The Configuration of Pyrazolone Azomethine Dyes

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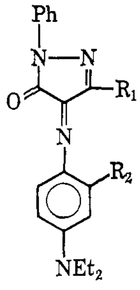
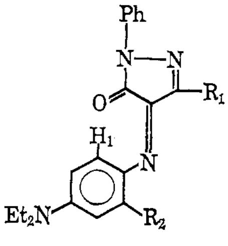
Abstract: Evidence from an nmr study confirms that pyrazolone azomethine dyes exist with the *p*-phenylenediamine ring *syn* to the pyrazolone carbonyl group when there is a 4-methyl substituent present. In the absence of a 4-substituent, the dyes exist as a mixture of *syn* and *anti* forms with the latter predominating. In dyes formed from 4-amino-N,N-diethylaniline, the *p*-phenylenediamine ring "flips" over between two planar conformations.

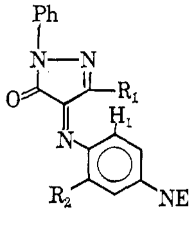
Pyrazolone azomethine dyes such as I are of great importance as magenta image formers in color photography.[1] As a consequence of this they have been much studied[2,3] with a view to determining the effects which structural changes have upon their visible spectra. No nuclear magnetic resonance studies have been reported, however, and it is the purpose of this paper to present the results of such an investigation.



I



IIa



IIb

III, $R_1 = CH_3$; $R_2 = H$
IV, $R_1 = CH_3$; $R_2 = CH_3$
V, $R_1 = H_1$; $R_2 = H$
VI, $R_1 = H$; $R_2 = CH_3$

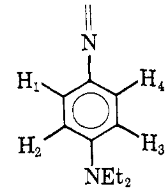
Two configurations (*IIa* and *IIb*) are possible for pyrazolone azomethine dyes as a result of the departure of the =N— bond angle from 180°. From a study of the effects of solvents upon their visible spectra, it has been concluded[2] that the dyes adopt the *syn* configuration (IIa) except when $R_1 = H$, in which case the alternative *anti* configuration (IIb) is preferred. The results of some more recent molecular orbital calculations[3] are in agreement with this conclusion, but no direct experimental evidence supporting it has yet been presented. The presence of a carbonyl group in the molecule, with its associated[4] long-range shielding effect, makes the dyes particularly susceptible to study by nmr for determining their configuration.

Results

The dyes are thought[2] to adopt a conformation in which the pyrazolone and *p*-phenylenediamine rings are coplanar, which would account for their color. If dyes in the *syn* configuration adopt such a conformation, one proton (H_1, IIa) will be close to and coplanar with the carbonyl group and should thus experience a deshielding effect, causing it to resonate at lower field than the other aromatic protons. The corresponding proton in the *anti* configuration (H_1, IIb) would not be close to the carbonyl group and no deshielding would be expected. On the basis of this argument it should be possible to distinguish between dyes in the *syn* and *anti* configurations by observing whether or not low-field signals are present in their nmr spectra.

Four dyes (III–VI) have been selected, and their nmr spectra have been determined at 60 Mc/sec in deuteriochloroform in order to test this hypothesis. The chemical shifts and coupling constants of the *p*-phenylenediamine aromatic protons are summarized in Table I. The spectrum of dye IV showed a low-field signal (intensity 1H) centered at 8.92 ppm downfield from internal tetramethylsilane, and on full analysis this was found to constitute the X part of an ABX spectrum, the AB part being centered at 6.54 ppm. The coupling constants extracted from the spectrum indicated that the low-field signal was due to H_1, and that this was coupled to H_2 and H_3.

Table I. Nmr Parameters of *p*-Phenylenediamine Aromatic Protons[a]



Dye	Chemical shift				Coupling constant		
	δ_1	δ_2	δ_3	δ_4	$J_{1,2}$	$J_{2,3}$	$J_{1,3}$
III	8.29	6.67	6.67	8.29	9	3	0
IV	8.92	6.50	6.57	...	9	3	1
V (*syn*)	8.34	6.60	6.66	8.34	~9	?	?
(*anti*)	7.49	6.68	6.68	7.49	~9	?	?
VI (*syn*)	8.92	?	?	...	~9	?	?
(*anti*)	7.65	6.54	6.60	...	9	3	1

[a] Chemical shifts are expressed in ppm downfield from TMS as internal reference.

Examination of the spectrum from dye III also revealed a low-field signal, but this had an intensity corresponding to two protons, which were coupled with two more protons resonating at high field to give an AA'XX' spectrum. By analysis[5a] of this spectrum to

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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] G. H. Brown, B. Graham, P. W. Vittum, and A. Weissberger, *J. Am. Chem. Soc.*, **73**, 919 (1951).

[3] W. F. Smith, Jr., *J. Phys. Chem.*, **68**, 1501 (1964).

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

[5] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press Ltd., Oxford, England, 1965: (a) p 392; (b) p 552; (c) p 482.

yield the coupling constants, and by analogy with dye IV, the low-field portion of the spectrum had to be assigned as being generated by protons H_1 and H_4 (see Table I). The significance of this observation will be discussed later.

The spectrum of dye V provided good evidence for the existence of the compound in two forms, presumed to correspond to the *syn* and *anti* configurations. Three quasi-doublet signals of unequal intensity were of interest, and these were centered at 6.66, 7.49, and 8.34 ppm. A double resonance experiment conducted at 100 Mc/sec facilitated the interpretation of this spectrum. On irradiation at the frequency of the 6.66-ppm protons, the signals centered at 7.49 and 8.34 ppm collapsed to singlets. However, on irradiation in turn at the frequencies of the 7.49- and 8.34-ppm protons, the signal at 6.66 ppm was only partially collapsed. In both cases a new singlet appeared (at 6.68 and 6.66 ppm, respectively), but the original pattern did not disappear completely, although it was greatly reduced in intensity. This behavior can be interpreted on the basis of a mixture of isomers, one giving rise to an AA′XX′ spectrum with components at 6.68 and 7.49 ppm and the other to a similar pattern at 6.66 and 8.34 ppm. Irradiation at the frequencies corresponding to the 7.49- or 8.34-ppm protons would then cause only the collapse of that part of the 6.66-ppm signal due to protons in the same molecule as those being irradiated. Further support for the existence of two forms was provided by an examination of the quadruplet due to the methylene protons of the N-ethyl groups. At 100 Mc/sec two quadruplets of unequal intensity centered at 3.41 (strong) and 3.44 ppm (weaker) could be observed; these can be ascribed to methylene protons in different compounds.

The spectrum of dye VI again provided evidence for the existence of two isomers although, in this case, one of them was present in only small amounts, as evidenced by the occurrence of a very weak signal centered at 8.92 ppm. The major component of the mixture gave rise to an ABX pattern centered at 6.57 and 7.65 ppm.

Discussion

The two dyes (III and IV) expected to exist in the *syn* configuration give rise to low-field signals at 8.29 and 8.92 ppm for proton H_1. This observation is in accord with the predicted effect of the pyrazolone carbonyl group in causing a downfield shift. One form of each of dyes V and VI also gives rise to a low-field signal (at 8.34 and 8.92 ppm), but the corresponding signals in the second form of these dyes occur at higher field (7.49 and 7.65 ppm). The isomers of V and VI responsible for the low-field signals can be assigned the *syn* configuration, leaving the other isomers (in each case the major component of the mixture) as having the *anti* configuration. It is not known whether the relative intensities of the signals corresponding to the different isomers are significant, because the chromatographic purification technique used could have affected the balance. It is noteworthy, however, that there was much less of the *syn* isomer of VI than of V, and this might be a reflection of the steric demands of the aromatic methyl group present in VI but not in V.

An observation of interest concerning the conformations adopted by the dyes is that protons H_1 and H_4 in dyes III and V are equivalent and give rise to the low-field portions of AA′XX′ spectra. This equivalence necessarily implies that both protons are subject to the same deshielding effects, and, if these originate in the diamagnetic anisotropy of the carbonyl group, the spectra are not easily accounted for on the basis of the accepted fixed planar conformation for the dyes. To account for this equivalence either the *p*-phenylenediamine ring must be in a plane perpendicular to that of the pyrazolone ring, so that H_1 and H_4 are symmetrically disposed with respect to the carbonyl group, or it must be undergoing rotation about the =N—Ar bond at a sufficient rate to average the chemical shifts of the two protons. Both of these situations appear at first sight to be difficult to reconcile with the colored nature of the compounds; however, it should be noted that 4-oximino-5-pyrazolones are strongly colored.[6]

The proposition that the *p*-phenylenediamine ring lies in a plane perpendicular to the pyrazolone ring can be regarded as unlikely in view of the fact that in such circumstances the carbonyl group would not be expected to exert a very large deshielding effect on H_1 and H_4 since they would no longer be coplanar with it. The magnitude of the deshielding effect, which can be estimated by comparing the chemical shifts of H_1 in the *syn* and *anti* forms of dyes V and VI, provides some evidence that rotation does in fact take place. For dye V the resonance of H_1 shifts by 0.85 ppm in going from the *syn* to the *anti* form, whereas in dye VI the corresponding shift is 1.27 ppm. Now, in dye VI, H_1 would be expected to occupy the position close to the carbonyl group depicted in IIa (R_2 = CH_3), since examination of molecular models indicates that complete rotation about the =N—Ar bond is prevented by the presence of the aromatic methyl substituent; it would therefore experience the full deshielding effect of the carbonyl group. In dye V, where the models do permit rotation, the chemical shift observed for H_1 will be that resulting from the averaging of those of H_1 and H_4 if the molecule were held in a fixed planar conformation. The carbonyl group will exert little influence on the chemical shift of H_1 in the *anti* forms of V and VI, so that the larger *syn–anti* shift is to be expected for VI if there is rotation in V.

Additional evidence in favor of the rotational model for dyes III and V may be obtained by calculating the expected value for the chemical shifts of H_1 and H_4 in these compounds. This may be done by taking the mean of the chemical shifts observed for H_1 in dyes IV and VI (*syn*), where it experiences the full effect of the carbonyl group, and in dye VI (*anti*), where this effect is at a minimum. The value of 8.29 ppm obtained in this way corresponds well with the values of 8.29 and 8.34 ppm observed for H_1 and H_4 in dyes III and V (*syn*), respectively. Furthermore, the chemical shift difference of 1.27 ppm for H_1 between dyes IV and VI (*syn*), on the one hand, and VI (*anti*), on the other, enables the minimum rate of rotation at room temperature for the observance of averaging to be calculated[5b] at 27 sec^{-1}.

The proposition that rotation about the =N—Ar bond exists is potentially capable of being tested by ob-

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[6] R. H. Wiley and P. Wiley in "The Chemistry of Heterocyclic Compounds," A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 85.

serving the nmr spectra of dyes III and V at low temperatures when it might be expected that the rotation would be slowed sufficiently to inhibit the averaging process. The spectra of III and V have been determined at −60° in deuteriochloroform, but in neither case was any change in the AA′XX′ pattern observed. This information enables the maximum possible height of the energy barrier to free rotation to be estimated at about 10 kcal.[5c]

An acceptable model for the dye molecules under consideration would seem to be that they exist in a planar conformation, thus accounting for the observed deshielding effect of the carbonyl group, but that the *p*-phenylenediamine ring "flips" over rapidly between the two positions in which it is coplanar with the pyrazolone ring. The preference for the planar conformation, rather than the less hindered conformation in which the *p*-phenylenediamine ring is perpendicular to the rest of the molecule, suggests that it is stabilized by resonance.

Experimental Section

3-Methyl-1-phenylpyrazolin-5-one and 4-amino-3-methyl-N,N-diethylaniline were obtained from Eastman Kodak Co., and 4-amino-N,N-diethylaniline was purchased from May and Baker Ltd. 1-Phenylpyrazolin-5-one was prepared from 1,1,3,3-tetraethoxycarbonylpropene[7] and phenylhydrazine according to the procedure of Ruhemann and Morrell.[8]

Dyes III–VI were prepared using the method previously described[9] for the preparation of indoanilines and since used[2] for the preparation of these pyrazolone azomethine dyes. They were purified by plc on silica gel.

The 60-Mc/sec spectra were run on a Varian A-60A spectrometer and the 100-Mc/sec spectra on a Varian HA-100 spectrometer.

Acknowledgments. The author is indebted to Dr. J. Feeney of Varian Associates Ltd. for facilities in carrying out this work, and to Miss A. Heinrich for running some of the spectra.

(7) C. K. Ingold and E. A. Perren, *J. Chem. Soc.*, 119, 1582 (1921).

(8) S. Ruhemann and R. S. Morrell, *ibid.*, 61, 791 (1892).

(9) P. W. Vittum and G. H. Brown, *J. Am. Chem. Soc.*, **68**, 2235 (1946).

Conformational Analysis of Bridgehead Carbonium Ions

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Abstract: Solvolysis rates of bridgehead substituted polycyclic bromides vary over 12 powers of ten. A computer conformational analysis of these systems shows that this variation can be accounted for satisfactorily in terms of the increase of strain in going from ground to transition state. For five substrates, *t*-butyl, 3-homoadamantyl, 1-adamantyl, 1-bicyclo[2.2.2]octyl, and 1-norbornyl, the average deviation of the rates calculated from the experimental values was $10^{\pm 0.8}$. This deviation is extremely creditable in view of the numerous simplifying assumptions which had to be made in carrying out the computations. The ground states were approximated by the parent bridged hydrocarbons, and the transition states by the corresponding carbonium ions. The energy minimization program developed by Wiberg and Harris was employed. The chief modifications were the use of "harder" nonbonded potential functions and necessary changes owing to the presence of the charged sites in the carbonium ions. Meaningful results were obtained only when the $C-C^+-C$ bending force constants were at least four times "stiffer" than the normal C–C–C values. Although the most important effect influencing brideghead solvolysis rates, according to this analysis, is increase in angle strain during ionization, other effects cannot be dismissed. In particular, a large measure of the 5000-fold rate difference between solvolysis rates of 1-adamantyl and 1-bicyclo[2.2.2]octyl bromides is due to the development of very unfavorable nonbonded $C_1 \cdot\cdot C_4$ interactions in the latter case on going to the ion. Solvolysis rates of three systems have been predicted, the 1-homoadamantyl, the 1-bicyclo[3.3.1]nonyl, and the 1-bicyclo[3.2.1]octyl.

Many effects govern organic chemical reactivity. These can be divided into two main classes depending on their electronic or steric origin. Electronic effects, such as inductive and resonance interactions, are now commonly treated quantitatively, by empirical or by quantum mechanical approaches.[2] Steric effects, by contrast, are seldom evaluated precisely, despite the availability of a body of attractive theory.[3] There exist, however, simple and often highly empirical correlations of steric effects with chemical reactivity.

An especially pertinent example is the relationship observed by Foote[4] between the rate of unassisted solvolyses of certain secondary tosylates and the carbonyl frequency of the corresponding ketones. The rational behind this correlation is that both carbonyl stretching frequencies and tosylate solvolysis rates should be some (not necessarily the same) function of bond angle, and they should therefore be related to one another. In other words, solvolysis rates should depend on angle strain,[3] and ketone carbonyl frequencies are a convenient method of evaluating this strain.

The Foote relationship applies to a limited number of cases where only angle strain factors affect reaction rates significantly. In order to generalize this ap-

(1) Alfred P. Sloan Foundation Fellow, 1962–1966.

(2) A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1961.

(3) H. C. Brown, *J. Chem. Soc.*, 1248 (1956). *Cf.*, however, R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13.

(4) C. S. Foote, *J. Am. Chem. Soc.*, **86**, 1853 (1964).