[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF UNION COLLEGE]

The Ultraviolet Absorption of Benzotriazole[1a]

BY JOHN E. FAGEL, JR.,[1b] AND GALEN W. EWING

The ultraviolet absorption spectra of benzotriazole and 5,(6)-chlorobenzotriazole have been determined in numerous aqueous solutions in the region 220–290 mμ. An attempt has been made to correlate the absorption spectra with molecular structure. The acidic dissociation constant of each compound has been determined graphically.

Since relatively little[2-7] has appeared in the literature on the physical properties of benzotriazole, and in view of its photographic and analytical applications, it was felt that a detailed study of its ultraviolet absorption might prove valuable from both the theoretical and practical viewpoints.

Discussion

The ultraviolet absorption of benzotriazole was determined initially in solvents of varying polarity. As may be seen in Fig. 1, a bathochromic shift accompanies the change from non-polar to polar solvents. This shift is in accord with that usually noted in similar situations.

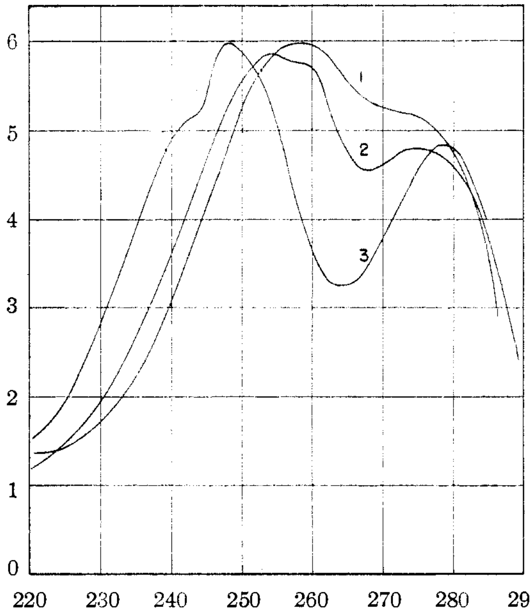


Fig. 1.—Benzotriazole—change of solvent: 1, *p*H 7.0; 2, 95% ethanol; 3, isoöctane.

Upon examining the spectra of benzotriazole in solutions of widely varying *p*H (Figs. 2–3), two fundamental spectral types are noted. The spectra of strongly acidic and basic solutions exhibit a single maximum, whereas the spectra of mildly acidic and neutral solutions exhibit two maxima.

By analogy with the known spectra of benzene and *o*-quinone, it is assumed that the lower wave length absorption band is characteristic of a benzenoid chromophore and that the higher wave length band is characteristic of a quinoid chromophore. It is further assumed that the principal contributing forms of the molecule in neutral and mildly acidic, acidic and basic solutions are, respectively, the neutral molecule, the cation and the anion. Therefore, we believe that the neutral form of the molecule is best characterized by a benzenoid structure (I) and that both the cation and anion are best characterized by quinoid structures (II and III).

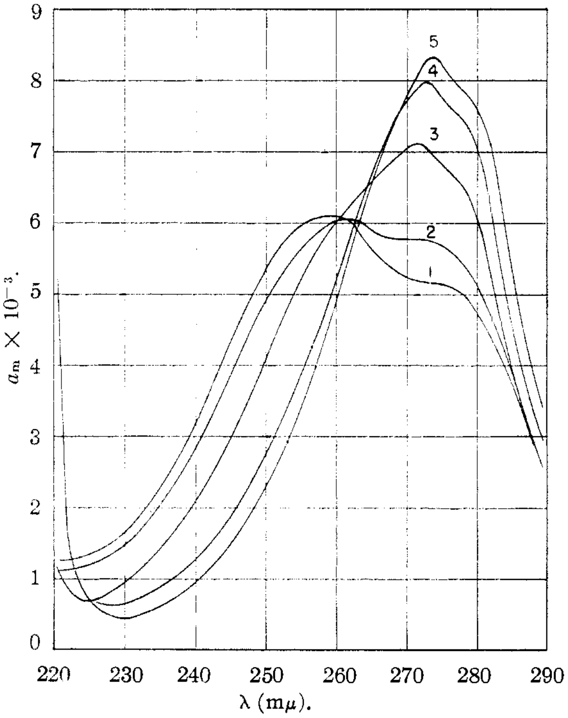
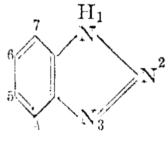
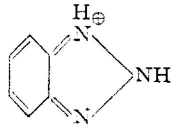


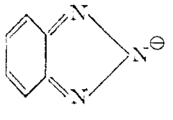
Fig. 2.—Benzotriazole in aqueous acids: 1, *p*H 2.0; 2, 0.1 *N* HCl; 3, 0.5 *N* HCl; 4, 6 *N* HCl; 5, 12 *N* HCl.



I



II



III

Evidence in support of the postulation of a mono-acid form in strongly acidic solutions was obtained by analyzing a sample of benzotriazole hydrochloride.[3] The hydrochloride was dissolved in water and passed through a cation exchange column saturated with hydrogen ions. The effluent was then titrated with standard base. Within the limits of experimental error, one equivalent of hydrogen ion was found per equivalent of benzotriazole, indicating the salt to be a mono-hydrochloride.

---

(1) (a) This work was supported by a grant from the Research Corporation, New York. (b) Research Laboratory, General Electric Co., Schenectady 5, N. Y.

(2) P. Griess, *Ber.*, **15**, 1878 (1882).

(3) F. Krollpfeiffer, H. Pötz and A. Rosenberg, *ibid.*, **71B**, 596 (1938).

(4) A. Macbeth and J. Price, *J. Chem. Soc.*, 111 (1936).

(5) K. Auwers, *Ber.*, **71B**, 604 (1938).

(6) H. Specker and H. Gawrosch, *ibid.*, **75B**, 1338 (1942).

(7) T. Heafield and L. Hunter, *J. Chem. Soc.*, 420 (1942).

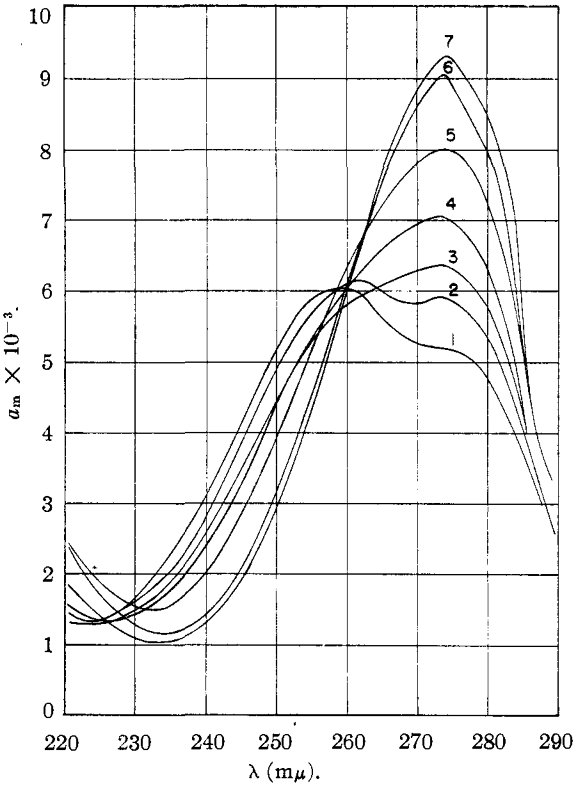


Fig. 3.—Benzotriazole in aqueous alkali: 1, pH 7.0; 2, pH 7.6; 3, pH 7.9; 4, pH 8.2; 5, pH 8.5; 6, pH 10.0; 7, 6 N NaOH.

There are two probable forms of the cation: the 1,2-form and the 1,3-form. Since the spectra in strongly acidic and basic solutions are similar, it seems reasonable to assume that the structures of the cation and anion are also similar. Upon examining typical resonance structures of each cation form and comparing them with the resonance structures of the anion and neutral molecule, it is observed that the principal structures of the 1,2-form are similar to those of the anion (quinoid), whereas the structures of the 1,3-form are similar to those of the neutral molecule (benzenoid). Therefore, we conclude the cation exists in the 1,2- rather than the 1,3-form.

5,(6)-Chlorobenzotriazole.—The absorption spectra of 5,(6)-chlorobenzotriazole (Figs. 4–5) exhibit roughly the same shape and variation with pH as do the spectra of the parent compound. Therefore, we conclude that the substitution of chlorine for hydrogen at the 5,(6)-position does not significantly alter the structures of the various molecular forms of the compound.

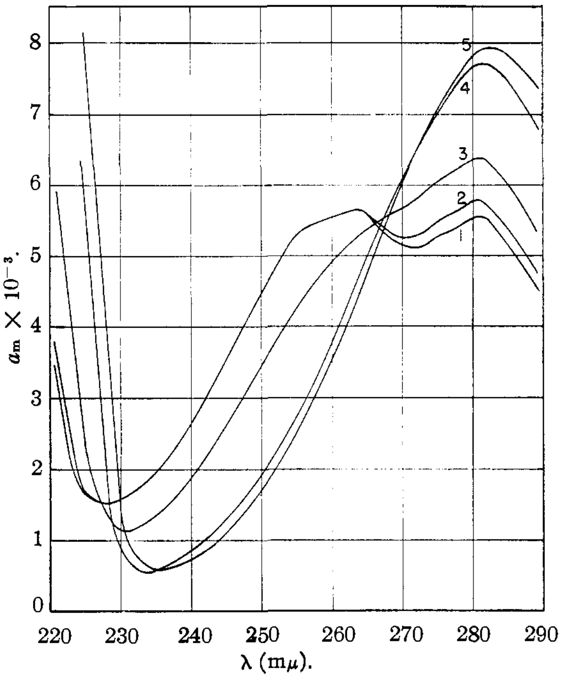


Fig. 4.—5,(6)-Chlorobenzotriazole in aqueous acids: 1, pH 5.0; 2, pH 1.2; 3, 1 N HCl; 4, 6 N HCl; 5, 12 N HCl.

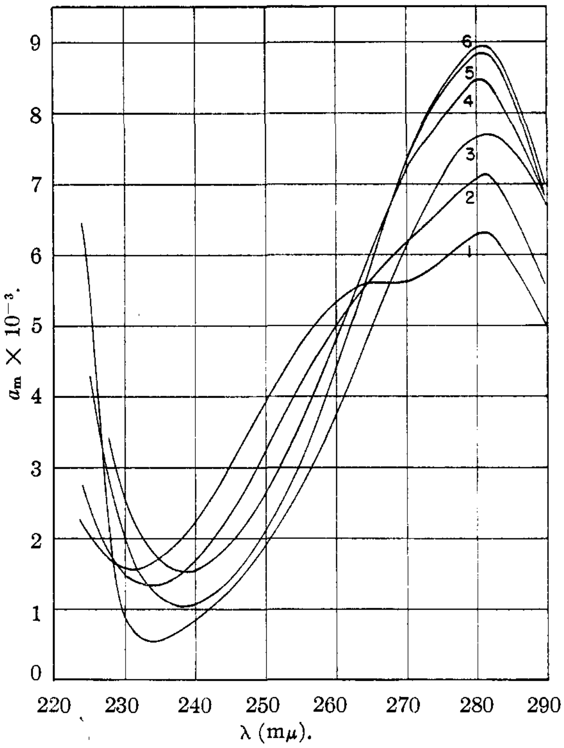


Fig. 5.—5,(6)-Chlorobenzotriazole in aqueous alkali: 1, pH 7.0; 2, pH 7.5; 3, 6 N NaOH; 4, pH 8.5; 5, pH 11.6; 6, pH 9.4.

Graphical Determination of the Acidic Dissociation Constants

According to Stenström and Goldsmith,[8] it is possible to determine the apparent dissociation constant of a compound by measuring its absorption in solutions of varying acidity. In Figs. 6–7, the molar absorbancy index (a_M) is plotted against the pH of the solutions. The apparent pK is equal to that value of the pH at which a_M is midway between its upper and lower limits.

The values of the acidic dissociation constants so determined at several different wave lengths agree closely with those shown in Figs. 6–7. The lower value for the chloro-derivative is in line with the expected inductive influence of the chlorine.

---

[8] W. Stenström and N. Goldsmith, *J. Phys. Chem.*, **30**, 1683 (1926).

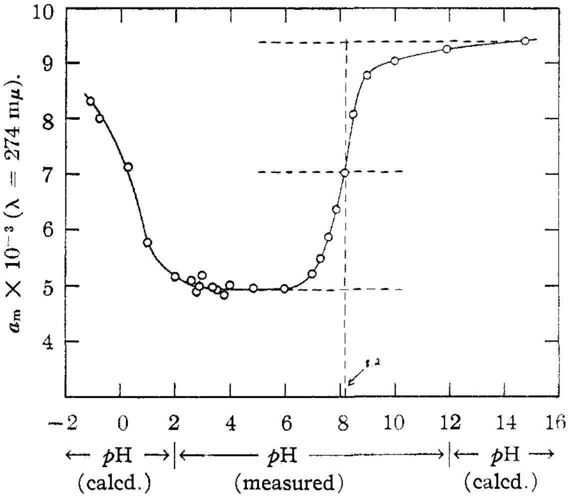


Fig. 6.—Graphical determination of acidic dissociation constant: benzotriazole, pK 8.2.

Experimental

The spectra were determined with a model DU Beckman spectrophotometer,[9] serial No. 3210.

The instrument was set at minimum sensitivity for all determinations, thus allowing measurements to be made at wave lengths as low as 210 mμ. Slit widths were varied from approximately 1.6 to 0.3 mm. Except in the lower wave length region, the nominal band width isolated was approximately 1 mμ.

Readings were taken at wave length intervals of 5 mμ. In the immediate vicinity of the maxima and minima readings were taken every 1 mμ.

Matched, fused-silica cells of square cross-section, 10 ± 0.01 mm. on the inside, were used.

Melting point determinations were made with a calibrated Thiele apparatus. All buffer solutions were checked with a glass-electrode pH meter.

Benzotriazole.—The material used in this study was obtained by benzene extraction from a photographic anti-foggant, *Orthazite*, manufactured by the Edwal Laboratories and purchased from a retail photographic dealer.

After extraction, the material was recrystallized from benzene until a sharp melting point was obtained. The melting point of the white product after drying *in vacuo* at 77°, was 98–99° (cor.). Literature values are 98.5°[10] and 96–97°.[11]

5,(6)-Chlorobenzotriazole.—The chloro-derivative was synthesized from 4-chloro-*o*-phenylenediamine by diazotization and self-coupling, by adaptation of the procedure[11] for the synthesis of benzotriazole from *o*-phenylenediamine.

The crude material was recrystallized from xylene. After drying *in vacuo* at 100°, the white product melted at 156–157° (cor.). The literature value is 156°.[12]

Preparation of Solutions.—The solutions of both the parent compound and the chloro-derivative varied in concentration between 10 and 15 mg. per liter. The reference liquid used in each determination was from the same batch of solvent used in preparing the solution.

Because of the extremely limited solubility of the chloro-derivative in aqueous buffers, it was found expedient to affect solution of the compound by first dissolving it in a few ml. of ethanol. No solvent effect on the spectra was observed.

Except in the pH range 2–6, the Clark and Lubs buffers were found ideally suited as solvents for the present work. (In the range excepted, a biphthalate salt which absorbs below 300 mμ renders these buffers unsuitable.) Sørensen's glycine–hydrochloric acid buffers were found to possess the necessary transparency in the range not covered by the Clark and Lubs buffers.

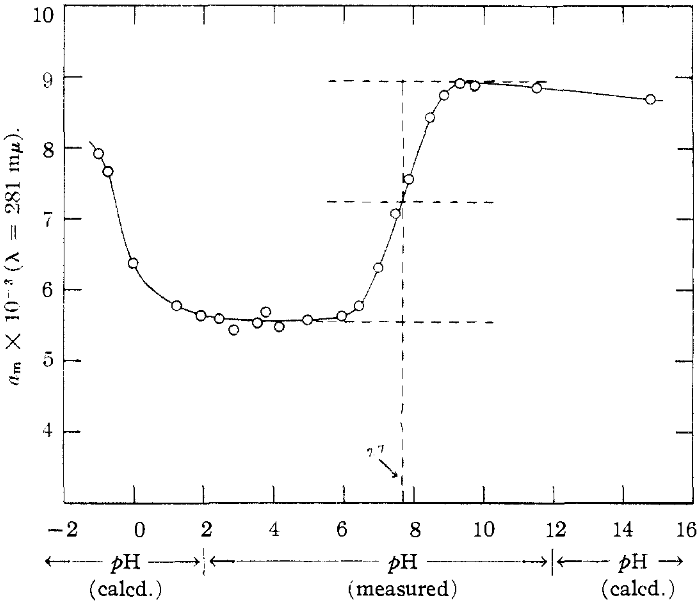


Fig. 7.—Graphical determination of acidic dissociation constant: 5,(6)-chlorobenzotriazole, pK 7.7.

SCHENECTADY 8, N. Y. RECEIVED NOVEMBER 27, 1950

---

[9] H. Cary and A. Beckman, *J. Optical Soc. Am.*, **31**, 682 (1941).

[10] Ladenburg, *Ber.*, **9**, 222 (1876).

[11] R. Damschroder and W. Peterson, *Org. Syntheses*, **20**, 16 (1940).

[12] F. Ullmann and F. Mauthner, *Ber.*, **36**, 4028 (1903).