

( $\theta_m - \theta_m^{qa}$ ) and  $\Delta E_m^{qa}/\Delta E_m$  corresponding to  $n = 7$  [or 10] we estimate  $\theta_m$  to be  $98.1^\circ$  (or  $98.9^\circ$ ) and  $\Delta E_B$  to be 5.7 kcal/mol (or 4.6 kcal/mol). These values compare with previous estimates by Holmes, *et al.*, (field B) of  $91.4^\circ$  and 15.3 kcal/mol in which a guess of the effect of anharmonicity was made, but in which  $F_{67}$  was neglected since it was not known at the time.<sup>15</sup> A more recent value of 3.0 kcal/mol based on an observed bending anharmonicity in  $\text{VF}_5$  scaled to  $\text{PF}_5$  has also been estimated by Holmes.<sup>14</sup> It will be interesting to investigate whether a transition metal complex conforms to the POS model as well as do compounds of nonmetals. In any event, we have more or less bracketed the barrier to pseudorotation in  $\text{PF}_5$  and find a value low enough to permit facile intramolecular exchange but a value somewhat higher than given by the EHMO method.

### Concluding Remarks

The POS variant of the valence shell electron pair repulsion model has shown sufficient promise in its application to force fields of  $\text{XY}_5$  compounds that further studies are underway. Unanswered in the present investigation are its merits in treating simpler cases where *all* bonds are equivalent by symmetry (*cf.*  $\text{SnCl}_4$ ,  $\text{TeF}_6$ ), decidedly more complex cases where auxiliary ideas are needed to interpret observations in a consistent way (*cf.*  $\text{IF}_7$ ), and cases in which bonds are nonequivalent chemically as well as geometrically (*cf.*  $\text{IOF}_5$ ). Preliminary results for the latter com-

pound<sup>49</sup> reveal that the POS and EHMO models are again strikingly parallel in their predictions of force fields and, moreover, are successful in accounting for radial forces governing the distribution of bond lengths as well as angular forces.

Applied to  $\text{XY}_5$  molecules the POS scheme has the following salutary features. (1) It accounts in an elementary way for the symmetry and distribution of bond lengths<sup>3,4</sup> and force constants. (2) It provides a rough physical criterion for selecting the proper solution from among several alternative force field solutions derived from vibrational spectra. (3) It offers a plausible method for relating pseudorotational barriers to force constants, a heretofore elusive undertaking. (4) It affords provocative evidence, in view of the harder than coulomb repulsions found and close correspondence between POS calculations, *ab initio* MO calculations, EHMO calculations devoid of coulomb interactions, and experiment, that the mutual avoidance (Pauli avoidance) of occupied, localized molecular orbitals is, as originally proposed by Gillespie and Nyholm, the proper basis for the valence shell electron pair repulsion theory.

**Acknowledgments.** We thank Miss Susan Fitzwater for assistance with some of the calculations. We are pleased to acknowledge partial support for the computing by the Michigan Computing Center. Helpful discussions with Dr. H. B. Thompson are also gratefully acknowledged.

(49) L. S. Bartell, F. B. Clippard, and E. J. Jacob, *Acta Crystallogr.*, in press.

## Reaction Pathways for the Photochemical Conversion of Ortho-Substituted Benzylideneanilines to Azoles

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*Contribution from the Max-Planck-Institut für Biophysikalische Chemie, D-3400 Göttingen, Germany. Received July 15, 1972*

**Abstract:** Benzylideneanilines substituted in the ortho position of the aniline ring by hydroxy, sulfhydryl, or amino groups are photochemically converted to the corresponding azoles. The possible reaction pathways depend on the substituent. Benzylidene-*o*-hydroxyaniline is stable at room temperature. Two photons are required to convert it first to the thermally unstable 2-phenylbenzoxazoline and then to 2-phenylbenzoxazole. Benzal-*o*-sulfhydrylaniline (Ib) is unstable at room temperature. It converts thermally to 2-phenylbenzothiazoline (IIb). Illumination of IIb yields 2-phenylbenzothiazole and Ib. Benzylidene-*o*-aminoaniline is stable at room temperature. Only one photon is required for the ring closure to 2-phenylbenzimidazole. The corresponding imidazoline could not be detected as an intermediate. It is either too short lived or nonexistent. All photo-reactions are accompanied by trans  $\rightarrow$  cis photoisomerizations of the Schiff bases.

Benzylideneanilines (I) substituted in the ortho position of the aniline ring by a hydroxy (Ia), mercapto (Ib), or an amino group (Ic) are photochemically converted to the respective heterocycles 2-phenylbenzoxazole (IIIa), 2-phenylbenzothiazole (IIIb), and 2-phenylbenzimidazole<sup>1</sup> (IIIc). (The reason for including the azoline II in Scheme I will be explained below.)

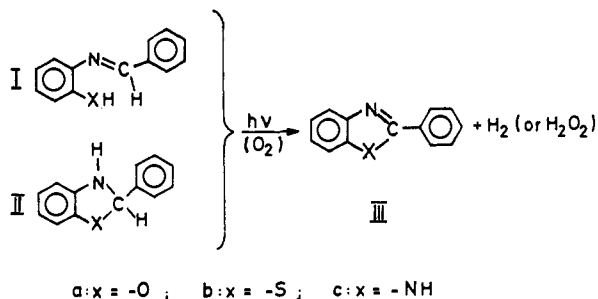
The reaction takes place in degassed as well as in air-

(1) K. H. Grellmann and E. Tauer, *Tetrahedron Lett.*, 1909 (1967).

saturated solutions. In the latter case the quantum yield is higher and stoichiometric amounts of  $\text{H}_2\text{O}_2$  are found; without oxygen the formation of hydrogen has been observed by means of gas chromatography. The products were identified by comparison with authentic samples.

The reaction depends somewhat on the nature of the solvent. Ib and Ic yield in hexane as well as in ethanol the corresponding azoles, whereas Ia photohydrolyzes in ethanol into *o*-hydroxyaniline and benzaldehyde and

Scheme I



cyclizes only in aprotic solvents. In spite of the similarity of the final photoproducts the reaction pathways of the three compounds differ substantially, as can be shown by means of steady-state and flash-spectrophotometric experiments.

Since the discussion of the reaction pathways we wish to present here is mainly based on the spectroscopic properties of the species involved, we shall briefly summarize the results of several papers<sup>2-7</sup> concerned with the interpretation of the absorption spectra of the parent compound benzylideneaniline (BA) and some of its derivatives. The following conclusions drawn from experimentally and theoretically derived data are generally accepted.

1. The thermodynamically stable form of BA is the trans configuration. This is also true for a great number of BA derivatives, including Ia and Ic (the stable form of the sulfur homolog is the thiazoline IIb, which will be discussed below).

The cis form is unstable at room temperature<sup>8</sup> and has a lifetime of about 1 sec. Its absorption spectrum can be studied by means of the flash technique, or more conveniently at low temperatures, since the thermal reaction cis  $\rightarrow$  trans has a high activation energy. At  $-120^\circ$  for instance aromatic cis Schiff bases are practically stable.<sup>8</sup> The light induced trans  $\rightarrow$  cis isomerization can, of course, still take place at low temperatures. There exists no wavelength region where only the trans form absorbs, and since the photochemical cis-trans conversion has a comparable efficiency, only a mixture of cis and trans can be generated at low temperatures.

2. The uv spectrum of *trans*-BA has an absorption band with a peak at 320 nm, thereafter called band A. It is due to resonance interaction between the aromatic rings through the  $\text{—C=N—}$  linkage. Its intensity is much weaker compared to the corresponding peak for the isoelectronic stilbene, because the aniline ring is twisted out of the molecular plane, thus reducing resonance interaction. In Ia and Ic band A is shifted to 360 nm due to the chromophoric ortho substituents.

3. In the sterically hindered cis configuration the angle of twist of the aniline ring is still greater than in the trans form, leading to a weakening of the intensity of the A band; however, at its long wavelength end an

(2) H. H. Jaffé, S.-J. Yeh, and R. W. Gardner, *J. Mol. Spectrosc.*, **2**, 120 (1958).

(3) J. Schulze, F. Gevson, J. N. Murrell, and E. Heilbronner, *Helv. Chim. Acta*, **44**, 428 (1961).

(4) J. D. Margerum and J. A. Sousa, *Appl. Spectrosc.*, **19**, 91 (1965).

(5) W. Krauss and C. G. J. Wagner, *Z. Naturforsch. A*, **22**, 746 (1967).

(6) E. Haselbach and E. Heilbronner, *Helv. Chim. Acta*, **51**, 16 (1968).

(7) A. van Putten and J. W. Pavlik, *Tetrahedron*, **27**, 3007 (1971).

(8) E. Fischer and Y. Frei, *J. Chem. Phys.*, **27**, 808 (1957).

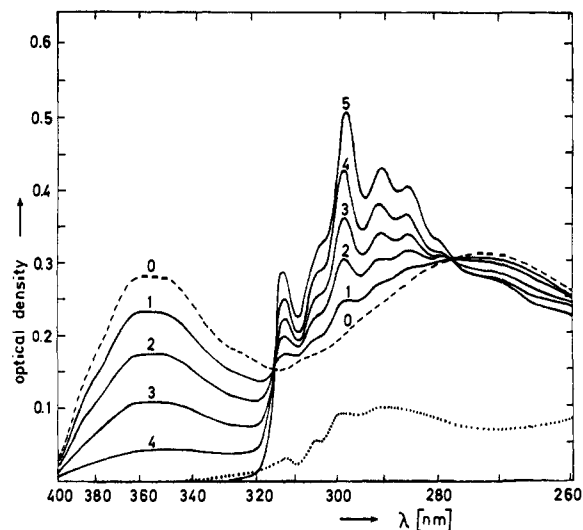


Figure 1. Absorption spectra of a  $2.5 \times 10^{-5} M$  solution of benzylidene-*o*-hydroxyaniline in air-saturated methylcyclohexane (MCH) at room temperature before illumination (0, - - -), and after polychromatic illumination (1-4, —). Absorption spectrum of a  $2.5 \times 10^{-5} M$  solution of 2-phenylbenzoxazole (authentic sample) in MCH at room temperature (5, —). Same solution as 0 illuminated at  $-80^\circ$  with a cutoff filter (.....) (see text). Optical path length  $d = 1$  cm.

absorption appears at about 400 nm which is stronger compared with that of the trans configuration. It is presumably due to an  $n \rightarrow \pi^*$  transition.

#### Experimental Results and Discussion

1. **Benzylidene-*o*-hydroxyaniline (Ia).** In Figure 1 we have depicted the absorption spectrum of Ia in methylcyclohexane (MCH) at room temperature before and after illumination with polychromatic light. The structured spectrum of the photoproduct is identical with that of 2-phenylbenzoxazole (IIIa). The isosbestic points at 317 and 278 nm indicate a clean conversion of the educt Ia to the product IIIa without side reactions. A spectrum of an authentic sample of the photoproduct with the same concentration as the educt before illumination has been added. Obviously, exhaustive illumination would lead to the same final curve.

Polychromatic illumination at  $-80^\circ$  also yields IIIa, but isosbestic points are not observed. The explanation for this behavior is the formation of an intermediate which is thermally stable at  $-80^\circ$  and which is photochemically converted to IIIa in a consecutive reaction. This intermediate can be selectively generated without subsequent formation of IIIa by exciting a solution of Ia at  $-80^\circ$  with the isolated 366-nm line of a medium pressure mercury lamp or by using a cutoff filter (Schott WG 3) which absorbs all light below 330 nm. The spectrum of the intermediate so formed is also given in Figure 1. It is stable in degassed as well as in air-saturated solution.

Its formation is accompanied by the relatively fast establishment of a photo cis-trans equilibrium of Ia. Therefore, if one measures the rate at which the A-band disappears at  $-80^\circ$ , one first observes a faster decrease of the optical density at, say, 360 nm because the A-band of cis Ia is less intense than that of trans Ia, followed by the slower decrease due to the continued formation of the intermediate. We assign the latter to 2-phenylbenzoxazoline IIa on the following grounds.

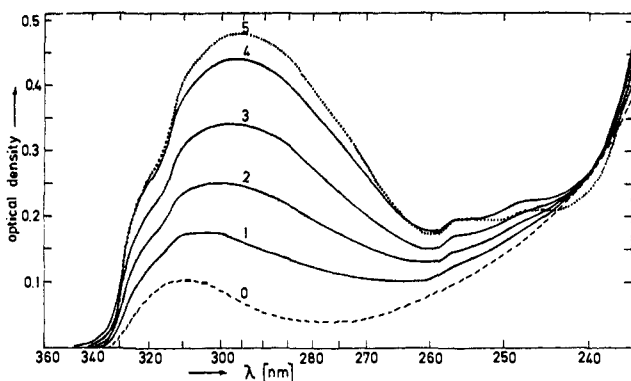


Figure 2. Absorption spectra of a  $2.5 \times 10^{-5} M$  solution of 2-phenylbenzothiazoline in air-saturated MCH at room temperature before illumination (0, ---), and after polychromatic illumination (1-4, —). Absorption spectrum of a  $2.5 \times 10^{-5} M$  solution of 2-phenylbenzthiazole (authentic sample) in MCH at room temperature (5, . . . .). Optical path length  $d = 1$  cm.

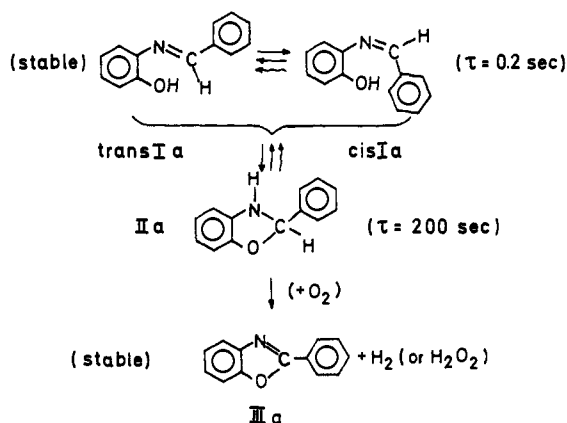
1. Similar to the stable 2-phenylbenzothiazoline IIb (*vide infra*), the compound does not absorb in the region of the A-band, because resonance interaction is interrupted.

2. The original spectrum of the educt is completely recovered if the solution is allowed to warm to room temperature in the dark. The product must therefore be an isomer of Ia; its lifetime at room temperature is about 200 sec. Dimerization can be excluded because the reaction also takes place in very diluted ( $10^{-5} M$ ) solutions. Furthermore, the para-substituted analog benzylidene-*p*-hydroxyaniline does not undergo the same spectral change; only *trans*  $\rightarrow$  *cis* isomerization but no cyclization takes place in this case.

3. Illumination of the new compound at  $-80^\circ$  (using the 254-nm line of a low pressure mercury lamp or a medium pressure mercury lamp without cutoff filter) results in the formation of Ia and IIIa; *i.e.*, the photochemical ring opening reaction IIa  $\rightarrow$  Ia competes with the photodehydrogenation to benzoxazole.

In Scheme II the photo- (solid arrows) and dark

Scheme II<sup>a</sup>



<sup>a</sup> Solid arrows indicate photoreactions, wavy arrows indicate dark reactions (lifetimes  $\tau$  are those at room temperature).

(wavy arrows) reactions are summarized. The lifetimes  $\tau$  given are those at room temperature. It is not known whether *trans* Ia, *cis* Ia, or both are reactive. The determination of quantum yields as a function of the wavelength of the exciting light would be necessary

to clarify this question. It is also not known whether the ring opening reaction IIa  $\rightarrow$  Ia produces *cis*-Ia, *trans*-Ia, or both.

The conversion of Ia to IIIa requires two photons according to Scheme II. The quantum yield is however independent of light intensity, because the thermal ring opening reaction IIa  $\rightarrow$  Ia is very slow and seems to be the only dark process competing with the photodehydrogenation. The relative quantum yields at different light intensities were measured by inserting wire mesh screens of known transmittance between the sample and the exciting light beam. The time of illumination was increased (1.5, 2, and 3.5 times) proportional to the decreased light intensity. In all cases the same amount of photoproduct was formed.

2. **2-Phenylbenzothiazoline (IIb).** The stable form of the condensation product of benzaldehyde and *o*-aminothiophenol is without doubt not the Schiff base Ib but the isomeric heterocycle IIb.<sup>9</sup> Charles and Freiser<sup>10</sup> have shown that the condensation product of salicylaldehyde and *o*-aminothiophenol is 2-(*o*-hydroxyphenyl)benzothiazoline. Like these authors we observed the N-H vibrations of the similar IIb at  $3390 \text{ cm}^{-1}$  in the infrared absorption spectrum. The ultraviolet absorption spectrum is also in agreement with the azoline structure. Unlike the other two Schiff bases Ia and Ic, the sulfur compound does not absorb in the region of the A-band because there is no resonance interaction between the two aromatic rings.

Although the five-membered ring of the stable photoproduct IIIb is already prefabricated in this case, the photoreactions of IIb are by no means simpler than those of the hydroxy compound. The absorption spectrum of the final photoproduct is depicted in Figure 2 together with the educt and an authentic sample of IIc. Obviously, side reactions occur in this case to some extent, in contrast to the other two substances Ia and Ic. These side reactions have not been further investigated.

Flash experiments reveal that the photodehydrogenation IIb  $\rightarrow$  IIIb is accompanied by the formation of an intermediate which has a lifetime of 5 sec and an absorption maximum at 360 nm, *i.e.*, in the region of the A-band. This absorption builds up within the lifetime of the flash and after the initial rise it increases further within 0.2 sec. The initial increase in absorption at 360 nm is in all probability due to the formation of a mixture of *cis*- and *trans*-Ib. The *cis* configuration has the expected lifetime of less than a second, its absorption is less intense than the *trans* absorption in this region and the build-up of the absorption at 360 nm after the flash is due to the thermal *cis*  $\rightarrow$  *trans* isomerization (Figure 3a). *trans*-Ib recyclizes to IIb with a rate of  $0.2 \text{ sec}^{-1}$  (Figure 3b). In Scheme III, a tentative reaction sequence is given.

Further kinetic studies are necessary to answer the interesting question as to whether the ring opening of IIb is stereospecific or whether a mixture of *cis*- and *trans*-Ib is formed simultaneously. It is also possible that in the thermal back reaction a small fraction of *cis*-Ib converts directly to IIb.

3. **Benzylidene-*o*-aminoaniline (Ic).** Figure 4 shows

(9) In our first communication on this subject<sup>1</sup> we have erroneously assigned the azomethine structure Ib to this compound.

(10) R. G. Charles and H. Freiser, *J. Org. Chem.*, **18**, 422 (1953).

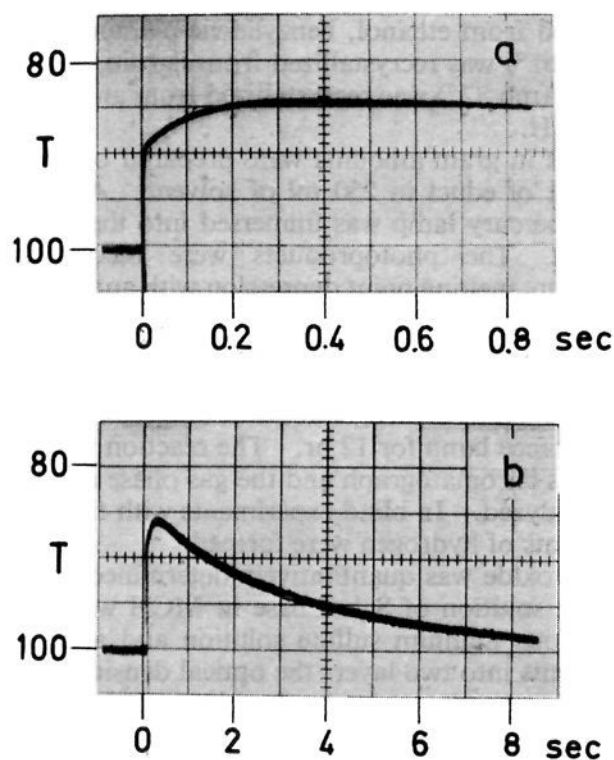
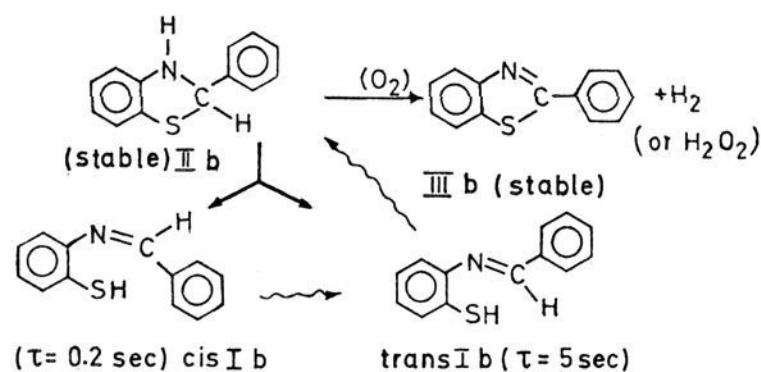


Figure 3. Oscilloscope traces at 360 nm after flashing a  $\sim 5 \times 10^{-5}$  M solution of 2-phenylbenzothiazoline in air-saturated MCH at room temperature: (a) time base 0.1 sec/div; (b) time base 1 sec/div, vertical scale, per cent transmission ( $T$ ). The optical path length for the monitoring light was 10 cm.

#### Scheme III<sup>a</sup>



<sup>a</sup> Solid arrows indicate photoreactions, wavy arrows indicate dark reactions (lifetimes  $\tau$  are those at room temperature).

the absorption spectra of the educt Ic and the subsequent formation of the photoproduct 2-phenylbenzimidazole (IIIc). The two preceding examples have shown that in each case a photon is required to dehydrogenate the azolines IIa and IIb to the corresponding azoles IIIa and IIIb. The difference of the two compounds lay in the thermodynamic stability of the open chain and the cyclic isomers I and II. In the case of the amino compound Ic, however, it was not possible to prove the existence of 2-phenylbenzimidazole (IIc) as an intermediate in spite of the otherwise similar properties of this molecule to Ia. The Schiff base Ic is the stable form of the condensation product of *o*-phenylenediamine and benzaldehyde and has an absorption spectrum similar to that of Ia. In addition, *trans*-Ic is photochemically converted to *cis*-Ic and the latter has a lifetime of less than a second at room temperature, also in close similarity to Ia.

The two compounds differ, however, if one compares the wavelength dependence of the quantum yield with which the azoles IIIa and IIIc are produced. While excitation of Ia at room temperature with long wavelength light in the region of the A-band led only to the formation of 2-phenylbenzoxazoline (IIa), the amine homolog is directly converted to 2-phenylbenzimidazole (IIIc) under the same conditions; *i.e.*, the quantum

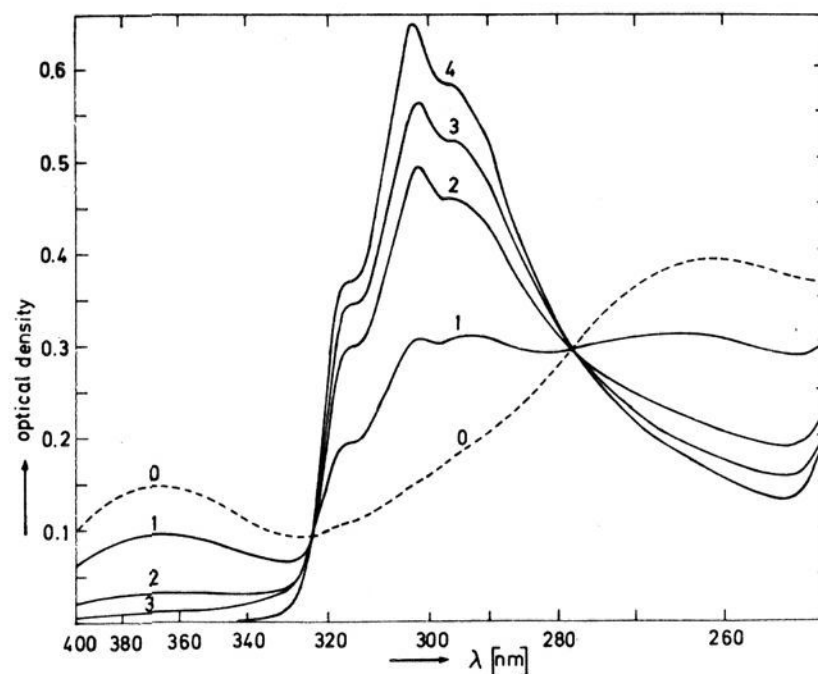
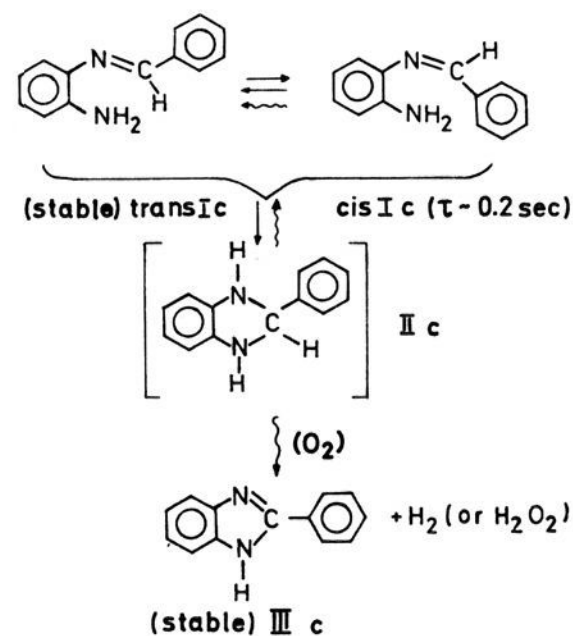


Figure 4. Absorption spectra of a  $2.5 \times 10^{-5}$  M solution of benzyldene-*o*-aminoaniline in air-saturated MCH at room temperature before illumination (0, ---), and after polychromatic illumination (1-3, —). Absorption spectrum of a  $2.5 \times 10^{-5}$  M solution of 2-phenylbenzimidazole (authentic sample) in MCH at room temperature (4, —). Optical path length  $d = 1$  cm.

yield in this case does not depend on the wavelength of the exciting light. If we make the reasonable assumption that 2-phenylbenzimidazole (IIc) like the other two compounds IIa and IIb does not absorb in the region of the A-band, then we have to conclude that IIc is thermally converted to IIIc if it is formed at all. Its formation had to be a rapid reaction because in flash experiments the absorption of the A-band of Ic disappears within the lifetime (5  $\mu$ sec) of the exciting flash-light. Steady-state illumination at low temperatures yields no further information because at  $-80^\circ$  only the usual *cis*-*trans* photoequilibrium is established, all other photoreactions are completely suppressed. In Scheme IV we have included the imidazoline IIc as a

#### Scheme IV<sup>a</sup>



<sup>a</sup> Solid arrows indicate photoreactions, wavy arrows indicate dark reactions (lifetimes  $\tau$  are those at room temperature).

possible intermediate, although it is not certain whether it exists.

The striking differences in the reaction pathways of the three compounds are obviously closely related to the different stabilities of the azolines IIIa-c. Apparently the higher acidity of the -SH group facilitates the formation of the thiazoline ring system; with the

less acidic -OH group the five-membered ring becomes more unstable which is even more so in the case of the basic amino group. The very interesting finding that molecular hydrogen is formed under anaerobic conditions will be quantitatively investigated in further studies.

### Experimental Section

**Spectra.** The flash apparatus used has been described elsewhere.<sup>11</sup> Uv absorption spectra were measured at room temperature with a Zeiss RPQ 20 spectrophotometer, at low temperatures a Cary 14 spectrophotometer with a thermostated cell holder essentially as described by Fischer,<sup>12,13</sup> *et al.*, was employed.

**Compounds.** The solvents used were uv grade (Uvasol Merck). All compounds were synthesized using methods described in the literature. Benzylidene-*o*-hydroxyaniline<sup>14</sup> (mp 92°, lit. mp 95°)

(11) K. H. Grellmann, E. Heilbronner, P. Seiler, and A. Weller, *J. Amer. Chem. Soc.*, **90**, 4238 (1968).

(12) Y. Hirschberg and E. Fischer, *Rev. Sci. Instrum.*, **30**, 197 (1959).

(13) S. Malkin and E. Fischer, *J. Phys. Chem.*, **66**, 2482 (1962).

(14) G. Smets and A. Delvaux, *Bull. Soc. Chim. Belg.*, **56**, 106 (1947).

was recrystallized from ethanol, benzylidene-*o*-aminoaniline<sup>15</sup> (mp 61°, lit. mp 60–61°) was recrystallized from ligroin, and 2-phenylbenzthiazoline<sup>10</sup> (mp 82°) was recrystallized from an ethanol-water mixture and MCH.

Photoproducts in gram amounts were prepared by the illumination of 1 to 2 g of educt in 250 ml of solvent. A high-pressure 125-W Osram mercury lamp was immersed into the stirred, water cooled solution. The photoproducts were recrystallized and showed no mixture melting point depression with authentic samples.

The qualitative determination of hydrogen was carried out with a Perkin-Elmer F7 gas chromatograph using a 5-Å molecular sieve column. About 100 ml of a 0.05 M solution of educt in MCH was bubbled with oxygen-free nitrogen for 1 hr and then irradiated with a mercury resonance lamp for 12 hr. The reaction vessel was connected to the gas chromatograph and the gas phase above the reaction mixture analyzed. In blind experiments with the pure solvent negligible amounts of hydrogen were formed.

Hydrogen peroxide was quantitatively determined with TiOSO<sub>4</sub>. The illuminated solution of Schiff base in MCH was shaken with the acidic aqueous titanium sulfate solution and after separation of the two solvents into two layers the optical density of the orange TiO<sub>2</sub><sup>2+</sup> solution was determined. In blind experiments it was shown that the hydrogen peroxide is quantitatively transferred into the aqueous phase.

(15) O. Hinsberg and P. Koller, *Chem. Ber.*, **29**, 1497 (1896).

## Reaction Patterns and Kinetics of the Photoconversion of *N*-Methyldiphenylamine to *N*-Methylcarbazole<sup>1a</sup>

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Contribution from the Max-Planck-Institut für Biophysikalische Chemie, D-3400 Göttingen, Germany, and the Department of Chemistry, Brandeis University, Waltham, Massachusetts. Received September 23, 1972

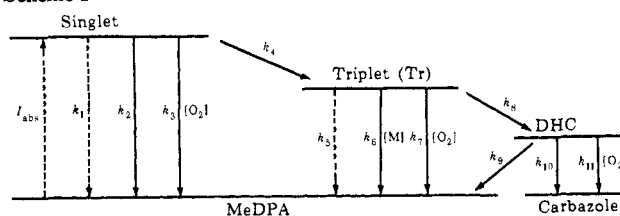
**Abstract:** The photoconversion of *N*-methyldiphenylamine (MeDPA) to *N*-methylcarbazole (C) has been studied by steady illumination measurements of carbazole quantum yields and flash photolytic measurements of transient yields and decay kinetics, in degassed and aerobic solution, from room temperature to -140°. The results establish that the reaction proceeds *via* the amine triplet (Tr), which transforms into another intermediate, absorbing at 610 nm, and assigned to *N*-methyl-4a,4b-dihydrocarbazole (DHC). This transient may either revert back to amine or react aerobically or anaerobically to form carbazole. The complex dependence of carbazole and dihydrocarbazole yield on oxygen concentration and temperature is discussed. The processes Tr → DHC and DHC + O<sub>2</sub> → C are demonstrated by flash photolysis, despite unfavorable overlapping absorptions in the latter case. Extinction coefficients of Tr and DHC are obtained, and four rate constants which are involved in the kinetics above -140° are determined directly by flash photolysis. The results are closely consistent with a diffusion-controlled rate for oxygen quenching of the amine triplet. Activation energies are: Tr → DHC,  $E_A = 5.5$  kcal mol<sup>-1</sup>; DHC → MeDPA (ring opening),  $E_A = 17.0$  kcal mol<sup>-1</sup>. The interesting anaerobic reaction DHC → carbazole, with  $E_A < 100$  cal mol<sup>-1</sup>, is discussed.

The oxidative photocyclization of diphenylamines to carbazoles is a complex reaction whose detailed steps exhibit some remarkable kinetic features. However, despite much research, there is still debate and confusion regarding the general reaction scheme. Before any of the interesting mechanistic problems can be treated, it is necessary to resolve these disagreements.

In earlier publications on the photoconversion of *N*-methyldiphenylamine (MeDPA) and triphenylamine to

the corresponding carbazoles,<sup>2</sup> the reaction pattern in Scheme I was proposed for the overall process (the

Scheme I



broken arrows ( $k_1$  and  $k_3$ ) indicate unimolecular transi-

(1) (a) A substantial fraction of this work forms part of a Ph.D. thesis by E. W. F. submitted to Stuttgart University and carried out at the Max-Planck-Institut für Biophysikalische Chemie, Göttingen. Other parts of this work were supported by a grant from the U. S. Atomic Energy Commission to Brandeis University (No. AT (30-1-2003)). (b) Max Planck-Gesellschaft Predoctoral Fellow, 1968–1971. (c) Guggenheim Fellow, 1971–1972.

(2) (a) K. H. Grellmann, G. M. Sherman, and H. Linschitz, *J. Amer. Chem. Soc.*, **85**, 1881 (1963); (b) H. Linschitz and K. H. Grellmann, *ibid.*, **86**, 303 (1964).