the 12.8 μ band to the Si—N function. The second complication is considerably more serious. Since primary amines exhibit absorption in this region and as the *N*,*N*-diethyltriethylsilane failed to show any characteristic absorption, no assignment of this region to the Si—N function can be made. The spectrum of a *N*,*N*-dideuterosilazane would shed considerable light upon this problem.

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Photochemical Reactions of Azo Compounds. I. Spectroscopic Studies of the Conjugate Acids of *cis*- and *trans*-Azobenzene

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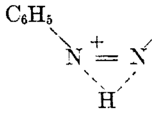
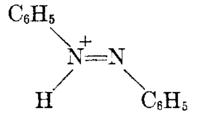
As part of the investigation of the photocatalyzed cyclization of azobenzene in acidic solution, the behavior of the conjugate acids of *cis*- and *trans*-azobenzene in the presence and absence of light has been studied spectroscopically. The basicities of the isomers and of benzo[c]cinnoline have also been examined.

It has been reported recently that azobenzene is oxidatively cyclized to benzo[c]cinnoline when exposed to light in strongly acidic solutions.[1] The properties of the conjugate acids of *cis*- and *trans*-azobenzene are of special interest in this reaction because no difference could be detected between their rates of cyclization. As irradiation of azobenzene in neutral solutions is known to result in *cis* ⇌ *trans* equilibration[2] it seemed that the photocatalyzed cyclization is most probably preceded by rapid *cis* ⇌ *trans* isomerization of the cations. A plausible alternative assumption, however, is that *cis*- and *trans*-azobenzene could form conformationally identical cations immediately upon protonation, such being consistent with Jaffé's[3] contention that even the conjugate acid derived from *trans*-azobenzene should be assigned the *cis*-structure (I) in preference to the commonly accepted classical structure (II).


(I)


(II)

The properties of *cis*- and *trans*-azobenzene in strongly acidic solutions, alternatively in the absence and presence of light, have now been studied by means of absorption spectroscopy. The results show conclusively that the former of the above alternatives is correct. Spectroscopic determinations of the ionization constants of the azobenzene isomers and benzo[c]cinnoline have also been made and satisfactorily correlated.

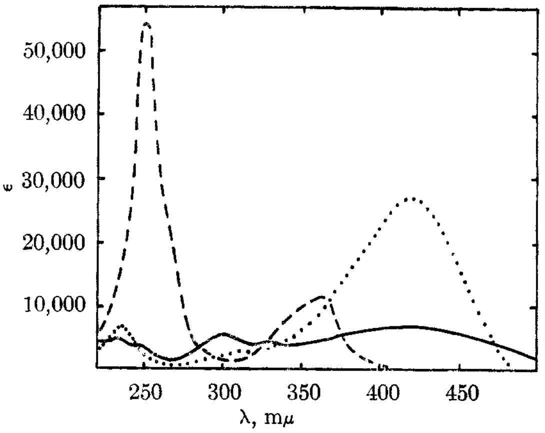


Fig. 1. Absorption spectra of conjugate acids in 22*N* 10% (v.:v.) ethanolic sulfuric acid: *cis*-azobenzene(——); *trans*-azobenzene (· · · ·); benzo[c]cinnoline (– – – –)

In Fig. 1 are recorded the absorption spectra of *cis*- and *trans*-azobenzene and benzo[c]cinnoline measured in 22*N* sulfuric acid containing 10% (v.:v.) ethanol. At this acidity all three compounds exist as the first conjugate acids.

Apart from the periods required for spectral measurements the solutions were protected from light. Under these conditions the conjugate acids of *trans*-azobenzene and benzo[c]cinnoline were stable, but the absorption of the *cis* cation changed over the course of several days to that of the *trans*. The half-time for the *cis*→*trans* conversion was 10.5 ± 0.5 hr. A small amount of extrapolation at certain wave lengths was therefore necessary in constructing an accurate curve for the *cis* ion. When concentrated sulfuric acid alone was tried as solvent, isomerization occurred too rapidly to permit reliable measurements. In this respect it is interesting that some authors,[2,4] although not employing solutions of sufficient acidity for examination of the conjugate acid, found that the rate of *cis*→*trans* isomerization of the free base increases with acidic strength of solution.

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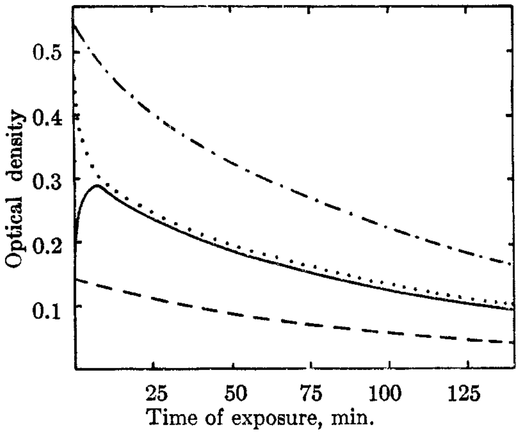


Fig. 2. Variations in optical density at 420 mμ following exposure to light of solutions (2 × 10 $^{-5}$ M) of conjugate acids of *cis*- and *trans*-azobenzene: (a) observed: *cis*(——); *trans*(· · · ·) (b) expected from the rate of formation of benzo[c]cinnoline: *cis*(- - - -); *trans*(-·-·)

The differences in spectra recorded in Fig. 1 show beyond doubt that the conjugate acids derived from *cis*- and *trans*-azobenzene are conformationally distinct. Protonation of *trans*-azobenzene does not, therefore, result in a *cis* conjugate acid as contended by Jaffé.[3]

Solutions of the *cis* and *trans* cations at spectroscopic concentrations are rapidly decolorized when exposed to direct sunlight. The fading, as shown by redetermination of spectra, is the result of cyclization. In order to study more closely the effect of light, subdued illumination had to be employed. The following procedure was both convenient and reproducible.

Freshly prepared solutions (2 × 10^{-5}M) of *cis*- and *trans*-azobenzene in 22N 10% (v.:v.) ethanolic sulfuric acid were exposed in 1 cm. spectrophotometer cells to a 160 watt tungsten filament lamp centered at a distance of 16 cm. Irradiation was interrupted only for periodic reexamination of the spectra.

The rate of cyclization was determined from increases in optical density at 252 mμ, the half-time for both solutions being 78 ± 4 min. Weakening of absorption at 420 mμ, however, was in each case irregular with respect to the appearance of the 252 mμ band.

The graphs in Fig. 2 illustrate the observed optical density changes at 420 mμ and those expected to occur at this wave length solely on the basis of the rate of formation of benzo[c]cinnoline. The decrease in absorption shown by the *trans* cation appeared to be abnormally fast, while the solution of the *cis* compound displayed an initial rapid increase. Furthermore, the optical densities of both solutions became almost equal within a short time, and subsequently decreased at the same rate.

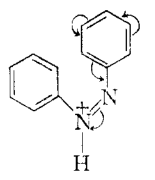
It was concluded that a *cis* ⇌ *trans* equilibrium is established in both cases. The half-time for equilibration was approximately 100 times less than that for the formation of benzo[c]cinnoline, thereby accounting for the failure of *cis*-azobenzene to undergo cyclization at a noticeably higher rate than the *trans* compound.

From the calculated and observed optical densities illustrated in Fig. 2, it was estimated that the *cis* cation constitutes approximately 55% of the equilibrium. Confirmatory evidence was obtained by examining a preformed mixture of *cis*- and *trans*-azobenzene (11:9) under the same conditions, in which case alterations in the 420 mμ and 252 mμ bands were consistently inversely proportional.

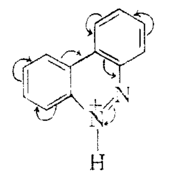
The ionization constants of *cis*- and *trans*-azobenzene and benzo[c]cinnoline were evaluated spectroscopically in 10% (v.:v.) ethanolic sulfuric acid. The pKa values found are: *cis*-azobenzene (−1.6 ± 0.2), *trans*-azobenzene (−2.6 ± 0.2) and benzo[c]cinnoline (1.8 ± 0.2). No evidence was found for addition of a second proton to benzo[c]cinnoline in 22N acid. The basicity of *cis*-azobenzene has not been reported previously but constants obtained in purely aqueous media for the other compounds are: *trans*-azobenzene (−2.48)[5] and benzo[c]cinnoline (2.2).[6]

It is necessary to emphasize that the currently reported values are suitable for qualitative comparisons only, in view of the application of Michaelis and Granick's scale[7] for estimation of pH in the regions of high acidity. Nevertheless, *cis*-azobenzene is clearly a stronger base than the *trans* compound, a fact which harmonizes with previous evidence for higher electron availability at the nitrogen atoms of the *cis* compound.[8]

Significance is also attached to the comparatively high basicity of benzo[c]cinnoline. Azo-compounds in general are much weaker bases than N-heterocyclic compounds, and, in the present case, consideration of comparable electron shifts in the conjugate acids of azobenzene (III) and benzo[c]cinnoline (IV) suggests that the latter ion has a considerably greater resonance energy. Such a difference should, in fact, be related to the enthalpy change in the cyclization reaction.



III



IV

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EXPERIMENTAL

Materials. Trans-azobenzene, m.p. 68°, was obtained free from traces of the *cis* isomer by chromatography on alumina and recrystallization from ethanol in darkness. *Cis*-azobenzene, m.p. 71°, was prepared by irradiation of the *trans* compound[2] and chromatographic purification on alumina. Immediately before each occasion of use it was recrystallized from pentane in order to remove any spontaneously formed *trans*-azobenzene. The benzo[c]cinnoline used in these experiments was prepared according to Badger, Seidler, and Thompson.[9] After recrystallization from aqueous ethanol it melted at 154°. Isolation of benzo[c]cinnoline from irradiated acidic solutions of azobenzene has been described already.[1]

Absorption spectra. Solutions for spectroscopy were prepared by diluting stock solutions in absolute ethanol with aqueous sulfuric acid of appropriate normality. All spectra were measured in an Optica CF_4 Double Beam Recording Spectrophotometer at a wave-length drive of 0.4 $m\mu$ $sec.^{-1}$ Spectral changes in the absence and presence of light were studied through the entire range, 220–500 $m\mu$, at every stage.

Ionization constants. The *p*Ka values were evaluated by a standard procedure[10] following measurement of the spectra in various normalities (0.1–22*N*) of 10% (v.:v.) ethanolic sulfuric acid and neutral solution. Thermostatic control was not employed. All data therefore refer to room temperature (19–23°). Calculations for benzo[c]cinnoline were based on *p*H determinations with a glass electrode. The extended *p*H scale of Michaelis and Granick[7] was used for solutions of the azobenzenes. Although this scale is strictly applicable to purely aqueous sulfuric acid systems constant *p*Ka values were obtained in 10% (v.:v.) ethanolic sulfuric acid over reasonably wide ranges of normalities. The values found, however, must be considered suitable for qualitative comparisons only.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF HOUSTON]

Kinetics of the Acetolysis of Some Alkyl-Substituted Neopentyl *p*-Bromobenzenesulfonates[1]

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Kinetics of the acetolysis of a series of alkyl-substituted neopentyl *p*-bromobenzenesulfonates, $R\text{-}C_\beta(CH_3)_2\text{-}C_\alpha H_2\text{-}OBs$, has been investigated. First-order rate constants have been determined at three temperatures and values for ΔH^* and ΔS^* derived for nine esters. Relative rates (CH_3 member = 1.0) show that (1) lengthening of the chain in R without branching beyond C_γ (C_2H_5, n-C_3H_7 and n-C_4H_9 members) gives a constant relative value of 2.4; (2) the effect of substitution of one, two, and three alkyl groups on C_γ (C_2H_5, i-C_3H_7 and *sec*-C_4H_9, t-C_4H_9 members) results in relative rates of 2.4, 7–8, and 34, respectively; (3) branching of R at C_δ (i-C_4H_9 member) gives a relative rate of 4.1. The overall variation of rate with structure corresponds closely to that observed in the structurally-related tertiary chlorides and appears to be explained best by a combination of carbon participation and a release of B-strain.

The behavior of alcohols of the type R_3C_β-$C_\alpha H_2OH$ (I) when subjected to conditions favorable to dehydration and rearrangement was first considered by Haller and Bauer[2] and later by Favorsky, who studied 2,2-dimethyl-1-butanol and 2-methyl-2-ethyl-1-butanol.[3] The extensive investigations of Whitmore on neopentyl alcohol (I, R = CH_3) and its derivatives[4] and of Meerwein and van Emster on camphene hydrochloride[5] led to formulation of an ionization mechanism for the rearrangements. Whitmore also investigated the relative migratory powers of the CH_3 and n-C_4H_9 groups during dehydration of 2,2-dimethyl-1-hexanol.[4c] This early work was later verified and extended by Dostrovsky, Hughes, and Ingold[6] and by Winstein[7] using kinetic methods. Numerous other investigators employed a stereo-chemical approach[8] and the labelling technique[9] in an effort to arrive at a better understanding of 1,2-saturated nucleophilic rearrangements. In most of the cases investigated, relative reactivities and rearranged

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