5° yielded colorless needles of 2-pyridone-6-alanine which were recrystallized from water to yield 1.07 g (58.6%). The analytical sample had mp 278–280° dec, λ_{max}^{Nujol} 6.15 μ. A ferric chloride test of this compound was negative, showing that the N–OH group had been removed.

Anal. Calcd for $C_8H_{10}N_2O_3$: C, 52.74; H, 5.53; N, 15.38. Found: C, 52.76; H, 5.69; N, 15.50.

Registry No.—1-Benzyloxy-4-methyl-2-pyridone, 16753-75-6; VI, 16753-76-7; VII, 16753-77-8; VIII, 16753-78-9; IX, 16753-79-0.

Color and Conformation in Pyrazolone Azomethine Dyes

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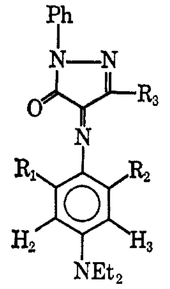
Pyrazolone azomethine dyes related to I and II are well known in color photography as image formers,[1] and are generated from pyrazolones and the *p*-phenylenediamines used as color developers through the action of silver ion as the oxidizing agent. The *p*-phenylenediamines usually employed are based upon 4-amino-N,N-diethylaniline and 4-amino-3-methyl-N,N-diethylaniline, and with these the dyes are magenta in hue, showing peak absorption near 520 nm in ethyl acetate. When, however, 4-amino-3,5-dimethyl-N,N-diethylaniline is used, the resulting dyes are cyan and absorb near 640 nm. The bathochromic shift of the absorption maximum is consistent with the twisting of a double bond in the conjugated system[2] and evidence has now been obtained from an nmr study that the developer-derived aromatic ring and the pyrazolone ring are not coplanar in these compounds.

Results

The nmr spectra of dyes I–IV have been determined at 100 MHz in deuteriochloroform solution and Table I gives the chemical shifts of the relevant aromatic protons and methyl substituents. From this it will be seen that in dyes II and III the aryl methyl group resonates at approximately 2.53 ppm whether the dye exists with the aromatic ring *syn* or *anti* with respect to the pyrazolone carbonyl group.[3] It may thus be assumed that the chemical shift of the methyl protons is determined largely by the electron density on the aromatic ring, rather than by any long-range shielding effects.

Table I

Chemical Shifts of *p*-Phenylenediamine Aromatic Protons and Methyl Substituents[a]



I, $R_1 = H_1$; $R_2 = H_4$; $R_3 = CH_3$
II, $R_1 = CH_3$; $R_2 = H_4$; $R_3 = CH_3$
III, $R_1 = CH_3$; $R_2 = H_4$; $R_3 = H$
IV, $R_1 = CH_3$; $R_2 = CH_3$; $R_3 = CH_3$

Dye	Chemical shift, ppm Ar–CH_3	H_1	H_4	H_2	H_3
I		8.29	8.29	6.67	6.67
II	2.53		8.92	6.57	6.50
III *syn*	2.50		8.92	*b*	*b*
III *anti*	2.53		7.65	6.60	6.54
IV	2.19			6.42	6.42

[a] Chemical shifts are expressed in parts per million (ppm) downfield from TMS as an internal reference. [b] Chemical shifts for these protons could not be obtained in the original analysis,[3] since the relevant signals were hidden under aromatic resonances from the other stereoisomer.

On introduction of the second methyl group (IV), the methyl resonance shifts to 2.19 ppm, corresponding to a shielding of 0.34 ppm; this is approximately twice the magnitude of the shifts undergone at the same time by the aromatic proton resonances, and is thus unlikely to be accounted for by electronic considerations alone. It should be noted that the introduction of the second methyl group produces the same effect on the aromatic proton resonances as the introduction of the first methyl group. It is thought that the observed shielding of the methyl groups is a consequence of their situation within the shielding cone of the pyrazolone carbonyl group.[4] If this assessment is correct, these observations constitute direct evidence for the nonplanarity of such dyes since, if they were planar, a large deshielding of the methyl groups by the carbonyl group would be expected. Such deshieldings have been observed[3] for the aromatic protons of planar members of this series of dyes, and are shown by R_2 in dyes I–III (*syn*). Examination of Courtauld models supports these findings, since it is revealed that, whereas coplanarity of the aromatic and pyrazolone rings can be achieved in dyes I–III, it is impossible for dye IV.

Discussion

The visible absorption spectra of pyrazolone azomethine dyes exhibit two maxima,[5] a low-intensity y band near 440 nm and an x band of higher intensity near 520 nm. It is known that the x bands of these dyes are solvent sensitive, shifting to longer wavelengths and becoming more intense with increasing solvent polarity.[5] This normally indicates that the resonance of the chromophoric system of the dyes is energetically asymmetric, the energy of the classical structure Va being lower than that of the dipolar extreme structure Vb.

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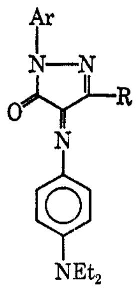
(1) C. E. K. Mees and T. H. James, Ed., "The Theory of the Photographic Process," 3rd ed, The Macmillan Co., New York, N. Y., 1966, Chapter 17.

(2) L. L. Ingraham in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 493.

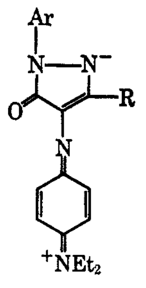
(3) P. J. S. Pauwels, *J. Amer. Chem. Soc.*, **89**, 580 (1967).

(4) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Ltd., London, 1959, p 122.

(5) G. H. Brown, B. Graham, P. W. Vittum, and A. Weissberger, *J. Amer. Chem. Soc.*, **73**, 919 (1951); W. F. Smith, Jr., *J. Phys. Chem.*, **68**, 1501 (1964).



Va



Vb

In terms of the present dyes, this indicates that the pyrazolinyl-N bond order is higher than that of the adjacent phenyl-N bond. Loss of coplanarity of the pyrazolone and phenyl rings, occasioned by overcrowding, might well be expected to occur by the twisting of the weaker of these bridge bonds, *i.e.*, the phenyl-N bond. Such twisting would, however, lower its bond order even more thus increasing the energetic asymmetry of the dye, and cause a shift to shorter wavelengths.

If, however, the overcrowding results in the twisting of the pyrazolinyl-N bond, a point can be reached at which the bond orders of both bridge bonds are identical or nearly so. A result of this would be an increase in the polarity of the dye chromophoric system and an approach to an isoenergetic resonance system. In this case introduction of the crowding substituent would cause a shift to longer wavelengths accompanied by a decrease in the intensity of the absorption resulting from a reduction in π electron overlap. Support for this proposition is provided by the fact that the molecular extinction coefficient falls from[5] about 36,000 to 12,000 (for IV in ethyl acetate) on introduction of the second methyl group.

The x band for the crowded dye (IV) is, however, at a longer wavelength (640 nm) than that expected for an isoenergetic resonance system of the structure. This can be calculated[6] as the mean of the peaks of the related symmetrical dyes of which the present dyes are hybrids, *i.e.*, 578 nm, the mean of the pyrazolone oxonol anion (437 nm) and the Bindschedler's Green analog (725 nm).

It is known however that in isoenergetic dyes, *e.g.*, symmetrical cyanines, any loss of coplanarity of the end nuclei caused by steric hindrance will result in a shift to longer wavelength accompanied by a decrease in intensity, the magnitude depending on the degree of twisting.[7-9] This same effect may be operative in the present case.[10]

Experimental Section

Dyes I-III were prepared as described elsewhere.[3] Dye IV was prepared, by the same procedure, from 1-phenyl-3-methylpyrazolone and 4-amino-3,5-dimethyl-N,N-diethylaniline. It was purified by recrystallization from ethanol.

Anal. Calcd for $C_{22}H_{26}N_4O$: C, 72.9; H, 7.18; N, 15.5. Found: C, 72.9; H, 7.47; N, 15.2.

Visible absorption spectra were measured on a Unicam SP800 spectrophotometer and nmr spectra were measured on a Varian HA-100 spectrometer.

Registry No.—I, 4595-01-1; II, 4719-41-9; III (*syn*), 14071-78-4; III (*anti*), 14071-79-5; IV, 4719-38-4.

Acknowledgment.—We thank Dr. P. W. Vittum of the Eastman Kodak Co. for supplying a generous sample of 4-amino-3,5-dimethyl-N,N-diethylaniline.

[6] L. G. S. Brooker, G. H. Keyes, R. H. Sprague, R. H. VanDyke, E. VanLare, G. VanZandt, F. L. White, H. W. J. Cressman, and S. G. Dent, Jr., *J. Amer. Chem. Soc.*, **73**, 5332 (1951).

[7] K. J. Brunings and A. H. Corwin, *ibid.*, **64**, 593 (1942).

[8] L. G. S. Brooker, F. L. White, R. H. Sprague, S. G. Dent, Jr., and G. VanZandt, *Chem. Rev.*, **41**, 325 (1947).

[9] R. A. Jeffreys and E. B. Knott, *J. Chem. Soc.*, 1028 (1951).

[10] Since this work was completed, molecular orbital calculations carried out by J. Figueras of the Eastman Kodak Co. (private communication) have indicated that the absorption characteristics of the hindered dye IV can be accounted for by a twist of approximately 40° about the pyrazolinyl-N bond. Twisting the phenyl-N bond would give rise only to a shift to shorter wavelengths. An alternative possibility is that twisting about both the pyrazolinyl-N and phenyl-N bonds occurs such that the relative amounts of twist are inversely proportional to the bond orders involved. Molecular orbitals based on such a doubly twisted model are also in agreement with observed spectral effects.

The Reaction of Azirines with Diazomethane to Produce Allylic Azides[1]

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As an extension of work carried out in this laboratory on the reactions of azirines,[2,3] it was considered of interest to determine the course of a cycloaddition reaction between diazomethane and representative azirines. 1,3-Dipolar cycloadditions of diazoalkanes to π bonds are well documented.[4,5] In particular, reaction of diazomethane with the C=C bond furnishes pyrazolines[6,7] and with the C=N bond, triazolines.[8] The related cycloaddition of azides to olefins gives triazoline adducts of varying stability.[9-14] Reported here is the reaction of diazomethane with the C=N in a three-membered ring,[15] the azirine system. The choice of the monomethyl azirine **1**, 3-methyl-2-phenyl-1-azirine, was dictated in part by the sluggish nature of the reaction with the dimethyl azirine **6**, 3,3-dimethyl-2-phenyl-1-azirine, and in part because the single substituent in the 3 position provided a marker for the ring carbon ($CHCH_3$) *vs.* the diazomethane carbon (CH_2) in following product formation.

When a chilled solution of diazomethane was added to a cold solution of 3-methyl-2-phenyl-1-azirine (**1**), both in ether, and the resulting solution was allowed to

[1] The support of this work by Research Grant GP-2012 from the National Science Foundation is gratefully acknowledged.

[2] N. J. Leonard and B. Zwanenburg, *J. Amer. Chem. Soc.*, **89**, 4456 (1967).

[3] N. J. Leonard, E. Muth, and V. Nair, *J. Org. Chem.*, **33**, 827 (1968).

[4] (a) R. Huisgen, *Angew. Chem.*, **2**, 633 (1963); (b) R. Huisgen, *Proc. Chem. Soc.*, 357 (1961).

[5] C. G. Overberger, N. Weinshenker, and J-P. Anselme, *J. Amer. Chem. Soc.*, **87**, 4119 (1965).

[6] T. V. van Auken and K. L. Rinehart, Jr., *ibid.*, **84**, 3736 (1962).

[7] R. J. Crawford and A. Mishra, *ibid.*, **87**, 3768 (1965).

[8] P. K. Kadaba and J. O. Edwards, *J. Org. Chem.*, **26**, 2331 (1961).

[9] L. Wolff, *Ann.*, **394**, 23, 59, 68 (1912).

[10] K. Adler and G. Stein, *ibid.*, **485**, 211 (1931); **501**, 1 (1933).

[11] G. D. Buckley, *J. Chem. Soc.*, 1850 (1954).

[12] G. Komppa and S. Beckman, *Ann.*, **512**, 172 (1934).

[13] L. H. Zalkow and C. D. Kennedy, *J. Org. Chem.*, **28**, 3303, 3309 (1963).

[14] P. Scheiner, J. H. Schomaker, S. Deming, W. J. Libbey, and G. P. Nowack, *J. Amer. Chem. Soc.*, **87**, 306 (1965).

[15] A. L. Logothetis, *J. Org. Chem.*, **29**, 3049 (1964).