

Concentration Effects in Photochemical *cis-trans* Isomerization.A Study of Difurylethylene and Dithienylethylene^{1,2a}A. A. ZIMMERMAN,^{2b} C. M. ORLANDO, JR., M. H. GIANNI,

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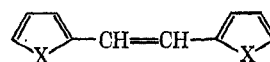
Received April 11, 1968

A study has been made of the effect of total concentration on the unsensitized photochemical *cis-trans* isomerization of 1,2-di(2-furyl)ethylene and 1,2-di(thienyl)ethylene in benzene solution. As expected, thermal equilibration produces only the *trans* isomer with both compounds. At low concentration ($<10^{-2} M$), the *cis* isomer predominates in the photostationary state. The *trans/cis* isomer ratio increases with increasing concentration. These results, and those of an earlier study with a substituted stilbene, are consistent with the collisional quenching of the first excited singlet state of the *trans* isomer and of a twisted triplet configuration by ground-state *trans*-ethylene molecules. Owing to experimental scatter, it could not be established whether the ground-state *cis* isomer also participates in the quenching processes. The lower limits of the lifetimes of the twisted triplet states are inferred to be of the same order of magnitude as those of the first excited singlet states of the *trans* isomers ($\sim 10^{-9}$ sec).

The direct and sensitized photoisomerizations of olefins have been extensively studied in recent years. That the sensitized isomerization involves triplet states of the olefins is strongly supported by all the available experimental evidence.³ The direct photoisomerization is still the subject of controversy, and both triplet^{3,4} and singlet⁵ mechanisms have been proposed. In the case of the stilbenes, substantial evidence in favor of the participation of the triplet state in the unsensitized isomerization has now accumulated.⁶

These mechanistic considerations are based on results obtained in dilute solution and apply strictly only when interactions between olefin molecules are absent. The picture is complicated by several reports of a concentration effect in direct photoisomerization. Thus the photostationary *cis/trans* isomer ratio for the irradiation of liquid *cis*-stilbene is different from that for a dilute ($10^{-5} M$) solution in *n*-hexane.^{7,8} The effect has been studied in more detail with two substituted stilbenes.^{9,10} In each case it was found that a high olefin concentration enhances the fraction of *trans* isomer in the photostationary state. Although no comprehensive interpretation of these findings has been offered, it has been suggested that a short-lived intermediate is generated which is capable of inducing *cis* \rightarrow *trans* isomerization.¹⁰ In this paper we report the concentration-dependent photoisomerization behavior

of two heterocycle-substituted olefins, 1,2-di(2-furyl)ethylene (I, X = O) and 1,2-di(2-thienyl)ethylene (I, X = S). The mechanistic implications of the results of this study and of the earlier reports on the concentration effect are examined.



I

Experimental Section

General.—The melting points reported here are uncorrected. The spectral measurements were made with a Perkin-Elmer Model 137B Infracord spectrometer, a Beckman DK-1 spectrophotometer, and a Varian A-60 nmr spectrometer.

1,2-Di(2-furyl)ethylene. **A. *trans* Isomer.**—Butyllithium (2.17 g, 0.034 mol) in heptane (27.4 wt % solution) was added, with stirring under an atmosphere of nitrogen, to triphenylfurfurylphosphonium chloride¹¹ (13.0 g, 0.034 mol) in 100 ml of anhydrous ether. Furfural (3.3 g, 0.034 mol) in 20 ml of ether was added slowly, and the mixture was heated for 2 hr at 80° in a pressure bottle. The liquid and solid phases were separated and the latter was extracted with several portions of ether. Evaporation of the combined liquids and vacuum sublimation gave 2.4 g (44%) of colorless crystalline material consisting of *trans*- and *cis*-1,2-di(2-furyl)ethylene in the ratio 7:3. Crystallization from hexane afforded the *trans* isomer as plates: mp 100–101° (lit.¹² mp 100°); $\lambda_{\text{max}}^{\text{Nujol}}$ 13.7 μ (m) (*trans* -CH=CH-); ultraviolet maxima (cyclohexane) at 339 m μ (log ϵ 4.57), 321 (4.62), and 307 sh (4.46); nmr peaks (CCl₄) at τ 3.69, 3.75, and 2.72 (ring H), and 3.24 (*trans* -CH=CH-).¹³

Anal. Calcd for C₁₀H₈O₂: C, 75.00; H, 5.00. Found: C, 75.18; H, 5.41.

B. *cis* Isomer.—The hexane filtrate from the above crystallization furnished a solid which was fractionally sublimed (0.05 mm, 25°) to yield a 90% pure sample of the *cis* isomer: mp 38.5–42.5°; $\lambda_{\text{max}}^{\text{Nujol}}$ 13.7 μ (s) (*cis* -CH=CH-);¹⁴ ultraviolet maxima (cyclohexane) at 339 m μ (log ϵ 4.37), 322 (4.45), and 307 sh (4.29); nmr peaks (CCl₄) at τ 3.63, 3.24, and 2.63 (ring H), and 3.88 (*cis* -CH=CH-).

Anal. Calcd for C₁₀H₈O₂: C, 75.00; H, 5.00. Found: C, 74.64; H, 4.98.

1,2-Di(2-thienyl)ethylene. **A. *trans* Isomer.**—A mixture of isomers was prepared by the method of Bohlmann and Hebst,¹⁵

(11) Obtained in 52% yield from furfurylchloride and triphenylphosphine in refluxing xylene.

(12) P. F. Bruins, *J. Amer. Chem. Soc.*, 51, 1270 (1929).

(13) Cf. M. H. Gianni, E. L. Strogyn, and C. M. Orlando, Jr., *J. Phys. Chem.*, 67, 1385 (1963).

(14) This absorption, which is present in the spectrum of the *trans* isomer as well, can in part be attributed to the *cis* protons of the furan ring.

(15) F. Bohlmann and P. Hebst, *Chem. Ber.*, 95, 2945 (1962).

(1) This research was supported, in part, by the Air Force Cambridge Research Laboratories, Office of Aerospace Research, under Contracts No. AF19(628)-3836 and F19628-67-C-0118.

(2) (a) A preliminary report on part of this study was presented at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964; see also *Chem. Eng. News*, 42, 43 (April 20, 1964). (b) To whom all correspondence should be directed at Esso Research and Engineering Co., Linden, N. J.

(3) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowam, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, 86, 3197 (1964). This and the following three references cite most of the pertinent literature.

(4) S. Malkin and E. Fischer, *J. Phys. Chem.*, 68, 1153 (1964).

(5) (a) J. Saltiel, E. D. Megarity, and K. G. Kneipp, *J. Amer. Chem. Soc.*, 88, 2336 (1966); (b) J. Saltiel, *ibid.*, 89, 1037 (1967).

(6) (a) K. A. Muszkat, D. Gegiou, and E. Fischer, *ibid.*, 89, 4814 (1967); (b) D. Gegiou, K. A. Muszkat, and E. Fischer, *ibid.*, 90, 12 (1968); (c) *ibid.*, 90, 3907 (1968).

(7) H. Stegemeyer, *Z. Naturforsch.*, 16a, 634 (1961).

(8) H. Stegemeyer, *J. Phys. Chem.*, 66, 2555 (1962).

(9) D. Schulte-Frohlinde, H. Blume, and H. Gsten, *ibid.*, 66, 2486 (1962).

(10) D. Schulte-Frohlinde and H. Gsten, *Z. Physik. Chem. (Frankfurt)*, 45, 209 (1965).

and the *trans* isomer was separated by vacuum sublimation and crystallization from petroleum ether. The colorless crystals had mp 134–135° (lit.¹⁶ mp 132–133.5°); $\lambda_{\text{max}}^{\text{ul}}$ 10.6 μ (*trans* -CH=CH-); ultraviolet maxima (acetonitrile) at 357 m μ sh (log ϵ 4.21), 338 (4.41), 325 sh (4.34), and 263 (3.72); nmr peaks (acetone- d_6) at τ 3.52, 3.45, and 3.22 (ring H), and 3.42 (*trans* -CH=CH-).

Anal. Calcd for $C_{10}H_8S_2$: C, 62.50; H, 4.16. Found: C, 62.32; H, 4.19.

B. *cis* Isomer.—A 0.1 *M* solution of the *trans* isomer in benzene was irradiated as described below to furnish a mixture containing ca. 85% of the *cis* isomer. The latter was isolated by trituration with petroleum ether and column chromatography (silica gel) using benzene as eluent. The *cis* isomer was obtained as a pale yellow oil of 93.3% purity; ultraviolet maxima (acetonitrile) at 322 m μ (log ϵ 3.90) and 250 (4.00); nmr peaks (acetone- d_6) at τ 3.49 and 3.17 (ring H), and 3.90 (*cis* -CH=CH-).

Anal. Calcd for $C_{10}H_8S_2$: C, 62.50; H, 4.16. Found: C, 62.46; H, 4.73.

Iodine-Catalyzed Thermal Isomerization.—A mixture of 75 mg of the substituted ethylene in 1 ml of benzene and 2 ml of a 0.2% solution of iodine in benzene was refluxed for 3–4 hr. Both isomers of the two compounds I were subjected to this treatment. The isomeric composition was determined by glpc using a 150-ft-long capillary column loaded with Dow-Corning DC-200 silicone fluid. It was established by separate tests that no isomerization occurs on the column.

Photoisomerization Experiments.—The photolyses were carried out in 10-cm-long cylindrical Pyrex vessels fitted with a side arm for connection to a vacuum line, a cold finger which reaches close to the bottom of the vessel, and a magnetic stirrer. The size of the tube used was appropriate for the size of the sample. Thus for small solution volumes (2–3 ml) the diameter of the vessel was such that the annular space surrounding the cold finger was 0.2 cm wide, while for 15–30-ml samples this space was 0.9 cm wide. The circulation of water kept the temperature below 35° throughout the irradiation. An unfiltered GE 275-W sun lamp situated 12 in. from the photolysis tube served as light source. The lamp emits all the mercury lines above 290 m μ and, considering the transmission of Pyrex and the absorption spectra of difurylethylene and dithienylethylene (Figures 1 and 2),¹⁷ it is evident that light at the wavelengths 366, 334, 313, 303, and 296 m μ is absorbed. It can readily be shown (*cf.* Appendix) that, for a photoisomerization brought about by polychromatic light, the photostationary isomer composition is not *per se* concentration-dependent provided that all the incident light at every active wavelength is absorbed. The concentrations employed were such that this criterion was always satisfied. The solutions were prepared with Baker Analyzed reagent benzene, which was used without further purification. They were degassed by three freeze-pump-thaw cycles and were placed under an atmosphere of nitrogen for photolysis.¹⁸ Irradiation times were in the range 4–10 hr and, at every concentration, equilibrium was established with both isomers. Analysis was accomplished by glpc as described above.

To express the results for different compounds in a comparable manner, the photostationary composition is given as the product $Rf(\epsilon)$, where R is the equilibrium ratio of *trans/cis* isomer concentration and $f(\epsilon)$ is the excitation ratio which reflects the extinction coefficients of the isomers. This function is given by eq 1 where a_i is the ratio of the intensity of the absorbed light

$$f(\epsilon) = \sum_i \left(\frac{a_i r_i}{1 + r_i R} \right) / \sum_i \left(\frac{a_i}{1 + r_i R} \right) \quad (1)$$

at the i th wavelength to the intensity at one wavelength arbitrarily chosen as standard (*i.e.*, $a_i = 1$), and $r_i = (\epsilon_{\text{trans}}/\epsilon_{\text{cis}})_i$, the ratio of the extinction coefficients at wavelength i . The summation is carried out over all the emitted lines which are

(16) Y. K. Yur'ev and D. Eckhardt, *Zh. Obshch. Khim.*, **31**, 3526 (1961); *Chem. Abstr.*, **57**, 4621b (1962).

(17) The spectrum of *cis*-difurylethylene is unusual in that it mirrors the absorption of the *trans* isomer and shows structure. The nmr, infrared, and glpc measurements, however, leave no doubt about the configuration of this isomer.

(18) In undegassed solutions, the irradiation of difurylethylene and dithienylethylene gives rise to products other than isomers. The photocyclo-dehydrogenation of these compounds under these conditions and in the presence of iodine has recently been reported; *cf.* C. E. Loader and C. J. Timmons, *J. Chem. Soc., C*, 1677 (1967); R. M. Kellogg, M. B. Groen, and H. Wynberg, *J. Org. Chem.*, **32**, 3093 (1967).

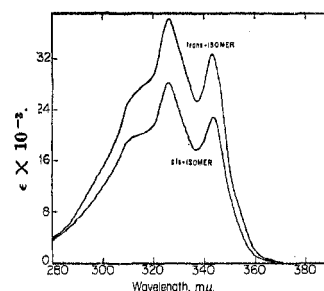


Figure 1.—Absorption spectra of the isomers of 1,2-di(2-furyl)ethylene in benzene.

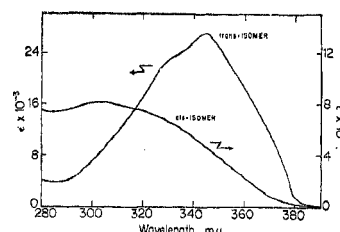


Figure 2.—Absorption spectra of the isomers of 1,2-di(2-thienyl)ethylene in benzene.

absorbed by the isomers. In the case of monochromatic irradiation at wavelength λ , $f(\epsilon) = (\epsilon_{\text{trans}}/\epsilon_{\text{cis}})\lambda$.

Values of a_i were obtained by measuring the emission of the sunlamp with a spectrophotometer whose spectral response had been determined with a lamp calibrated against an NBS standard lamp.^{19,20} The sunlamp shows no continuum emission <400 m μ . The relative intensities in quanta per unit time and area for the various mercury lines (λ , m μ) are 2.62 (578), 1.78 (546), 0.98 (435), 0.43 (405), 1.00 (366), 0.080 (334), 0.28 (313), 0.11 (303), and 0.041 (296).

Results

The *cis* and *trans* isomers of difurylethylene and dithienylethylene have been prepared and unequivocally characterized by nmr, infrared, and ultraviolet spectral analyses. The photostationary isomer compositions attained with total light absorption at 366, 334, 313, 303, and 296 m μ are given in Table I. These data indicate the final compositions to be markedly dependent upon the total olefin concentration. As with the stilbenes,^{7,9,10} high concentrations favor the *trans* isomer. With the technique and apparatus employed, the limiting composition at very low concentration could only be approximately determined, since under these conditions less than total light absorption takes place at some wavelengths. It is clear that, under all conditions, the photostationary *trans*- to *cis*-isomer ratio (R) is greater for difurylethylene than for dithienylethylene.

Thermal equilibration of the two compounds at high concentration (0.4–0.5 *M*) in benzene was achieved by iodine catalysis. In both cases, the equilibrium is, within experimental error, entirely on the *trans*-isomer side (99% *trans* and 1% *cis* olefin).

Figure 3 shows the plots of $Rf(\epsilon)$ against the photostationary *trans*-isomer concentration, $[trans]_{\infty}$. The data of Schulte-Frohlinde and coworkers for 4-nitro-4'-methoxystilbene,¹⁰ which was equilibrated in 1-methylnaphthalene solution with 366-m μ light, are included.

(19) R. Starr, W. E. Schneider, and J. K. Jackson, *Appl. Opt.*, **2**, 1151 (1963).

(20) C. A. Parker and W. T. Rees, *Analyst*, **85**, 587 (1960).

TABLE I
PHOTOSTATIONARY-STATE ISOMER COMPOSITION FOR
DIFURYLETHYLENE AND DITHIENYLETHYLENE IN BENZENE^a

Total concn, $M \times 10^2$	Difurylethylene		Dithienylethylene	
	<i>trans</i> isomer, %	$Rf(\epsilon)^b$	<i>trans</i> isomer, %	$Rf(\epsilon)^b$
1.01	49	1.20	9.0	0.79
10.0	70	2.88	13	1.10
29.9			30	2.80
52.0			69	11.65
100	97	34.0		

^a At 25–35°. The values are the average of those obtained for the *cis* and *trans* isomer as the starting material. The relative error in composition is estimated to be $\pm 5\%$. ^b See Experimental Section.

The curves are fitted well by eq 2, where a , b , and c

$$Rf(\epsilon) = a + b[\text{trans}]_{\infty} + c[\text{trans}]_{\infty}^2 \quad (2)$$

are constants having the values indicated in Figure 3. It must be pointed out, however, that the distinction between eq 2 and more complex expressions involving the concentration of the *cis* isomer as well is rendered difficult by the magnitude of the experimental uncertainty.

Discussion

At low concentration ($<10^{-2} M$), the photoisomerization behavior of difurylethylene and dithienylethylene in benzene is not too different from that of stilbene. Thus the limiting values of $Rf(\epsilon)$ for the two compounds are approximately 1.1 and 0.8, respectively, while the value for stilbene is 0.67.³

In seeking an explanation for the increase in $Rf(\epsilon)$ with concentration, two possibilities immediately come to mind. These are (1) association between ground-state molecules which gives rise to dimers and higher aggregates, and (2) specific interactions between excited and ground-state olefin molecules. With respect to the first possibility, theoretical considerations indicate that association should lead to new absorption at longer or shorter wavelengths than that due to the monomer.²¹ We have examined difurylethylene and dithienylethylene over a wide concentration range and have found no evidence of spectral change; both the position of the absorption bands and the extinction coefficients are, within experimental error, independent of the concentration. Similar behavior has been noted for the absorption and emission spectra of 4-nitro-4'-methoxystilbene.¹⁰ It is worthy of mention that ground-state association has been invoked in a case where spectral changes with concentration are absent²² and, also, that it may well play a role in the photoisomerization of neat *cis*-stilbene where the concentration is $>5 M$.

In contrast with ground-state association, the quenching of excited olefin molecules is experimentally well documented.^{3,5} In the concentration range employed ($<1 M$), it is considered probable that the change in equilibrium isomeric composition is, in fact, due to

(21) (a) T. Förster, "Fluoreszenz Organischer Verbindungen," Vandenhoeck and Ruprecht, Göttingen, 1951, Chapter 11; (b) R. M. Hochstrasser, "Molecular Aspects of Symmetry," W. A. Benjamin, Inc., New York, N. Y., 1966, p 321 ff.

(22) The photodimerization of acenaphthylene is postulated to involve a ground-state dimer whose existence was inferred from an almost negligible increase in molecular weight with concentration; cf. R. Livingston and K. S. Wei, *J. Phys. Chem.*, **71**, 541 (1967).

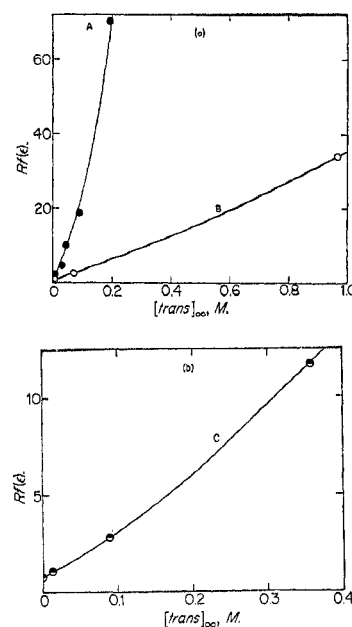


Figure 3.—Plots of $Rf(\epsilon)$ vs. $[\text{trans}]_{\infty}$. The solid lines are calculated from eq 2 with the indicated values (a , b , and c). (a) Curve A, 4-nitro-4'-methoxystilbene (1.58, 114, 1190); curve B, difurylethylene (1.075, 25.0, 9.50). (b) Curve C, dithienylethylene (0.85, 19.0, 31.3).

interactions between excited- and ground-state olefin molecules, and further discussion of the concentration effect is based on this assumption. In this connection it is pertinent that the fluorescence of *trans*-4-nitro-4'-methoxystilbene is subject to concentration quenching.¹⁰ The *cis* isomer, which is itself nonfluorescent, is without effect on the emission of the *trans* isomer. The data for this compound indicate further that the isomerization is more sensitive to concentration changes than the fluorescence.^{23,24} With respect to the concentration effect in isomerization, these findings suggest that specific interactions involving more than one excited species are operative.

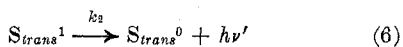
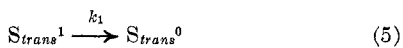
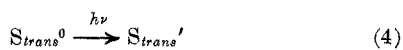
The photoisomerization of stilbene has been examined theoretically with the aid of SCF-MO calculations by Borrell and Greenwood.²⁵ The potential energy diagrams generated by this treatment are broadly consistent with the triplet mechanism proposed by Fischer and coworkers.^{4,6} The theoretical results indicate that neither the *cis* nor the *trans* configurations of the lowest triplet level are stable relative to a twisted triplet state. The mechanism we propose here for the concentration effect in *cis-trans* photoisomerization is based on a simplified version of Borrell and Greenwood's model. Inasmuch as vibrational relaxation in solution is rapid in relation to other decay processes, nonvertical transitions are formulated without attention to inter-

(23) This becomes quite evident if one considers the change in $Rf(\epsilon)$ to be solely due to the quenching of the excited singlet state of the *trans* isomer. Schulte-Frohlinde and Gütten¹⁰ also report concentration-dependent quantum yields for the *cis-to-trans* *trans-to-cis* isomerizations, which are claimed to have been computed by the method of Zimmerman, *et al.*²⁴ However, the equations derived by Zimmerman are specifically based on the assumption that the quantum yields are independent of the light intensity and the concentration. Consequently we believe that the quantum yields at high concentrations presented in ref 10 are without quantitative significance, although there is no reason to doubt that they vary with concentration.

(24) G. Zimmerman, L. Chow, and V. Paik, *J. Amer. Chem. Soc.*, **80**, 3528 (1958).

(25) P. Borrell and H. H. Greenwood, *Proc. Roy. Soc. (London)*, **A298**, 453 (1967).

mediate vibrational states. In the equations which follow, singlet states are represented by S, the common twisted first triplet state by T', and ground and excited levels by the superscripts 0 and 1, respectively. With the stated simplification, excitation of the *cis*-isomer ground state (S_{cis}^0) is considered to lead directly to a twisted cisoid excited singlet state (S'). Excitation of the *trans*-isomer ground state (S_{trans}^0) produces the singlet excited state S_{trans}^1 , the conversion of which into S' is considered to be the activated process. With the three postulated excited states (S_{trans}^1 , S', and T'), the minimum requirement imposed by the results is that S_{trans}^1 and one of the other excited states are collisionally quenched to S_{trans}^0 . In view of the short lifetimes inferred for excited cisoid configurations,^{9,25} deactivation of T' seems more realistic. The intersystem crossing $S' \rightarrow T'$, which is pictured to involve initial crossover to a second triplet level followed by internal conversion, can be expected to be very rapid.²⁶ The T' and S⁰ potential curves intersect, but the changes $T' \rightarrow S_{trans}^0$ or S_{cis}^0 require a sizable conversion of electronic into vibrational energy and the vibrational overlap integrals are likely to be small. A lifetime of T' comparable with that of S_{trans}^1 is, therefore, not unreasonable, and collisional quenching of the twisted triplet state T' can be expected. Equation 7 reflects



the fluorescence quenching results with 4-nitro-4'-methoxystilbene.¹⁰ For the quenching of T', only one reaction with S_{trans}^0 is included. Other reactions involving quenching by, and the formation of S_{cis}^0 , may well occur, but the experimental data are not accurate enough to distinguish between the given mechanism and those which include such additional steps. This simple formulation may further be inadequate in view of the "nearest neighbor" effects noted at high quencher concentrations.²⁷

With application of the steady state approximation to the short-lived states and the assumption that the isomerization quantum yields are independent of the wavelength of irradiation,²⁸ the mechanism leads to

(26) P. Seybold and M. Gouterman, *Chem. Rev.*, **65**, 413 (1965); S. K. Lower and M. A. El-Sayed, *ibid.*, **66**, 199 (1966).

(27) P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 5715 (1967).

(28) This holds rigorously for 4-nitro-4'-dimethylaminostilbene⁹ in cyclohexane and in benzene, and is approximately true for 4-nitro-4'-methoxystilbene¹⁰ in methylcyclohexane-decalin and for stilbene⁹ in *n*-hexane.

eq 2, with

$$a = \frac{k_7(k_1 + k_2 + k_4)}{k_4k_6}$$

$$b = \frac{k_8(k_1 + k_2 + k_4) + k_3k_7}{k_4k_6}$$

$$c = \frac{k_3k_5}{k_4k_6}$$

Clearly, a represents the limiting value of $Rf(\epsilon)$ at infinite dilution.

The fluorescence data for *trans*-4-nitro-4'-methoxystilbene provide at least a partial check for the mechanism. The concentration quenching of fluorescence may be expressed as $\phi_F^0/\phi_F = 1 + k_Q[trans]$, where ϕ_F^0 and ϕ_F are the fluorescence quantum yields without and with quenching, respectively, and $k_Q = k_3/(k_1 + k_2 + k_4)$. From the reported concentration which halves the fluorescence yield (0.25 M), $k_Q = 4M^{-1}$ is computed. Combination of the constants of eq 2 as defined above yields $k_Q^2 - (b/a)k_Q + (c/a) = 0$. Using the values of a , b , and c for 4-nitro-4'-methoxystilbene given in Figure 3, this equation gives $k_Q = 13$ and $59 M^{-1}$. Since $b/a = k_Q + (k_3/k_7)$, the corresponding values of k_3/k_7 are 59 and 13 M^{-1} , respectively. Thus unambiguous distinction between the two values for each of these constants is not possible. Further, the uncertainties in these numbers are large and are estimated to be $\pm 100\%$. Within these limitations, the isomerization and fluorescence results are consistent with the mechanism.

Fluorescence data are not available for difuryl-ethylene and dithienylethylene. For these compounds, the conjugate pairs of values for k_Q and k_3/k_7 derived from the isomerization results are 0.4 and 23 M^{-1} (difuryl-ethylene) and 2 and 22 M^{-1} (dithienylethylene).

With the reasonable assumption that the singlet state quenching (eq 7) occurs at close to the diffusion-controlled rate²⁹ ($k_3 \approx 2 \times 10^9$ l./mol sec in 1-methylnaphthalene³⁰ and 1×10^{10} l./mol sec in benzene), the lifetimes of the S_{trans}^1 states of the three compounds examined are estimated to fall in the range $1-5 \times 10^{-9}$ sec. These values compare favorably with average lifetimes of $1.5-3.3 \times 10^{-9}$ sec which have been reported for the S_{trans}^1 states of some substituted stilbenes.³¹ The more tenuous assumptions that the quenching of the triplet state (eq 12) is also diffusion controlled and that $k_8 \approx k_7$ provide lower limits of the lifetimes of the T' states which are of the same order of magnitude as those of the S_{trans}^1 states.

Registry No.—I (X = O, *trans*), 1439-19-6; I (X = O, *cis*), 18266-93-8; I (X = S, *trans*), 13640-78-3; I (X = S, *cis*), 18266-94-9.

Acknowledgments.—We gratefully acknowledge helpful discussions with Drs. R. Srinivasan and F. J. Wright, Mr. D. Bachert's experimental contributions, and Mr. E. Reid's assistance with the computations. The relative intensity calibration of the light source was performed by Dr. H. P. Wolf and Mr. W. N. Hall, whom we also thank. Dr. E. Fischer of the Weizmann

(29) *Cf.* ref 21a, pp 209, 244.

(30) The viscosity of this solvent at 25° is estimated as 30.5 mP from the data of H. F. Hipsher and P. H. Wise, *J. Amer. Chem. Soc.*, **76**, 1747 (1954).

(31) P. M. Shorygin and T. M. Ivanova, *Soviet Phys. "Doklady,"* **3**, 764 (1958).

Institute of Science kindly supplied us with several of his manuscripts prior to publication.

Appendix

Photostationary State Composition with Irradiation at Several Wavelengths. Consider the photoisomerization $A \rightleftharpoons B$ brought about by light of several discrete frequencies ν_i , with both isomers showing absorption at all these frequencies. In this derivation, the quantum yields are assumed to be independent of the concentration. Let C_A and C_B be the molar concentrations of A and B, respectively, at any time, and C_A^0 and C_B^0 the corresponding initial concentrations. Assuming that no side reactions occur, the total concentration is $C^0 = C_A + C_B = C_A^0 + C_B^0$. Other symbols are defined as follows, with the subscript i referring to the parameter at ν_i .

$X_A = C_A/C^0$, mole fraction of A
 X_A^∞ = mole fraction of A in the photostationary state
 ϕ_{A_i} = quantum yield for the change $A \rightarrow B$
 ϕ_{B_i} = quantum yield for the change $B \rightarrow A$
 I_{T_i} = total light absorbed (einsteins/second)
 I_{B_i} = incident intensity (einstein/second)
 D_{T_i} = the total optical density, which is equal to $D_{A_i} + D_{B_i}$
 V = volume, in liters of solution receiving radiation
 ϵ_{A_i} and ϵ_{B_i} are the molar extinction coefficients

Now $I_{T_i} = I_{A_i} + I_{B_i}$, the sum of the light absorbed by A and B, respectively. The latter quantities are clearly $I_{A_i} = D_{A_i}/D_{T_i}$ and $I_{B_i} = D_{B_i}/D_{T_i}$. From Beer's law, $I_{T_i} = I_{0_i}[1 - \exp(-2.3D_{T_i})]$, which is equal to I_{0_i} when D_{T_i} is large at high substrate concentrations.

The rate of formation of A is given by eq 13. Equat-

$$\frac{dC_A}{dt} = C^0 \frac{dX_A}{dt} = \frac{1}{V} \left[\sum_i \phi_{B_i} I_{0_i} D_{B_i} / D_{T_i} - \sum_i \phi_{A_i} I_{0_i} D_{A_i} / D_{T_i} \right] \quad (13)$$

ing this rate to zero at the stationary state, and defining the optical densities in the usual manner (e.g., $D_{A_i} = \epsilon_{A_i} C_A l$, where l is the path length), relative intensities by $a_i = I_{0_i}/I_{0_0}$, and the difference in extinction coefficients as $\Delta\epsilon_i = \epsilon_{A_i} - \epsilon_{B_i}$, we finally obtain

$$X_A^\infty = \frac{\sum_i a_i \epsilon_{B_i} \phi_{B_i} / (\epsilon_{B_i} + X_A^\infty \Delta\epsilon_i)}{\sum_i a_i (\epsilon_{A_i} \phi_{A_i} + \epsilon_{B_i} \phi_{B_i}) / (\epsilon_{B_i} + X_A^\infty \Delta\epsilon_i)} \quad (14)$$

This equation can, in principle, be solved for X_A^∞ with the boundary condition $0 < X_A^\infty < 1$. It shows that, if light absorption is complete at every frequency, X_A^∞ remains independent of the total concentration, C^0 . Concentration dependence appears when there is only fractional light absorption at some frequencies. If, however, there is partial light absorption at every frequency such that the approximation $1 - \exp(-2.3D_{T_i}) = 2.3D_{T_i}$ holds, eq 14 becomes

$$X_A^\infty = \frac{\sum_i a_i \epsilon_{B_i} \phi_{B_i}}{\sum_i a_i (\epsilon_{A_i} \phi_{A_i} + \epsilon_{B_i} \phi_{B_i})} \quad (15)$$

With monochromatic irradiation, eq 14 and 15 reduce to $X_A^\infty = \epsilon_{B_i} \phi_{B_i} / (\epsilon_{A_i} \phi_{A_i} + \epsilon_{B_i} \phi_{B_i})$, which is identical with eq 6 given in the appendix of Malkin and Fischer's paper.³²

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Concerning Back-Bonding and Polar Effects in Aminoalkylbenzene Derivatives

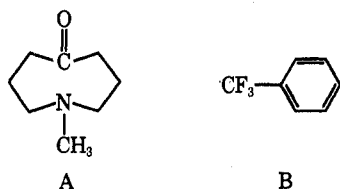
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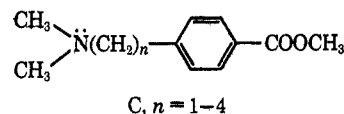
The infrared and ultraviolet spectral properties of $(CH_3)_2N(CH_2)_n C_6H_4COOCH_3$ ($n = 1-4$) were studied to determine the presence of intramolecular interactions between the nonbonded nitrogen electrons and the π system of the aromatic rings (i.e., back-bonding). The results show that such interactions do not contribute to either the ground or excited states. Kinetic data on the basic hydrolysis of the four esters likewise demonstrate the absence of nonconjugative orbital overlap. In the second portion of the paper we determine how the rate of alkaline hydrolysis of $(CH_3)_2N^+(CH_2)_n C_6H_4COOCH_3$ varies with the value of n . The compounds possess a quaternary nitrogen, a powerful electron-withdrawing group, and an ester functionality whose hydrolysis rate is sensitive to polar effects. The data are compared with Kirkwood-Westheimer calculations using spherical and ellipsoidal cavities. Hammett σ_p constants are reported for the $(CH_3)_2N(CH_2)_n$ and $(CH_3)_2N^+(CH_2)_n$ groups where $n = 1-4$.

Intramolecular interaction between a carbonyl carbon and nonbonded amino nitrogen electrons (as occurs in compound A) is well known.² Sheppard³ has proposed



a similar type of interaction in benzotrifluoride (B) between a nonbonded pair of electrons on fluorine

and the π system. Subsequent work,^{4,5} however, has shown that such back-bonding is of no importance in the case of benzotrifluoride. One of several arguments used against the back-bonding concept is that there is no analogy suggesting that this effect can be significant.⁴ In the present paper we examine a series of methyl *p*-(*N,N*-dimethylaminoalkyl)benzoates (C, $n = 1-4$) for the presence of $p-\pi$ overlap.



Back-bonding effects are much more likely in this set of compounds than in benzotrifluoride. The p

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