The Mechanism of Syn–Anti Isomerization of Azomethine Dyes

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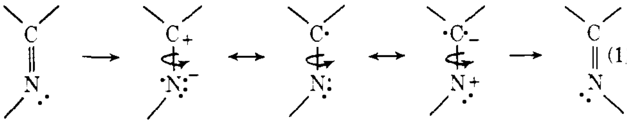
Abstract: In previous work it has been demonstrated that irradiation of azomethine dyes brings about syn–anti isomerization, a change in the configuration about the carbon–nitrogen double bond. We have now systematically measured substituent and steric effects on the rates of thermal isomerization following photochemical excitation of benzoylacetanilide and pyrazolone azomethine dyes. For all dyes, bulk added in the form of methyl groups adjacent to the azomethine bond increases the rate of thermal isomerization. With substituents in the para position of the aromatic ring attached to the nitrogen atom of the azomethine bond, both electron-donating and electron-withdrawing substituents provide rate enhancement; for each class of dye, plots of the logarithm of the rate constant *vs.* the substituent σ constant are V-shaped with the minima near σ equal to zero. We believe that our results can be interpreted in terms of different mechanisms of isomerization; with electron-donating substituents, the isomerization proceeds by torsion about the central azomethine bond and with electron attractors, inversion about the azomethine nitrogen is the preferred path.

Two basic mechanisms have frequently been proposed for isomerization about the carbon–nitrogen (azomethine) double bond: (a) the torsion, or twist, mechanism and (b) the linear inversion, or lateral shift, mechanism.[1] The torsion mechanism involves a rotation or twisting about the azomethine bond, as depicted in eq 1. To bring about this change in geometry, there must be a reduction in the double bond character of this bond in the transition state relative to the ground state. The C=N—C bond angle remains constant at 120° on proceeding through the transition state, as does the sp^2 conjugation of the nitrogen atom electrons. The inversion mechanism, shown in eq 2, is characterized by an increase in the angle of the C=N—C bond from approximately 120° in the ground state to 180° in the transition state. The double bond character of the azomethine bond remains intact in the transition state, as the nitrogen atom electrons rehybridize from sp^2 to sp with the formerly nonbonding electrons becoming available as p electrons for conjugation with other π-electron systems attached to the nitrogen atom. It has also been proposed that there may be a mechanistic continuum between torsion and inversion such that the conversion from one geometric isomer to the other need not proceed *via* a pure torsion or inversion mechanism, but may follow a path in which both make contributions in varying degrees.[2,3]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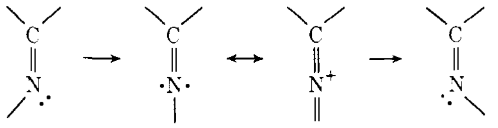
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Although several reports have appeared supporting the torsion mechanism, most people have favored the inversion mechanism for isomerization about the azomethine bond. One of the most frequent arguments for choosing inversion over torsion is the fact that the activation energies for aromatic imine isomerization are on the order of 20 kcal/mol or even less,[4] whereas approximately 40 kcal/mol activation energy is required to isomerize aromatic olefins.[5,6] The latter can isomerize only by the torsion mechanism. Because inversion at the nitrogen atom is known to have relatively low activation energies,[7,8] it has frequently been deduced that imines must isomerize by the same mechanism. More recent evidence has shown this argument to be less than compelling. Several substituted olefins are now known where the energy barrier to isomerization is less than 20 kcal/mol.[9–11] Also, guanidinium salts, where the extra pair of electrons is tied up and torsion becomes the only viable path for isomerization about the azomethine bond, have activation energies of this same order of magnitude.[1,12–14] Lehn reports that heteroatoms present in the substituents of alkyl- and aryl-substituted imines may appreciably perturb the C=N bond and lower the barrier to torsion below that of inversion.[8] Support for this view is also provided by the calculations of Raban on CH_2=NH and two of its heteroatom substituted derivatives.[15]

A second argument frequently cited in favor of inversion is based on steric evidence. Kessler has found that activation energies for arylimines (guanidines, in particular) with alkyl substituents R in the ortho posi-

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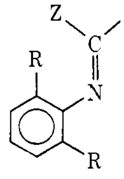
[1] H. Kessler, *Angew. Chem.*, **82**, 237 (1970).
[2] N. P. Marullo and E. H. Wagener, *Tetrahedron Lett.*, 2555 (1969).
[3] M. Raban and E. Carlson, *J. Amer. Chem. Soc.*, **93**, 685 (1971).
[4] E. Fischer and Y. Frei, *J. Chem. Phys.*, **27**, 808 (1957).
[5] G. B. Kistiakowsky and W. R. Smith, *J. Amer. Chem. Soc.*, **56**, 638 (1934).
[6] F. W. J. Taylor and A. R. Murray, *J. Chem. Soc.*, 2078 (1938).
[7] J. D. Andose, J. M. Lehn, K. Mislow, and J. Wagner, *J. Amer. Chem. Soc.*, **92**, 4050 (1970).
[8] J. M. Lehn, *Fortschr. Chem. Forsch.*, **15**, 311 (1970).
[9] A. S. Kende, P. T. Izzo, and W. Fulmer, *Tetrahedron Lett.*, 3697 (1966).
[10] Y. Shvo, E. C. Taylor, and J. Bartulen, *Tetrahedron Lett.*, 3259 (1967).
[11] G. Isakson, J. Sandstrom, and J. Wennerbeck, *Tetrahedron Lett.*, 2233 (1967).
[12] H. Kessler and D. Leibfritz, *Tetrahedron*, **25**, 5127 (1969).
[13] H. Kessler, P. F. Bley, and D. Leibfritz, *Tetrahedron*, **27**, 1687 (1971).
[14] H. Kessler and D. Leibfritz, *Chem. Ber.*, **104**, 2158 (1971).
[15] M. Raban, *Chem. Commun.*, 1415 (1970).

Table I. Hammett σ Constants for Para Substituents Determined from Ionization of Para-Substituted Benzoic Acids

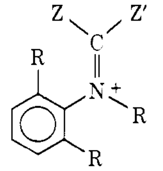
Para substituent	Benzoic acid p*K* in EtOH–H_2O	Lit. benzoic acid p*K* in EtOH–H_2O	σ in EtOH–H_2O	σ normalized to pure H_2O[a]	Lit. σ
$-NO_2$	4.57	4.53[b]	+1.17	+0.77	+0.78[c]
–CN	4.70	4.70[b]	+1.04	+0.68	+0.66[c]
–COMe	4.88	5.10[b]	+0.86	+0.56	+0.50[c]
–Cl	5.36	*d*	+0.38	+0.25	+0.23[c]
–H	5.74	5.70–5.80[b]	0.00	0.00	0.00[e]
–Me	5.95	6.00[b]	−0.21	−0.14	−0.17[e]
–OMe	6.05	6.12[b]	−0.31	−0.20	−0.27[c]
$-N(Ph)_2$	6.13	6.10[f]	−0.39	−0.26	*d*
–NHPh	6.43	*d*	−0.69	−0.45	*d*
$-NH_2$	6.53	*d*	−0.79	−0.52	−0.66[g]
$-N(Me)_2$	6.70	*d*	−0.96	−0.63	−0.60[h]
–NHMe	6.71	*d*	−0.97	−0.64	−0.59[h]
$-N(Et)_2$	6.84	*d*	−1.10	−0.72	*d*

[a] Each σ constant, measured in 50% aqueous ethanol, is divided by 1.522, the ρ value for ionization of para-substituted benzoic acids in this solvent mixture as reported in ref 17. [b] This value is taken from a compilation of p*K*'s measured in 50% aqueous ethanol as reported in ref 17. [c] This value is taken from a compilation of σ constants based on the ionization of substituted benzoic acids as reported in ref 17. [d] Not reported previously. [e] Standard, by definition. [f] E. N. Tsvetkov, D. I. Lobanov, and M. I. Kobachnik, *Akad. Nauk Ukr. SSR*, **1**, 729 (1965); *Chem. Abstr.*, **64**, 12523f (1965). [g] L. P. Hammett, "Physical Organic Chemistry, "McGraw-Hill, New York, N. Y., 1940, Chapter 7. [h] This value is taken from a compilation of σ constants using that value "which best fits the entire body of experimental data," from H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

tions of the aromatic ring attached to the N atom are lowered as the size of the alkyl groups increases.[1,12–14]



In guanidinium salts, however, in which the lone pair of electrons is fixed and inversion is no longer possible, increasing steric bulk raises activation energies of isomerization. Kessler interprets these data as support



for the inversion mechanism for sterically hindered imines. Lehn, however, regards such steric effects as inconclusive because of complications brought about by the action of substituents in the ortho positions of *N*-arylimines on the conjugation between the nitrogen site and the aryl group.[8]

In previous work we have demonstrated that irradiation of azomethine dyes and related model compounds brings about syn–anti isomerization, a change in the configuration about the C=N double bond.[16] The thermal barrier between the two isomers is sufficiently low that the photochemically induced shift in the configurational equilibrium is only temporary at ambient temperatures and is followed by a rapid, thermal relaxation to reestablish the initial configurational equilibrium between syn and anti isomers. Using flash photolysis techniques with the dyes in fluid solvents, the photochemical isomerization was detected by changes in the electronic absorption spectra of the dyes and the rates of the thermal relaxation were monitored with time. We now report the results of our investigations to elucidate the mechanism of azomethine dye isomerization.

Results and Discussion

A selected group of azomethine dyes and related model compounds was synthesized in order to investigate systematically substituent and steric effects on the rates of thermal syn–anti isomerization following photochemical excitation. Substituents spanning the range from strong electron donors to strong electron withdrawers were incorporated in the para position of the aromatic ring attached to the nitrogen atom. To provide bulk at sites adjacent to the azomethine bond, methyl groups were introduced in the ortho positions of the same ring.

One of the purposes of this investigation was to attempt a correlation between the measured isomerization rate constants for dyes with a series of para substituents and the Hammett para σ constants for these substituents. Because some substituents were utilized for which no σ constant had previously been reported and because many of the remaining σ constants had been determined under varied experimental conditions, it seemed advisable to measure under identical conditions σ constants for all substituents employed in this study. These measurements are based on the ionization of the para-substituted benzoic acids and were carried out in a 1:1 solvent mixture of water and ethanol owing to poor solubility of some of the acids in pure water. With the exception of the p*K* of *p*-acetylbenzoic acid, the measured p*K*'s in aqueous ethanol are in good agreement with literature values. McDaniel and Brown[17] had previously reported that para-substituted benzoic acids ionize in 50% aqueous ethanol with a ρ of 1.522. This value of ρ was used to normalize the σ values measured in our solvent mixture to pure water. Results are summarized in Table I.

Six classes of dyes have been investigated as reported here. These include pyrazolone azomethine and benzoylacetanilide azomethine dyes each with 0, 1, and 2 *o*-methyl groups in the aromatic ring; all

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(16) W. G. Herkstroeter, *Mol. Photochem.*, **3**, 181 (1971).

(17) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

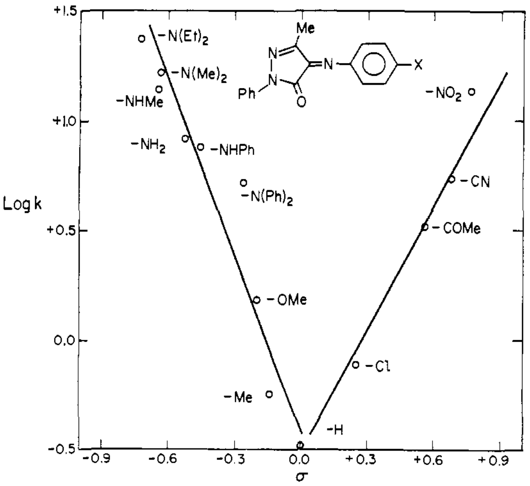

Figure 1. Test of the Hammett equation using σ-substituent constants for the thermal isomerization of the series of para-substituted pyrazolone azomethine dyes in benzene at 22°.

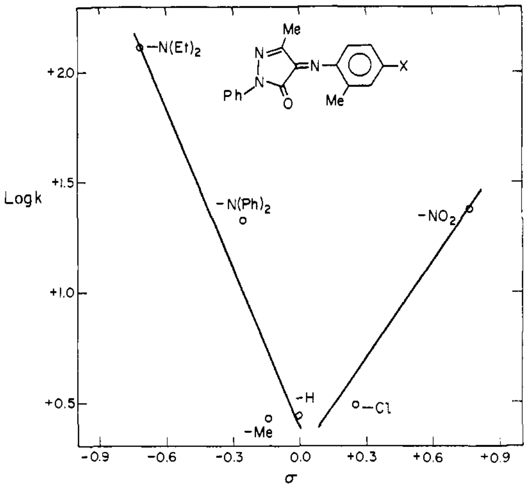

Figure 2. Test of the Hammett equation using σ-substituent constants for the thermal isomerization of the series of para-substituted o-methyl pyrazolone azomethine dyes in benzene at 22°.

contain selected substituents in the para position of this same ring. Kinetic measurements of dye isomerization were carried out in benzene solution at room temperature and in the presence of a triplet sensitizer, 7*H*-benz[*de*]anthracen-7-one, to generate larger initial yields of the metastable dye isomers.[16] For each of these classes of dye, the logarithms of the measured rate constants for thermal isomerization were plotted *vs.* the Hammett σ constants for the para substituents in the dyes. As is evident from Figures 1–6, the Hammett plots are all V-shaped. In the series of pyrazolone dyes in Figure 1, ρ changes from −2.70 (correlation coefficient −0.959) to +1.88 (correlation coefficient 0.989) near a σ of 0 and in the series of benzoylacetanilide dyes of Figure 4, ρ changes from −1.36 (correlation coefficient −0.968) to +1.60 (correlation coefficient 0.973) near a σ of −0.2. For the plots of Figures 2, 3, 5, and 6 the number of points is fairly sparse and ρ values cannot be measured with any degree of precision, but the general trend is the same as in those plots with numerous points.

There have been a number of reports of correlation of rate constants for *N*-arylimine isomerization with

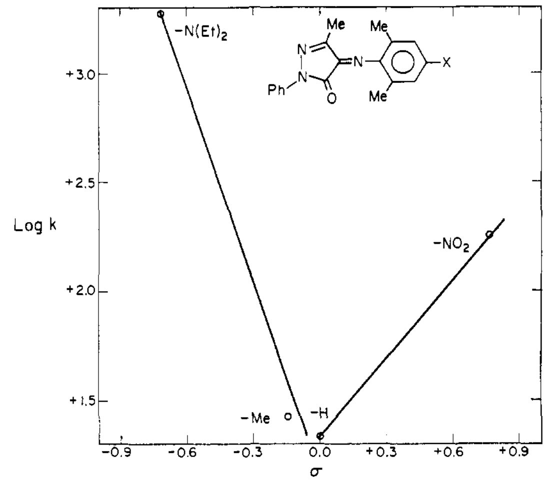

Figure 3. Test of the Hammett equation using σ-substituent constants for the thermal isomerization of the series of para-substituted o,o-dimethyl pyrazolone azomethine dyes in benzene at 22°.

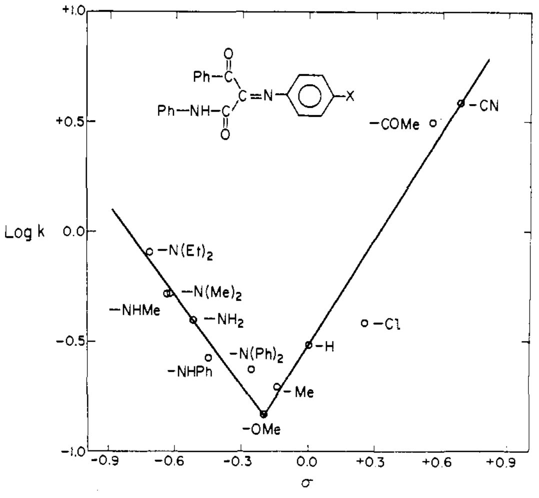

Figure 4. Test of the Hammett equation using σ-substituent constants for the thermal isomerization of the series of para-substituted benzoylacetanilide azomethine dyes in benzene at 22°.

Hammett σ constants and, with one exception, these all show positive ρ's.[1,11,13,18–27] The one exception is provided by the work of Hall, Middleton, and Roberts.[28] These workers correlated the Hammett σ^+ constants with the rate constants for the degenerate isomerization about the carbon–nitrogen double bond of hexafluoroacetone *N*-phenylimine and its para-substituted methoxy, methyl, fluoro, chloro, and nitro derivatives.

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(18) D. Y. Curtin and C. G. McCarthy, *Tetrahedron Lett.*, 1269 (1962).

(19) G. Wettermark, J. Weinstein, J. Sousa, and L. Dogliotti, *J. Phys. Chem.*, **69**, 1584 (1965).

(20) D. Y. Curtin, E. J. Grubbs, and C. G. McCarthy, *J. Amer. Chem. Soc.*, **88**, 2775 (1966).

(21) D. W. Gerlich, F. Voegtle, A. Mannschreck, and H. A. Staab, *Justus Liebigs Ann. Chem.*, **708**, 36 (1967).

(22) H. Kessler, *Angew. Chem.*, **79**, 997 (1967).

(23) A. Rieker and H. Kessler, *Tetrahedron*, **23**, 3723 (1967).

(24) H. Kessler, *Tetrahedron Lett.*, 2041 (1968).

(25) D. Leibfritz and H. Kessler, *J. Chem. Soc. D*, 655 (1970).

(26) H. Kessler and D. Leibfritz, *Tetrahedron*, **26**, 1805 (1970).

(27) K. Giebel, B. Staudinger, K. H. Grellmann, and H. Wendt, *Ber. Bunsenges. Phys. Chem.*, **76**, 1246 (1972).

(28) G. E. Hall, W. J. Middleton, and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 4778 (1971).

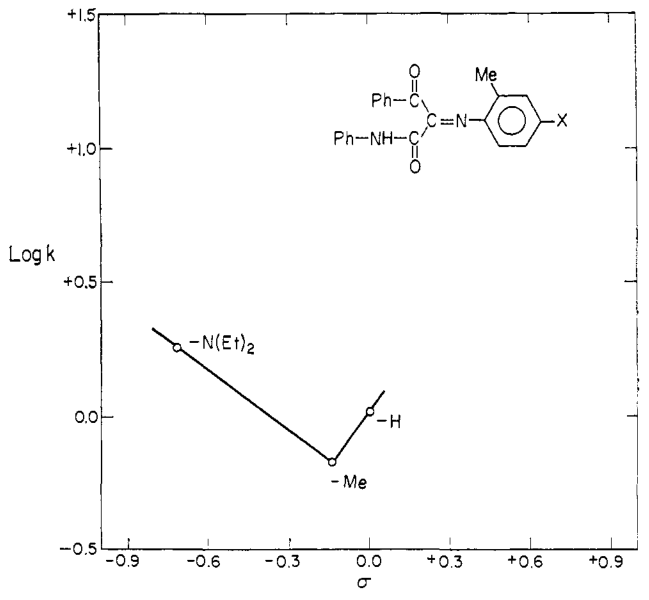


Figure 5. Test of the Hammett equation using σ-substituent constants for the thermal isomerization of the series of para-substituted o-methyl benzoylacetanilide azomethine dyes in benzene at 22°.

If the datum for the *p*-nitro compound is omitted, a linear Hammett plot with a ρ value of -0.980 (correlation coefficient -0.989) obtains; the isomerization of the nitro-substituted compound proceeds more efficiently than expected on the basis of this plot alone. Hall, Middleton, and Roberts interpret their results in terms of isomerization by different mechanisms such that torsion is the path for all compounds except the nitro-substituted one where inversion has taken over.[28]

Our results with the azomethine dyes are, in terms of the appearance of the Hammett plots, similar to the results of Hall, *et al.*,[28] with the hexafluoroacetone *N*-phenylimines; we also propose a similar interpretation. We believe that our results are completely consistent with a change in mechanism of isomerization at those points where the ρ's of the plots of Figures 1–6 change from negative to positive. Our interpretation is that the torsion mechanism is favored when the azomethine dyes have electron-donating substituents and that inversion is the preferred path when these dyes are substituted with electron-withdrawing substituents. The torsion and inversion mechanisms for the isomerization of a pyrazolone azomethine dye are illustrated in eq 3 and 4, respectively.

These equations also illustrate the precise configurational changes that take place in the pyrazolone azomethine dyes for which nmr and X-ray crystallographic studies have established the syn configuration as more stable.[29,30] Configurational assignments in benzoylacetanilide azomethine dyes are the subject of current investigations. For both the pyrazolone and benzoylacetanilide classes of dyes, nmr measurements indicate that the ground-state configurational equilibria predominantly favor the more stable isomers, so that our reported rate constants measure principally the reverse, thermal isomerizations and contain no significant contributions from the forward, thermal isomerizations.

Hall, *et al.*, found that their data for the hexafluoro-

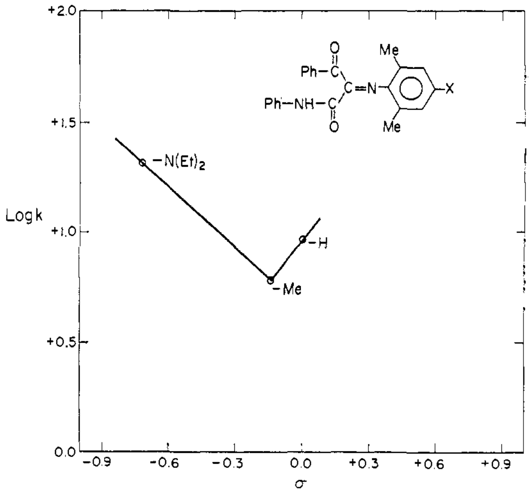
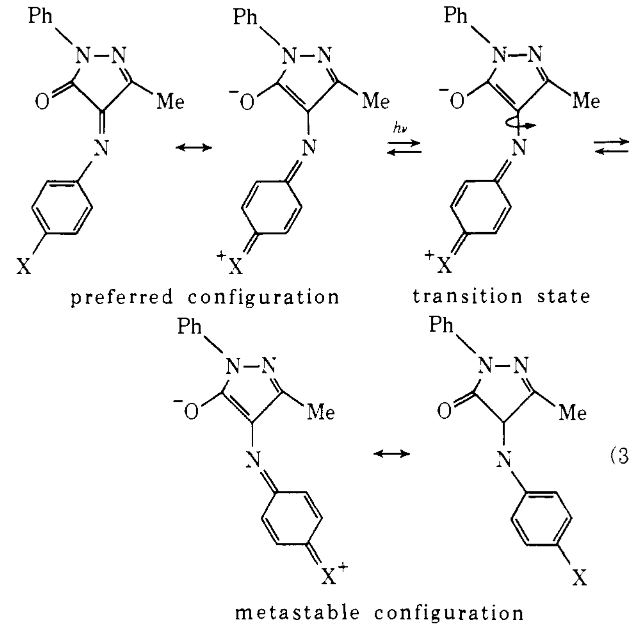


Figure 6. Test of the Hammett equation using σ-substituent constants for the thermal isomerization of the series of para-substituted o,o-dimethyl benzoylacetanilide azomethine dyes in benzene at 22°.



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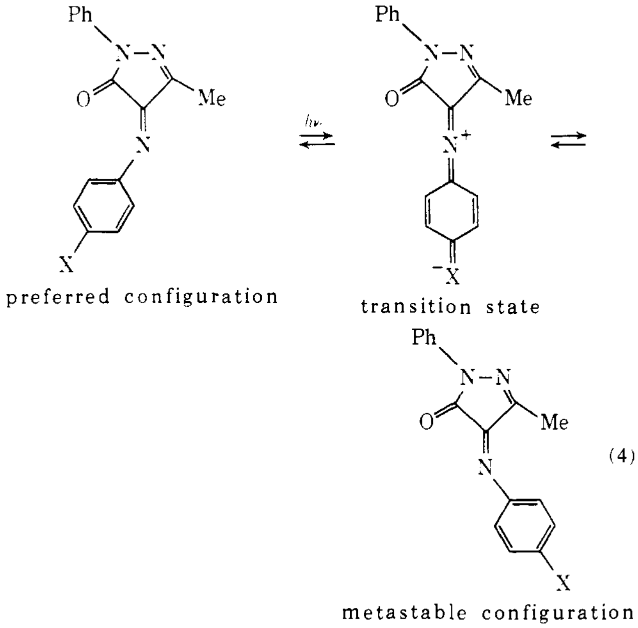

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[29] P. J. S. Pauwels, *J. Amer. Chem. Soc.*, **89**, 580 (1967).
[30] D. L. Smith and E. K. Barrett, unpublished results.

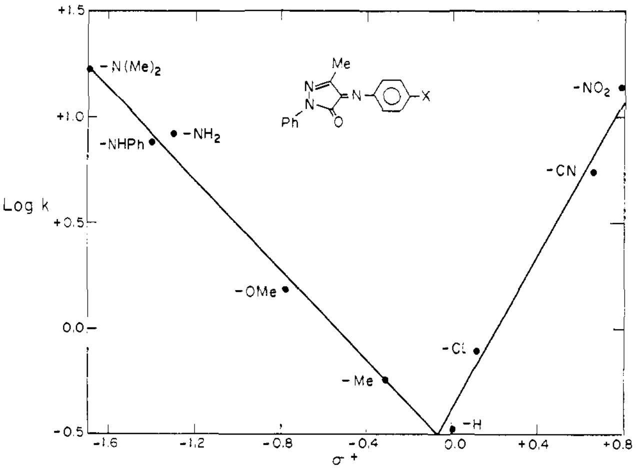


Figure 7. Test of the Hammett equation using σ^+-substituent constants for the thermal isomerization of the series of para-substituted pyrazolone azomethine dyes in benzene at 22°.

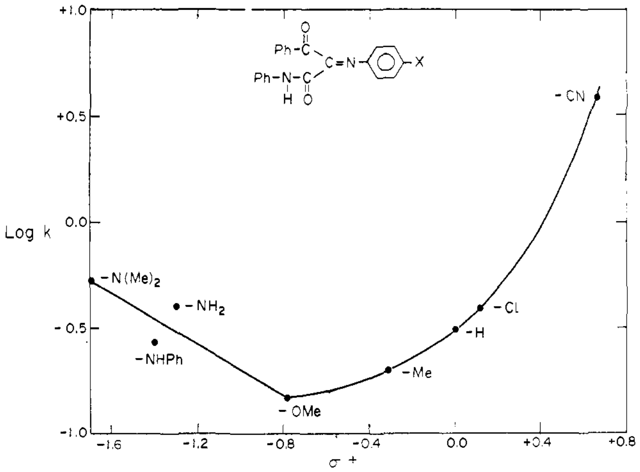
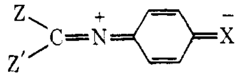


Figure 8. Test of the Hammett equation using σ^+-substituent constants for the thermal isomerization of the series of para-substituted benzoylacetanilide azomethine dyes in benzene at 22°.

acetone *N*-phenylimines correlated better with σ^+ than with σ.[28] This is interpreted by them to mean that ". . . resonance is important in the process which supplies electrons and favors formation of the transition state." Insofar as σ^+ constants were available for the para substituents in our azomethine dyes,[31] we plotted the logarithms of the rate constants for dye isomerization *vs.* σ^+. As shown in Figure 7 for the pyrazolone azomethine dyes, a V-shaped plot again obtains where the negative leg has a slope of -1.06 (correlation coefficient -0.995) and the positive leg has a slope of 1.84 (correlation coefficient 0.994). The correlation here is good and is comparable to that observed in Figure 1, which includes more data points. The plot for the benzoylacetanilide dyes in Figure 8 shows a pronounced curvature in moving to the right of the data point for the methoxy group. Actually, the whole plot could be regarded as U-shaped, because a U-curve could easily be drawn by omitting the point for the amino substituent. As plotted, the negative-sloped leg of Figure 8 has a slope of -0.60 (correlation coefficient -0.921). The remaining data points of Figure 8 do not correlate well with a straight line (correlation coefficient 0.683). In contrast to the isomerization rate constants for the pyrazolone azomethine dyes, it appears that the correlation of the kinetic data of the benzoylacetanilide azomethine dyes is poorer with σ^+ than with σ.

Two questions now arise. The first is what distinguishes the azomethine dyes and the hexafluoroacetone *N*-phenylimines from the other imines described in the literature where isomerization data result only in positive ρ's in Hammett plots. The second is whether substituent effects of *N*-arylimine isomerization can be used as a means of distinguishing between torsion and inversion mechanisms. The answer to the first question is that the azomethine dyes and the hexafluoroacetone *N*-phenylimines have electron-withdrawing groups attached to the imine carbon in contrast to the other imines which are substituted with electron donors in these positions. The significance of this difference as well as the answer to the second question are included in the following discussion.

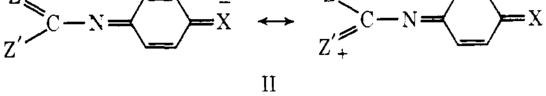
In the torsion mechanism, the barrier in the transition state will be lowered by substituents that reduce the double bond character of the azomethine bond. On the other hand, the mechanism for linear inversion should be facilitated by substituents that contribute to the stability of the inversion transition state. In this transition state, depicted by structure I, the valence



I

electrons of the nitrogen atom are sp hybridized: one of the two p orbitals is used for the C–N bond, but the second p orbital is free to overlap with the π-electron system of the para-substituted aromatic ring.[32] Lehn, in discussing pyramidal inversion, reports that ". . . delocalization of the nitrogen lone pair by conjugation diminishes the lone pair electron density and leads to a barrier *decrease*, through stabilization of the transition state."[8] Unlike imines, where both torsion and linear inversion can lead to isomerization, amines have no alternate or competitive route to pyramidal inversion for their change in geometry. According to Lehn, pyramidal nitrogen inversion and linear nitrogen inversion should show similar dependences on structural factors.[8] The logical conclusion here is that as the electron-withdrawing power of the substituent X grows, imine inversion is facilitated by increasing stabilization of the transition state (I).

When the imino carbon substituents Z and Z′ are electron donors, the *N*-aryl substituent X, as an electron withdrawer, will facilitate isomerization by both inversion and torsion; the respective transition states are illustrated by structures I and II. With X growing in



II

strength as an electron donor, neither inversion nor torsion is facilitated. Thus, when Z and Z′ are electron

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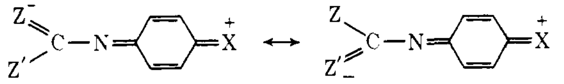
(31) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

(32) E. A. Jeffery, A. Meisters, and T. Mole, *Tetrahedron*, **25**, 741 (1969).

donors, the Hammett plots for both inversion and torsion would be expected to have a positive ρ as X is varied, so substituent effects do not distinguish mechanisms. With Z and Z′ as electron withdrawers, the situation changes. As the electron donor strength of X increases, isomerization by torsion is facilitated as indicated by transition-state structure III, whereas growing electron-withdrawing capacity of X facilitates the formation of the inversion transition state (I). Thus, when Z and Z′ are electron withdrawers, as is the case with the azomethine dyes as well as the hexafluoroacetone N-phenylimines of Hall, *et al.*,[28] torsion is expected to show a negative ρ and inversion a positive ρ in Hammett plots, so that substituent effects do distinguish between the two isomerization mechanisms.[33]



III

From the data presented here it is evident that introduction of methyl groups into the ortho positions of the aromatic ring attached to the azomethine nitrogen atom accelerates the rate of isomerization. Even though all rate constants increase in magnitude, there is no change in the character of the Hammett-type plots; the plots remain V-shaped with minima near σ equal to zero. As has been described above, Kessler has evidence for guanidinium salts, where only torsion is possible, that o-methyl groups retard isomerization and for guanidines, where both mechanisms are possible, that these same methyl groups enhance isomerization.[12-14] Kessler has concluded, therefore, that o-alkyl groups in N-arylimines hinder rotation and facilitate inversion. With azomethine dyes, by contrast, if our interpretation of data is correct, added methyl groups facilitate both torsion and inversion. It may be that methyl groups added to the ortho positions of the azomethine dyes with electron-donating substituents increase the contribution of inversion to the overall mechanism, but, even with these dyes, we believe torsion still makes the major contribution to the mechanism of isomerization.

Experimental Section

Materials. The benzoic acids, except for those listed specifically below, were Eastman reagent chemicals and were purified by multiple recrystallizations. p-Acetylbenzoic acid was purchased from Chemical Procurement Laboratories and N-phenylaminobenzoic acid was purchased from the Alfred Bader Division of the Aldrich Chemical Co.; both were purified by recrystallization. N,N-Diphenylamino-p-benzoic acid was synthesized according to the procedure of Gilman and Brown[34] and N,N-diethylamino-p-benzoic acid was synthesized according to the method of Seefelder.[35] The sensitizer, 7H-benz[*de*]anthracen-7-one, also was an Eastman chemical and was purified by recrystallization.

Dyes were synthesized either by oxidative coupling of benzoylacetanilide or 2-methyl-1-phenyl-2-pyrazolin-5-one with the appropriately substituted p-phenylenediamine, potassium ferricyanide being used as oxidizing agent, or by condensation of 1-phenyl-3-(N-phenylamino)propanetrione or 3-methyl-1-phenyl-2-pyrazoline-4,5-dione with the appropriately substituted aniline, utilizing boron trifluoride as catalyst.[36]

The benzene was Mallinckrodt Nanograde and was used as received.

Procedures. The pK's of the benzoic acids in 50% (by volume) aqueous ethanol were determined by reading at the half-neutralization points the pH scale of a pH meter (Corning Model 12) that uses glass and saturated calomel electrodes and had been calibrated for aqueous buffer solutions. No corrections for liquid junction potentials were made. Each of our pK values in Table I is the average of three determinations and is believed to be accurate within 0.1 pK unit.

Kinetic measurements were carried out on a conventional flash photoelectric apparatus. Two xenon flash lamps (Kemlite Z8H20) were positioned on opposite sides of a sample cell holder inside a cylindrical housing whose inside walls were coated with highly reflective paint (Eastman white reflectance paint). The energy of the flash discharge was 400 J (2-μF capacitor charged to 20 kV). The flash output returned to $^1/_3$ peak intensity within 15 μsec. The monitoring source was a quartz halide 100-W lamp (Osram 64625) powered by a regulated dc power supply (Sorensen QSB12-8). The lamp was mounted in an appropriate housing on an optical bench in series with a collimating lens, the flash chamber, a focusing lens, and a 0.25-m monochromator (Jarrell-Ash). The monitoring beam, after passing through the sample cell, was focused on the entrance slit of the monochromator. Light intensity as a function of time was measured by means of a photomultiplier tube (RCA 4463) located at the exit slit of the monochromator. The output from the photomultiplier was fed into a cathode-follower amplifier and then into a wide-band oscilloscope (Tektronix 555). Oscillographs were photographed with an oscillograph-record camera.

The cylindrical Pyrex-glass sample cells were 25 cm long and 15 mm o.d. with flat windows fused to the ends. The cells were connected by side arms to bulbs where solutions were contained during the degassing procedure. Solutions were degassed by subjecting them to several freeze–pump–thaw cycles on a high-vacuum manifold prior to sealing the sample containers.

The oscillographs were enlarged to facilitate more precise measurement of the transient phenomena. The lifetime of a transient species was measured by the recovery rate of the monitoring beam after the excitation flash. Kinetic analysis was by the method of Linschitz and Sarkanen.[37]

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