Tsunetsugu, H. G. Vilhuber, and E. Werstiuk, *J. Am. Chem. Soc.*, **94**, 5517 (1972). (c) A. Nickon, J. B. DiGirogio, and P. J. L. Daniels, *J. Org. Chem.*, **38**, 533 (1973). (d) The results cited by Nickon are per molecule and not per deuterium (personal communication).

(45) K. R. Kopecky, J. H. van de Sande, and C. Mumford, *Prepr., Div. Pet. Chem., Am. Chem. Soc.*, Abstr. No. 27 (Sept 1971).

(46) C. W. Jefford, M. H. Laffer, and A. F. Boschung, *J. Am. Chem. Soc.*, **94**, 8904 (1972).

(47) C. W. Jefford, A. F. Boschung, R. M. Moriarty, C. G. Rimbault, and M. H, Laffer, *Helv. Chim. Acta*, 2649 (1973).

(48) A. P. Schaap and G. R. Faler, *J. Am. Chem. Soc.*, **95**, 3381 (1973).

(49) (a) P. D. Bartlett, *Chem. Soc. Rev.*, 149 (1976); (b) C. W. Jefford and A. F. Boschung, *Tetrahedron Lett.*, 4771 (1976).

(50) W. Franke and R. Kraft, *Angew. Chem.*, **67**, 395 (1955).

(51) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. I, Wiley, New York, N.Y., 1967, p 584.

(52) 9 ft × $\frac{1}{4}$ in. aluminum column packed with 20% Carbowax 20M on Chromosorb W AW DMCS: flow, 75 mL/min; injection temperature, 200 °C; detector temperature, 250 °C.

(53) G. F. Woods, Jr., "Organic Syntheses," Collect. Vol. III, Wiley, New York, N.Y., 1975, p 470.

(54) Y. R. Naves, P. Oschner, A. F. Thomas, and D. Lamparsky, *Bull. Soc. Chim. Fr.*, 1608 (1963).

(55) For alternate preparations of **30**, see (a) C. D. Hurd and W. H. Saunders, *J. Am. Chem. Soc.*, **74**, 5324 (1952); (b) W. J. Gensler and G. L. McLeod, *J. Org. Chem.*, **28**, 3194 (1963).

(56) Each scintillation vial used was washed initially with distilled water, dried in an oven, and capped.

(57) The scintillation fluid was prepared by dissolving in 1 gal of toluene 0.76 g of *p*-bis[2-(5-phenyloxazolyl)]benzene (POPOP) and 18.9 g of 2.5-diphenyloxazole (PPO). These scintillation grade compounds were obtained from New England Nuclear, Boston, Mass.

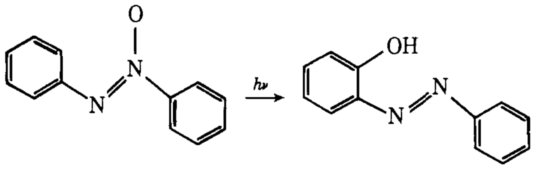
Photorearrangement of Azoxybenzene to 2-Hydroxyazobenzene. Evidence for Electrophilic Substitution by Oxygen

Nigel J. Bunce,* Jean-Pierre Schoch, and Michael C. Zerner

Contribution from the Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Guelph, Guelph, Ontario, N1G 2W1, Canada. *Received May 16, 1977*

Abstract: The excited state responsible for the azoxybenzene photorearrangement is deduced to be $^1n,\pi^*$, not $^1\pi,\pi^*$ as assumed previously. INDO calculations indicate this state to be almost classical $^1n,\pi^*$, with excellent agreement between the calculated and observed spectrum being obtained. The theoretical model predicts an electrophilic role for oxygen during the rearrangement. Experiments with substituted azoxybenzenes support this model; among isomeric compounds having different substituents on the two rings, the higher quantum yield of reaction is observed when oxygen is to migrate into the ring bearing more electron-donating substituents. The evidence is permissive only, since it has not been possible to relate these quantum yields to relative rate constants for reaction.

Photolysis of azoxybenzene and its derivatives causes photomigration of the azoxy oxygen atom to the ortho position of the more distant aromatic nucleus[1] (eq 1). In this paper we are concerned with (1) assignment of the reactive excited state and (2) correlation of the electron distribution in this excited state with the relative facility with which the photorearrangement takes place for simple substituted azoxybenzenes.



(1)

Assignment of Excited State. Tanikaga[2] noted that when azoxybenzene solutions are photolyzed together with benzophenone, the yield of the photorearrangement product drops and azobenzene is formed. He proposed that azobenzene emanates from the triplet state of azoxybenzene, and that photorearrangement is a reaction of the lowest observed singlet excited state (π,π^*). Monroe and Wamser demonstrated subsequently[3] that benzophenone acts in this reaction as a "chemical sensitizer" rather than as a source of triplet energy. Hence azobenzene is not a triplet state product at all, but the question of the state responsible for photorearrangement is unresolved.

We implicate a singlet excited state as the precursor of rearrangement on the following grounds. High-energy ketone sensitizers depress the photoefficiency owing to competing light absorption. The quantum yield for photorearrangement is unaffected by potential quenchers such as oxygen, piperylene, 1,3-cyclohexadiene, and pyrene. Heavy atom solvents, including 2-bromoethanol, methyl iodide, or xenon, do not affect the photoefficiency in ethanol.[4] Finally, in both benzene and ethanol, the quantum yield is unchanged over a wide temperature range, seeming to exclude a "hot" ground state intermediate.

What of the configuration of this excited state? The first observed absorption band of azoxybenzene in all solvents studied is associated with a π,π^* transition ($\nu_{\max} \approx 31\ 000$ cm^{-1}, $\epsilon \sim 14\ 000$). To understand the nature of the low-lying excited states of azoxybenzene, we have undertaken a series of molecular orbital calculations, using an intermediate neglect of differential overlap technique described elsewhere.[6] After the ground state self-consistent field MOs were obtained, the 35 lowest energy π,π^* configurations were interacted to obtain the lowest lying π,π^* states. Likewise, interaction of 38 σ,π^* and π,σ^* configurations afforded the low-lying n,π^* states.

Input to the program included idealized crystallographic coordinates based on the structure of Krigbaum et al.[7a] for ethyl *p*-azoxybenzoate. Notable features of this crystallographic study are the long C-N bonds (1.56 Å vs. the usual $R_{\text{C-N}}$ of 1.47 Å), the strong N-N bond of 1.155 Å (cf. $R_{\text{N}\equiv\text{N}}$ 1.10 Å and $R_{\text{N=N}}$ 1.24 Å), and the distortion from sp^2 hybridization at the N$_2$O bridge (∠NNO = 135°). Additionally, the azoxy oxygen is located almost equidistant from the nearest carbon atom of each ring (R = 2.67 Å).

Calculated and observed transition energies and assignments are given in Table I. The spectral location of the first π,π^* band is confirmed, but the lowest singlet state is n,π^* at 26 000 cm^{-1}. Even after configuration interaction, this state is still

Table I. Spectrum of Azoxybenzene

Obsd, cm^{-1} (ϵ)	Calcd Position, cm^{-1}	Calcd Oscillator strength	Comments[c]
~25 000 (?)[a]	26 476 (25 000)[d]	0	n,π^* O(n) → N-N antibond
31 200 (14 300)[b]	34 247 (31 200)[d]	0.35	π,π^* e_{1u}(B) → N-N antibond
33 330 sh (11 000)[b]	36 089 (33 100)[d]	0.13	π,π^* e_{1u}'(B) → N-N antibond
34 750 sh (8000)[b]	37 347 (34 300)[d]	0.01	n,π^* N(n) → N-N antibond
	37 816 (37 816)[d]	0.01	π,π^* $^1B_{2u}$(A)
38 760 (7100)[b]	41 174 (38 200)[d]	0.06	π,π^* e_{1u}(A) → N-N antibond
	41 992 (41 992)[d]	0.04	π,π^* $^1B_{2u}$(B)
43 103 (4 bands) (8700)[b]	44 525 (44 525)[d]	0.03	π,π^* $^1B_{1u}$(A) band spacing 1090 cm^{-1}
>48 800 (>20 000)[b]	49 151	0.00	π,π^* $^1B_{1u}$(B) plus B → A
	49 744	0.06	π,π^* delocalized
	50 818	0.12	π,π^* NO antibond → N-N antibond
	53 109	0.04	π,π^* B → A charge transfer plus $^1B_{1u}$(A)
	53 350	0.00	n,π^* O(n) → A
	54 169	0.33	π,π^* B → A charge transfer
	54 358	0.00	π,σ^* ring A
	54 510	0.00	n,π^* O(n) → B
	55 419	0.00	π,σ^* ring A
	55 445	0.95	π,π^* ^1E_u(B)
	55 952	0.00	n,π^* O(n) → A
	56 009	0.00	n,π^* O(n) → B
	56 085	0.58	π,π^* ^1E_u(A) and ^1E_u(B)

[a] Vapor. [b] Taken in mixed hexanes. [c] A is the benzene ring nearer the NO function. The group theoretical labels refer to localized D_{6h} benzenelike transitions and molecular orbitals. [d] Assuming $R_{(\mathrm{N-N})} = 1.23$ Å, first-order perturbation theory suggests the transition energies in parentheses. These shifts are mostly the result of a depressed eigenvalue for the N-N antibond.

almost pure n,π^* with 0.7 electron removed from an n orbital on oxygen and placed in the lowest vacant MO, which is the N-N antibond.

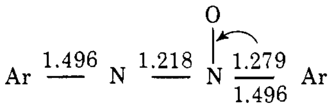
This assignment is confirmed tentatively by experiment. At 70 °C, the vapor phase spectrum of azoxybenzene shows a small bump near 25 000 cm^{-1} on the tail of the π,π^* band. It is possible that this is the n,π^* band.

Characteristics of this lowest ^{1}n,π^* state are a greatly reduced N-N bond order, making rotation easier, and a much lower N-O bond order, consistent with bond breaking. Both these features will be argued to be important photochemically.

A lowest n,π^* singlet state accounts for the previously inexplicable lack of fluorescence from azoxybenzene.[8] Moreover, its energy is low enough that it may intersect bound vibrational levels of the ground state. Hence internal conversion to the ground state is likely to be rapid. A short-lived ^{1}n,π^* reactive state is compatible with the experimental inability of bimolecular quenchers to intercept it before reaction or deactivation.

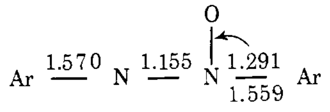
The calculations locate the first π,π^* band near 34 000 cm^{-1}, and suggest that it involves charge transfer from ring B (distant from the N-O function) into the N-N antibond. The next two resolved bands are calculated to be complex, each comprising ring to N-N antibond charge transfer components and localized excitations resembling the B_{1u} transition of benzene.

These first three π,π^* states are calculated ~3000 cm^{-1} higher than the observed values. This is poorer agreement with experiment than we have obtained previously.[6] Perturbation theory indicates that if the crystallographic N-N bond distance (for ethyl *p*-azoxybenzoate) were too small the effect would be to raise the calculated energy of the N-N antibond. As noted already, an N-N bond length of 1.155 Å represents a bond substantially stronger than a N═N double bond, while the N-O bond length of 1.29 Å ($R_{\mathrm{N\text{-}O}} \sim 1.48$ Å, $R_{\mathrm{N=O}} \sim 1.24$ Å) argues also for an N-N bond no stronger than double. If the N-N bond distance were greater than 1.155 Å, the energies of the first three π,π^* bands would be correspondingly reduced. Taking the "typical" N═N distance of 1.24 Å, first-order perturbation theory gives the results in parentheses in Table I. These are in excellent agreement with observation. Experimental justification for this approach comes from a second crystallographic study,[7b] showing the N-N distance in *p*-azoxyanisole to be 1.22 Å.



$$\mathrm{Ar} \overset{1.496}{—} \mathrm{N} \overset{1.218}{—} \overset{\mathrm{O}}{\mathrm{N}} \underset{1.496}{\overset{1.279}{—}} \mathrm{Ar}$$

p-azoxyanisole

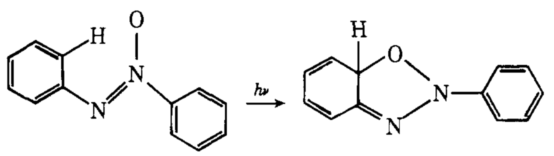


$$\mathrm{Ar} \overset{1.570}{—} \mathrm{N} \overset{1.155}{—} \overset{\mathrm{O}}{\mathrm{N}} \underset{1.559}{\overset{1.291}{—}} \mathrm{Ar}$$

ethyl *p*-azoxybenzoate

The remaining π,π^* band observable below 50 000 cm^{-1} is calculated to be almost pure benzenelike, and shows the usual fine structure of the benzene $^1B_{1u}$ band. It is calculated in excellent agreement with experiment, since the critical N-N antibond, and hence the N-N distance, are not involved.

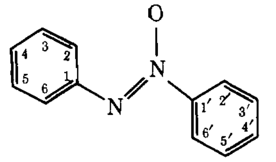
Substituent Effects. The assignment of a reactive n,π^* state suggests that the oxygen atom would play an electrophilic role in the rearrangement. The generally accepted mechanism of rearrangement involves a reaction such as 2 where the oxygen becomes bonded to the ortho carbon, i.e., an aromatic substitution (cf. ref 8 and 9). Originally, Badger and Buttery[9] conceived of this as nucleophilic attack of oxygen at carbon. However, the phenylazo is able to delocalize both positive and negative charge;[10] the observation[11] that the photorearrangement may be acid catalyzed supports an electrophilic oxygen, although participation of an n,π^* excited state is unlikely under these conditions.



(2)

In reactions involving cyclic transition states or intermediates, it is often not possible to ascribe electrophilic or nucleo-

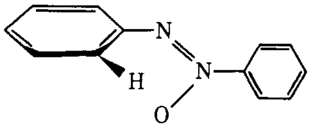
Table II. Identification and Photoreactivity of Substituted Azoxybenzenes



	Substituents	Mp, °C (lit.)[a]	λ_{max} (EtOH)	MS fragmentation[g] $Ar^+/C_6H_5^+$	ϕ_{rel}
1a	None	35-36 (36)	323		1.00[b]
2a	4-CH_3	46-47 (48)[e]	332	0.55 ± 0.02	0.75 ± 0.02
3a	4′-CH_3	63-64 (65)[e]	326	4.0 ± 0.1	0.37 ± 0.01
4a	4,4′-$(CH_3)_2$	69-70 (71)	332		0.47 ± 0.02
5a	4-CF_3	98.5-99.5	316	0.13 ± 0.01	0.27 ± 0.01
6a	4′-CF_3	63-65	327	0.62 ± 0.01	1.70 ± 0.05[c]
7a	4,4′-$(CF_3)_2$	105-106[f]	317		0.39 ± 0.02
8a	4-CH_3-4′-CF_3[d]	114-116	(328)		>1.25 ± 0.02
9a	3,5-$(CH_3)_2$[d]	Oil	>323	0.23 ± 0.01	>0.85 ± 0.01
10a	3′,5′-$(CH_3)_2$	56-57	321	1.68 ± 0.04	0.80 ± 0.01
11a	3,3′,5,5′-$(CH_3)_4$	111.5-112.5 (111)	331		1.16 ± 0.06
12a	3,5-$(CF_3)_2$	43-44	312	0.07 ± 0.01	<0.07 ± 0.01
13a	3′,5′-$(CF_3)_2$	72.5-73.5	331	0.67 ± 0.01	2.50 ± 0.12
14	3,3′,5,5′-$(CF_3)_4$	63-64	315		~0.00

[a] Unreferenced literature melting points are from Beilstein's "Handbuch". [b] Assumed: $\phi_r = 0.018 \pm 0.002$ in 0.5 M KOH/EtOH at 30 °C. [c] Extrapolation to zero conversion; correction for light absorption by **5a** as impurity suggests $\phi_{rel} \sim 2.2$. [d] Never obtained pure. Repeated fractional crystallization effected virtually no separation of **8a** from its isomer. Since **8b** was isolated pure, this suggests that ϕ_{rel} for **8a** should be ~2.5, since **8a** absorbed little more than half the light. Likewise, ϕ_{rel} for **9a** is probably substantially more than 0.85. [e] C-S. Hahn and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 949 (1962). [f] R. A. Abramovitch, S. R. Challand, and E. F. V. Scriven, *J. Org. Chem.*, **37**, 2705 (1972), report having prepared this compound in order to reduce it to the azo compound, but give no physical constants. [g] In each case the ratio of the two possible aryl fragments is given taking the height of m^+/e 77 as unity.

philic character to one of the cyclizing atoms. In this particular case, we have argued elsewhere[12] that the atoms cannot all be coplanar during cyclization, and that a transition state like that below may be involved. It should therefore be possible to discover whether the azoxy oxygen behaves as an electrophile or as a nucleophile through substituent effects.



Previously, Tanikaga showed that unsubstituted azoxybenzene photorearranged faster than any substituted analogue he studied.[2] Strongly electron-donating (e.g., $N(CH_3)_2$) or withdrawing (e.g., NO_2) groups at the 4,4′ positions inhibited the reaction completely. However, the absorption spectra of such compounds are markedly different from that of the parent molecule. This implies considerable alteration of the properties of the excited state. In planning our experiments, we wished to minimize the problem by using only inductive substituents, and CH_3 and CF_3 groups were chosen for study.

The compounds examined are identified in Table II as **1-14.** They were prepared by conventional means: the symmetrically CH_3 substituted ones by reduction of nitro compounds, the symmetrically CF_3 substituted ones by oxidation of anilines. Unsymmetrical compounds were prepared by coupling appropriately substituted nitroso compounds and anilines. The resulting azo compounds were then oxidized with H_2O_2/acetic acid, to give mixtures of azoxy compounds. These mixtures are notoriously difficult to separate,[13] and repeated fractional crystallization was required.

The purities of the compounds were determined by NMR. Fluorine-containing compounds were analyzed directly using ^{19}F NMR; those lacking fluorine were examined in the presence of the lanthanide shift reagent $Eu(fod)_3$.[13] In some cases, the less reactive of a pair of isomers could be obtained in higher purity by photolyzing to partial conversion. This method was used successfully for **5a, 10a,** and **12a,** which were thus obtained essentially free of their isomers.

Preparative scale irradiations were carried out to give reference samples of the *o*-hydroxyazo compounds. Compound **14** was very resistant to photolysis; it did not photorearrange, but was slowly reduced to the azo compound.

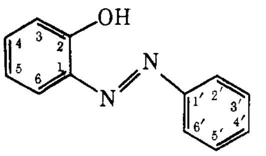
A major task was deciding which structure to assign to which isomer of an unsymmetrical azoxy compound. Our criteria follow.

(1) The products of irradiation, being azo compounds, are relatively easy to identify. Mass spectrometry gives strong peaks for the molecular ion, the two possible diazonium ion cleavage fragments, and the two aryl cations. Thus the location of the hydroxy substituent may be deduced (Table III). Further, the absorption spectrum of the product is shifted with respect to the parent compound, particularly if the substituent is in the phenolic ring. Thus the absorptions of **5b** and perhaps **12b** are blue shifted by comparison with **1b,** while **8b** and **9b** are red shifted. Charge transfer through the system as a whole contributes to the large red shifts of **6b, 8b,** and **13b.**

We now apply the criterion of Badger and Buttery[9] that the azoxy oxygen migrates to the distant aromatic ring. This cannot be used in isolation, because we have previously reported a case where two isomeric azoxy compounds gave the same photorearrangement product.[14] In that case, prior photoisomerization of the azoxy compounds was found to occur. Consequently, in this study, the preparative scale photolyses were carried out to less than complete conversion and the azoxy compound was recovered. In no case was the azoxy compound found to have isomerized.

(2) If we accept the structural assignments using the above arguments, the absorption spectra of the azoxy compounds present a self-consistent picture. Substitution of the aryl ring closer to the N-O function causes a much smaller shift in λ_{max} than does substitution in the aniline-like ring. Methyl substitution of the "aniline" ring causes a red shift, while CF_3 substitution consistently yields a blue shift.

Table III. Physical Properties of 2-Hydroxyazobenzenes



	Substituents	Mp, °C	In 0.5 M KOH/EtOH λ_{max}	In 0.5 M KOH/EtOH ϵ	Mass spectrum (major peaks)
1b	None	81-82	458	7 600	198 (M^+), 121, 105, 93, 77
2b	4-CH_3	121-122	460	11 800	212 (M^+), 135, 107, 105, 77
3b	4′-CH_3	80-81	460	9 700	212 (M^+), 121, 119, 93, 91
4b	4,4′-$(CH_3)_2$	151-152	460	11 300	226 (M^+), 135, 119, 107, 91
5b	4-CF_3	109-110	447	6 500	266 (M^+), 189, 161, 77
6b	4′-CF_3	108-109	480	11 000	266 (M^+), 145, 121, 93
7b	4,4′-$(CF_3)_2$	121-122	465	7 600	334 (M^+), 189, 161, 145
8b	4-CH_3-4′-CF_3	110-111	480	7 300	280 (M^+), 145, 135, 107, 91
9b	3,5-$(CH_3)_2$	*a*	>466		
10b	3′,5′-$(CH_3)_2$	72-74	460	7 800	226 (M^+), 121,[c] 105,[c] 93
11b	3,3′,5,5′-$(CH_3)_4$	161-162	484	10 400	254 (M^+), 149, 121, 105
12b	3,5-$(CF_3)_2$	*a*	<475		
13b	3′,5′-$(CF_3)_2$	128-129	490	12 300	334 (M^+), 213, 163, 121, 93

[a] Never obtained pure. λ_{max} values apply to a mixture containing some of the other isomer. [b] Since **8b** was obtained as a pure compound, we conclude that the isomer of **8a** is substantially less reactive than **8a** itself. [c] Exact masses: *m/e* 121; found 121.044 (calcd for $C_6H_5N_2O$, 121.040; calcd for C_8H_9O, 121.065; *m/e* 105, found 105.077 (calcd for $C_6H_5N_2$, 105.045; calcd for C_8H_9, 105.071).

(3) In unsymmetrical azoxybenzenes, mass spectral fragmentation of the molecule has previously been found to occur preferentially on the side closer to the N-O bond.[15] Our observations are consistent with that trend (Table II).

For azoxy compounds such as **9a, 11a, 12a,** and **14,** one might legitimately question whether steric effects might slow down migration of oxygen into the neighboring ring position. Previous work[2,12] indicates that this is not a problem in practice, a result we have now confirmed for a neighboring trifluoromethyl group,

Relative Rate Kinetics. The solvent selected was 0.5 M KOH in ethanol. The advantages of this medium are (1) the hydroxyazo compound product may conveniently be monitored as its anion ($\lambda_{max} \sim 460$ nm). (2) Formation of product is linear with time to greater conversions because the reactant and product spectra overlap less in base than in neutral solution. This causes less retardation by an "inner filter" effect. (3) Side products, which might arise by the diazonium ion fragmentation reaction,[12] are essentially completely suppressed in this medium. Control experiments showed that neither the product spread nor the quantum efficiency of the reaction of azoxybenzene was affected when KOH was added to ethanol.

The relative and absolute quantum yields are reported in Table II. These relative rates of reaction cannot be identified with relative rate constants because the lifetimes of the excited states of the azoxy compounds are unknown. Moreover, since neither luminescence nor quenching is observed, these lifetimes are currently unobtainable with the facilities available to us. It is not likely that all the compounds studied have comparable lifetimes. Deactivation of S_1 may involve either internal conversion or intersystem crossing to the triplet manifold. Internal conversion requires the electronic energy to be degraded to vibration; the largest vibrational quanta (C-H in this case) are believed to affect the rate most strongly.[16] We might consider whether increasing the number of C-H bonds through methyl substitution would shorten the lifetime substantially. However, the work of Froehlich and Morrison[17] on methylated benzenes indicates essentially no change in singlet lifetime when fewer than five methyl groups are present. This is consistent with our previous study[8] where were showed that perdeuteration of azoxybenzene affected the photorearrangement efficiency only slightly. As to the effect of substitution on the intersystem crossing rate, we have no information; however, cases are known, e.g., the 9- and 10-substituted anthracenes,[18] where substantial effects are observed.

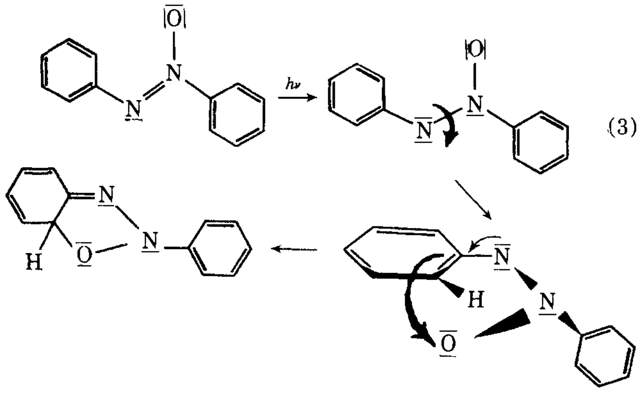
For this reason, we can interpret our data only qualitatively. Considering isomeric pairs of azoxy compounds, we note that in every case, the picture emerges of greater photoreactivity when the oxygen is to substitute into the more electron-rich ring. For example, **2a,** which has the methyl group in the ring under attack, photolyzes more efficiently than **3a.**[19] Based on a single pair of compounds, this would be a very suspect conclusion, for it is implicitly assumed that **2a** and **3a** have comparable lifetimes. However, the pattern is repeated for all the pairs of compounds studied; it is more pronounced for the trifluoromethylated compounds, for the inductive effect of this group considerably surpasses that of the methyl group in magnitude.[20] Thus the substituent effects are consistent with oxygenation being an electrophilic attack upon the aromatic nucleus.

Conclusions

Our calculations and experiments permit us to draw two related conclusions about the mechanism of the azoxybenzene photorearrangement. First, a low-lying $^1n,\pi^*$ excited state is almost certainly involved; second, attack by oxygen at the distant ortho carbon represents electrophilic attack at the aromatic ring. This second conclusion, supported by the calculated electron density of the lowest lying excited singlet state, receives only qualified experimental support because we cannot identify the relative quantum yields of reaction with rate constants for reaction 2. This is a particular problem when the observed quantum yield is so low; almost 98% of all photons absorbed are not accounted for. Nevertheless, we believe the conclusion to be justified on the grounds that the results of the calculations and the experiments present a consistent picture. The reactivity pattern of the isomeric unsymmetrical azoxybenzenes is in every case what could be expected from a consideration of the electronic distribution in a lowest $^1n,\pi^*$ state. Taken together, these reactivity patterns provide strong circumstantial evidence for this interpretation.

Finally, we attempt to consider the events that most probably take place following excitation. According to the crystallographic studies, the oxygen atom in the ground state of azoxybenzene is almost equidistant from the ortho carbon atoms of each ring. If we assume that the structure of the molecule is similar in solution, it is clear that there is attraction between the oxygen and the nearest ortho hydrogens in the ground state. This is because the distances (2.04 and 2.26 Å) are well within the van der Waals radii (2.6 Å). Population of the $^1n,\pi^*$ state causes severe reduction in the N-N bond order and removal of almost a full electron from oxygen. The oxygen-ortho hydrogen interaction must now be repulsive, and rotation about the N-N bond becomes facile. Since the nitrogen atoms are now pyramidal, the oxygen is situated conveniently for attack at the distant ortho carbon with formation of a five-membered ring. This is clearly shown in molecular models.

The substituent effects support this hypothesis, with electron-attracting groups in the distant ring disfavoring C-O bond formation, and electron-releasing groups facilitating it. Pictorially, we might represent the first states of the reaction by the crude valence bond formalism of eq 3.



(3)

Experimental Section

Methods for preparative photolysis and for the separation and identification of photoproducts have been described in detail previously.[8] In this work ethanol means the 95% constant boiling azeotrope. Melting points are uncorrected. Analytical data on new compounds are in Table IV.[25]

Preparation of Azoxy Compounds. Most physical constants are in Table II. Azoxybenzene was made as described previously.[8] Reduction of the nitro compound with Tl/ethanol[21] gave after purification 4,4′-dimethylazoxybenzene (55%) and 3,3′,5,5′-tetramethylazoxybenzene (34%). Purified samples of 4,4′-bis(trifluoromethyl)azoxybenzene (35%) and 3,3′5,5′-tetrakis(trifluoromethyl)azoxybenzene (43%) were obtained by oxidizing the aniline with H_2O_2/CH_3CO_2H at 60 °C. Unsymmetrical compounds were made by oxidizing azo compounds, prepared from the aniline and the nitroso compound. The isomeric azoxy compounds were separated by repeated fractional crystallization from methanol, but even so, 100% purity was not attained (Table V).[25]

Hydroxyazo Compounds. Authentic samples were prepared by photorearrangement of azoxy compounds. Physical constants are recorded in Table III. Compound **12a** rearranged very inefficiently and gave a mixture, which included the azo compound, and **14** afforded exclusively the azo compound **15**.

Visible spectra of these products were recorded on a Beckman Model 24 spectrophotometer in 0.5 M KOH in ethanol. At least two different stock solutions of each compound were prepared. Each stock solution was diluted to give three working solutions of different concentration. Beer's law was verified for each, and the extinction coefficients of Table III are thus the average of at least six determinations.

Mechanistic Studies. Rotating "merry-go-rounds" were used to ensure equal illumination of samples. Product formation was monitored by spectrophotometry at the wavelengths indicated; usually this was ~410 nm in neutral solution and ~460 nm in basic solution for **1a**. A Rayonet photoreactor equipped with eight RUL 3000 lamps having maximal output near 300 nm was operated at ambient temperature (≈40 °C). Temperature control was provided in a system in which a merry-go-round and a Hanovia 500-W medium-pressure mercury arc housed in a water-cooled Pyrex immersion well were contained in a constant temperature bath. Except as indicated, this could be held constant to ±0.1 °C. All figures reported below represent the average of two independent samples having good agreement between them. Since the geometry of the setup changed from experiment to experiment, comparison from one set of data to another is not possible.

Quantum Yield of Photorearrangement. This was determined relative to the ferrioxalate actinometer.[22] Five duplicate determinations in 0.5 M KOH-alcohol gave $\phi_r = 0.018 \pm 0.002$ (lit.[11] 0.008 at 320 nm). The value 0.22 ± 0.02 given in our earlier paper[8] should have been 0.022 ± 0.002.

Photolysis of 3,3′-Bis(trifluoromethyl)azoxybenzene. The azoxy compound (0.7 g, mp 43–44 °C (lit.[24] 46 °C), prepared by oxidation of *m*-trifluoromethylaniline), was irradiated in 0.1 M KOH-ethanol (500 mL) for 88 h. The product was separated from unreacted azoxy compound on alumina, but the two possible products could not be separated. ^{19}F NMR of the crude product showed three resonances at 2638, 2685, and 2732 Hz from internal $CFCl_3$, ratio 2:1:1, indicating that both hydroxyazo compounds has been formed in equal amount.

Relative Quantum Yields. These determinations were made at 30 °C. Ethanol-0.5 M KOH was the solvent. Concentrations of azoxy compounds were sufficient to give absorbance >20 to minimize light absorption by products. Duplicate samples of four different azoxy compounds, always including **1a**, were irradiated simultaneously. Illumination was stopped after different times (usually 2–20 min) and the solutions analyzed spectrophotometrically at the various λ_{max} values. Relative reactivities were calculated for each time and the average of four to ten values obtained. Always included were runs where the concentrations of all but **1a** were halved; this had no effect on the results. The data of Table I are the average of different experiments of the type described in which different combinations of azoxy compounds were photolyzed. New stock solutions were prepared for these new combinations. Good agreement between runs was always obtained. In the case of **6a**, the reaction was strongly retarded by products; the initial relative quantum yield was obtained by extrapolation of 15 runs to zero conversion.

Acknowledgment. We thank the National Research Council of Canada for financial support.

Supplementary Material Available: Experimental data on the effects of oxygen, heavy atoms, sensitizers, quenchers, base, and temperature on photorearrangement; analytical data on new compounds (Table IV); approximate purities of azoxy compounds (Table V) (6 pages). Ordering information is given on any current masthead page.

References and Notes

(1) G. G. Spence, E. C. Taylor, and O. Buchardt, *Chem. Rev.*, **70**, 231 (1970); E. Buncel in "Mechanisms of Molecular Migrations," Vol. I, B. S. Thyagarajan, Ed., Interscience, New York, N.Y., 1969, pp 104–110.

(2) R. Tanikaga, *Bull. Chem. Soc. Jpn.*, **41**, 1664, 2151 (1968).

(3) B. M. Monroe and C. C. Wamser, *Mol. Photochem.*, **2**, 213 (1970).

(4) Addition of large quantities of haloalkanes to ethanol indeed depresses the rate,[5] but this seems to be a solvent effect.

(5) N. J. Bunce, *Bull. Chem. Soc. Jpn.*, **47**, 725 (1974).

(6) J. E. Ridley and M, C. Zerner, *Theor. Chim. Acta*, **32**, 111 (1973); *J. Mol. Spectrosc.*, **50**, 457 (1974).

(7) (a) W. R. Krigbaum and P. G.Barber, *Acta Crystallogr., Sect. B*, **27**, 1884 (1971); (b) W. R. Krigbaum, Y. Chatani, and P. G. Barber, *ibid.*, **26**, 97 (1970).

(8) D. J. W. Goon, N. G. Murray, J-P. Schoch, and N. J. Bunce, *Can. J. Chem.*, **51**, 3827 (1973).

(9) G. M. Badger and R. G. Buttery, *J. Chem. Soc.*, 2243 (1954).

(10) J. Miller, "Aromatic Nucleophilic Substitution", Elsevier, Amsterdam, 1968, pp 77, 127; C. D. Houghton and W. A. Waters, *J. Chem. Soc.*, 1018 (1950); J. Burns, J. McCombie, and H. A. Scarborough, *ibid.*, 2928 (1928).

(11) R. H. Squire and H. H. Jaffé, *J. Am. Chem. Soc.*, **95**, 8188 (1973).

(12) N. J. Bunce, *Can. J. Chem.*, **55**, 383 (1977).

(13) M. A. Berwick and R. E. Rondeau, *J. Org. Chem.*, **37**, 2409 (1972).

(14) N. J. Bunce, *Can. J. Chem.*, **53**, 3477 (1975).

(15) J. H. Bowie, R. G. Cooks, and G. E. Lewis, *Aust. J. Chem.*, **20**, 1601 (1967).

(16) G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, **37**, 1962 (1962); **38**, 1187 (1963).

(17) P. M. Froehlich and H. A. Morrison, *J. Phys. Chem.*, **76**, 3566 (1972).

(18) R. S. Becker, "Theory and Interpretation of Fluorescence and Phosphorescence", Wiley, New York, N.Y., 1969, Chapter 11.

(19) However both **2a** and **3a** photolyze less efficiently than **1a**. We interpret this to mean that lifetime effects are important.

(20) T. H. Lowry and K. S. Richardson, "Mechanism and Theory in Organic

Chemistry", Harper and Row, New York, N.Y., 1976, p 62.

(21) A. McKillop, R. A. Raphael, and E. C. Taylor, *J. Org. Chem.*, **35**, 1670 (1970).

(22) J. G. Calvert and J. N. Pitts, "Photochemistry", Wiley, New York, N.Y., 1966, p 783.

(23) S. Hashimoto and K. Kano, *Bull. Chem. Soc. Jpn.*, **45**, 852 (1972).

(24) Y. Kobayaski, I. Kumadaki, Y. Hanzawa, and M. Mimura, *Chem. Pharm. Bull.*, **23**, 636 (1975).

(25) This material will appear in the microfilm edition; see paragraph at the end of the paper regarding supplementary material.

trans-Stilbene–Amine Exciplexes. Photochemical Addition of Secondary and Tertiary Amines to Stilbene

Frederick D. Lewis*[1] and Tong-Ing Ho

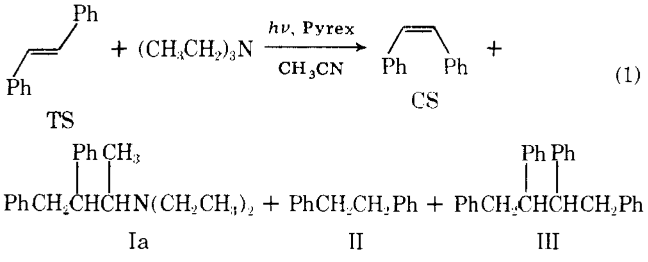
Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received April 22, 1977*

Abstract: The fluorescence of *trans*-stilbene is quenched by several secondary and tertiary amines. Quenching by tertiary amines in nonpolar solvents is accompanied by the appearance of exciplex fluorescence. The temperature dependence of fluorescence quenching by secondary and tertiary amines in polar and nonpolar solvents is indicative of reversible exciplex formation in all cases. Addition of the α C–H bond of tertiary amines to singlet stilbene occurs only in polar aprotic solvents. Electron transfer from the tertiary amine to stilbene apparently must precede proton transfer. The addition of the N–H bond of secondary amines to stilbene occurs in all aprotic solvents. The behavior of exciplexes formed from *trans*-stilbene with secondary and tertiary amines and conjugated dienes is compared.

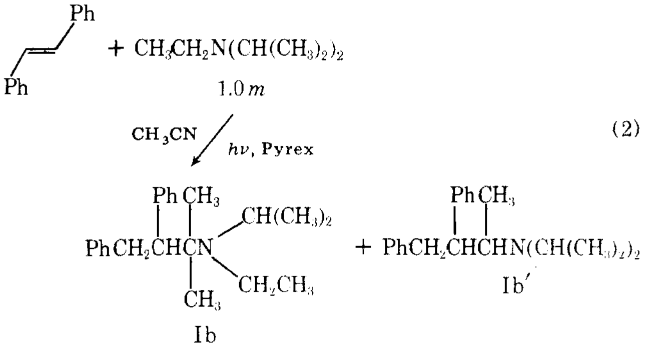
Stilbene and other diarylethylenes undergo a number of photochemical addition reactions with electron-rich[2,3] and electron-poor[4] alkenes, dienes,[5,6] and amines.[7] We have recently characterized the exciplex intermediates in the photochemical $[{}_\pi 2_s + {}_\pi 2_s]$ cycloaddition reactions of *trans*-stilbene and diphenylvinylene carbonate with conjugated dienes.[6] Frontier orbital interactions in these π-donor–π-acceptor exciplexes appear to determine product stereochemistry and regiochemistry. Recent investigations of the reactions of singlet *trans*-stilbene with amines have established that secondary amines add to stilbene in nonpolar solvents, whereas no reaction occurs with primary or tertiary amines.[7] Exciplex fluorescence has been observed from *trans*-stilbene–*N*-methylpyrrole and exciplex intermediates postulated for the addition of secondary amines.[7b] We were interested in comparing the behavior of n-donor–π-acceptor type exciplexes with our results for π–π type exciplexes and thus have investigated the interactions of singlet *trans*-stilbene with several secondary and tertiary alkyl amines.

Results

Product Studies. Irradiation of an acetonitrile solution of *trans*-stilbene (0.01 *m*) and triethylamine (1.0 *m*) results in the formation of diastereomeric *N,N*-diethyl-1-methyl-2,3-diphenylpropylamine (Ia), 1,2-diphenylethane (II), and 1,2,3,4-tetraphenylbutane (III) along with isomerized stilbene (eq 1). The diastereomeric amine adducts were not separable by vapor phase or column chromatography; however, the ^{13}C NMR spectrum of the mixture showed two signals of approximately equal intensity for all saturated carbons, indicating the formation of a mixture of diastereomers. The mass spectrum of Ia and other stilbene–amine adducts are remarkably simple and of considerable value in confirming structure assignments (see Experimental Section). Quantum yields for product formation at several amine concentrations are given in Table I. Formation of addition (Ia) and reduction (II, III) products was not detected when photolyses were carried out in hexane, diethyl ether, or ethyl acetate solvents. Quantum yields for formation of Ia in mixed ether–acetonitrile solvent increase with acetonitrile content (Table II). The failure of Kawanisi and Matsunaga[7a] to observe products from irradiation of stilbene in neat triethylamine (ϵ = 2.4 D) is consistent with these observations.



Irradiation of *trans*-stilbene and diisopropylethylamine in acetonitrile solution similarly results in addition of an amine α C–H bond to stilbene. The complicated ^{13}C NMR spectrum of the amine addition product indicated the formation of both possible adducts, one as a pair of diastereomers (eq 2). Quantum yields for formation of amine adduct (Ib and Ib′), diphenylethane, and tetraphenylbutane are given in eq 2.



$$\mathrm{Ib} + \mathrm{Ib}' \ (\Phi = 0.088) + \mathrm{II} \ (\Phi = 0.15) + \mathrm{III} \ (\Phi = 0.030)$$

Kawanisi and Matsunaga[7a] have reported the formation of *N,N*-diethyl-1,2-diphenylethylamine (Ic) and 1,2-diphenylethane (II) from the photolysis of stilbene in neat diethylamine. These products, alone with tetraphenylbutane (III), were isolated from photolyzed hexane solutions of 0.01 *m trans*-stilbene and 1.0 *m* diethylamine (eq 3). Quantum yields for formation of both addition and reduction products decrease