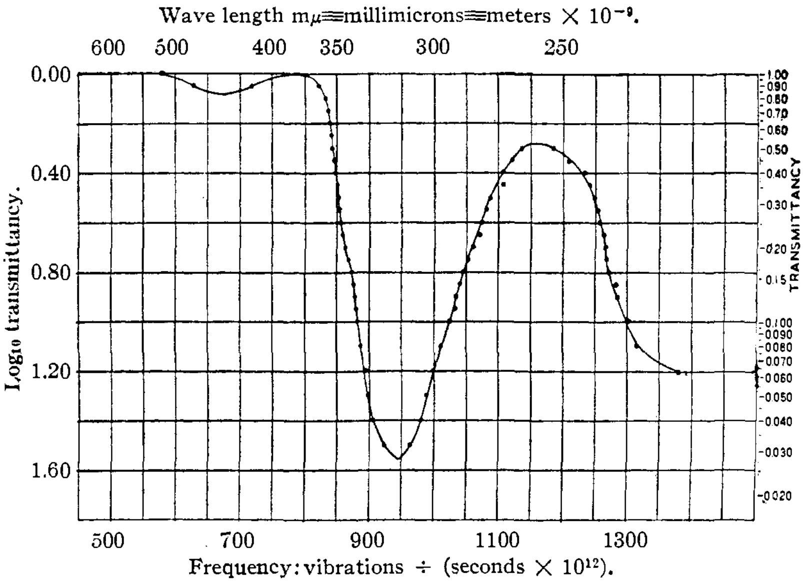

Fig. 2.—The absorption spectrum of benzene-azobenzene in ethyl alcohol (95%) concentration, 3.3 cg. per liter; cell thickness, 0.5 cm. (For numerical values see Table I).

Table I

The Absorption Spectrum of Benzene-azobenzene in Alcohol

$-\log_{10}$ trans-mittancy	No. obs.	Av. val., f	Av. dev.	Max. dev.	No. obs.	Av. val.,	Av. dev.	Max. dev.	No. obs.	Av. val., f	Av. dev.	Max. dev.
0.00	6	< 580	...	...								
.05	4	630	10.0	10.0	4	720	20	30	4	824	2.0	6.0
.10	6	835	1.5	5.0	..	....	...	...	.	......	...	...
.15	1	838	...	...	..	....	...	...	.	......	...	...
.20	5	840	0.4	1.0	..	....	...	...	.	......	...	...
.25	1	843	...	...	..	....	...	...	.	......	...	...
.30	10	845	1.5	3.0	10	1138.4	7.0	18.0	8	1187	11.0	26.0
.35	1	848	...	...	1	1123	...	...	1	1210	...	...
.40	6	849	1.0	2.0	6	1107.5	4.0	8.0	6	1235	4.0	7.0
.45	1	852	...	...	1	1110	...	...	1	1242	...	...
.50	5	855	1.0	2.0	5	1088	5.0	9.0	5	1250	2.0	6.0
.55	2	856.5	0.5	0.5	2	1083.5	0.5	0.5	2	1256.5	1.5	1.5
.60	11	859.4	1.0	4.5	11	1075.5	4.0	6.5	9	1259.5	2.5	5.5
.65	1	860	...	...	1	1071	...	...	1	1264	...	...
.70	6	865.3	2.0	3.7	6	1061	3.0	4.0	6	1266	3.0	4.0
.75	1	870	...	...	1	1054	...	...	1	1270	...	...
.80	6	875.3	1.0	2.7	6	1046	3.0	6.0	6	1273	3.0	3.0
.85	1	877	...	...	1	1043	...	...	1	1285	...	...
.90	6	880.6	1.0	2.4	6	1035.5	2.5	3.5	5	1287	5.0	11.0
.95	1	881	...	...	1	1036	...	...	0	......	...	...
1.00	11	885.3	1.0	2.7	11	1026	3.5	7.0	7	1306	7.0	16.0
1.10	4	889.8	0.2	0.8	4	1013	3.0	5.0	1	1325	...	...
1.20	4	898.5	0.8	1.5	4	1000.5	3.0	7.5	1	> 1380	...	...
1.30	4	900	0.2	1.0	4	990	4.0	6.0	.	......	...	...
1.40	7	908	4.0	9.0	7	981	4.0	7.0	.	......	...	...
1.50	12	927	7.0	17.0	12	965	8.0	15.0	.	......	...	...

Concentration, 3.3 cg. dissolved in 95% alcohol; cell thickness, 0.5 cm.

In Fig. 2 is given the average curve as determined by a number of separate observations on the alcoholic solution of benzene-azobenzene. These determinations were made on three samples from different sources, all of which melted between 68° and 69°. The points plotted in the graph are those of the mean values of several observations as given in Table I. There is no doubt as to the existence of the side band on the left of the principal band (at 870 *f*) as shown by the results obtained. In addition to the observations recorded in Table I a large number of measurements were made at other concentrations and thicknesses and it was found that Beer's law (that the $\log_{10}$ transmittancy is directly proportionate to the concentration and thickness) holds for this dye for the concentrations studied (3.3 to 0.4 cg. per liter), confirming the data of Macbeth and Maxwell[5] on this dye. The position of the principal absorption band of this dye, as determined by 22 separate observations was found to be at a frequency of $947 \pm 2f$ ($\lambda = 316\text{m}\mu$; $1/\lambda = 316 \times 10^{-5}$).

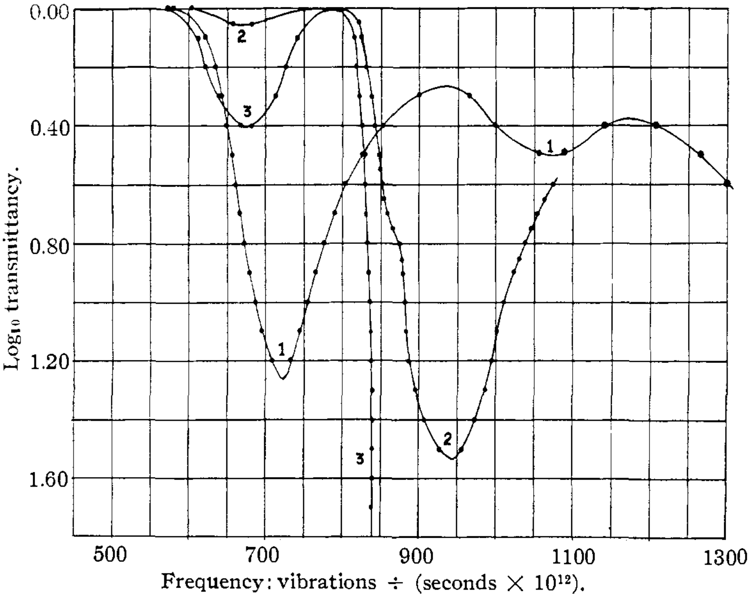

Fig. 3.—The absorption spectra of benzene-azobenzene in concd. hydrochloric acid; concentration, 1.65 cg. per liter (Curve 1); in ligroin of concentration 3.3 cg. per liter, (Curve 2), and in ligroin of concentration, 26.4 cg. per liter (Curve 3). The cell thickness in all cases is 0.5 cm.

In Fig. 3 are given the curves for benzene-azobenzene in ligroin (Curve 2) and in hydrochloric acid (Curve 1). The absorption spectrum of benzene-azobenzene in a benzene solution was also determined and found to be practically identical with the absorption spectrum in ligroin. There

[5] Macbeth and Maxwell, *J. Chem. Soc.*, **123**, 370 (1923).

was no extensive shift of the center of the band with different organic solvents, although such a shift was shown to occur with benzene-azophenol.[4b] On this same graph is also given the curve for eight times the original concentration in ligroin (Curve 3), showing the exact position and strength of the first weak band. In the absorption curve of the entire band, this first band appears so weak that some observers have missed it entirely.

Summary

1. The absorption spectra of benzene-azobenzene have been determined in a number of solvents, and there has been shown to be no extensive shift of the band with a change of typical organic solvents as was the case with benzene-azophenol.

2. It has been shown that the absorption band of benzene-azobenzene is not simple but consists of a smaller band on the lower frequency side of the principal band which adds to the principal band to produce the observed absorption curve.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF LOUISVILLE]

THE SYNTHESIS OF ACRIDINE-9-ETHYLAMINE

BY H. JENSEN AND L. HOWLAND[1]

RECEIVED APRIL 21, 1926 PUBLISHED JULY 6, 1926

Introduction

Among the alkaloids, strychnine and brucine,[2] as well as among the valuable pharmaceutical products, acriflavine and rivanol[3] are found acridine derivatives, and therefore this group of substances, about which only little is known, has gained new interest for the chemist.

For this reason one of the authors has undertaken a series of investigations on acridine derivatives. In this paper we shall report about the preparation of acridine-9-ethylamine.

Acridine itself has antiseptic properties, and it was thought that by introducing an ethylamine side chain the optimum effect would be obtained. In the pharmaceutical investigations of the amino-alkyl bases of the phenols and of the iminazoles it has been found that the carbon skeleton giving optimum sympathomimetic activity consists of a benzene-iminazole

---

[1] This paper is an abstract of a part of a thesis presented by Louis Howland in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at the University of Louisville.

[2] Perkin and Robinson, *J. Chem. Soc.*, **97**, 305 (1910).

[3] For the physiological effect of these compounds, see E. Laqueur, "Die neueren chemotherapeutischen Praeparate aus der Chinin- und aus der Akridinreihe," Julius Springer, Berlin, **1923**.