Acid Strengths of Various Substituted Formazans in Ethanolic Solution

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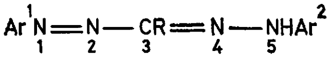
The acid strengths, pK_{ae}, of a number of substituted 1,5-diarylformazans have been determined by spectrophotometric titration with sodium ethoxide in ethanol. For the yellow non-intramolecularly hydrogen-bonded isomers, with alkyl and chloro-substituents in the 3-position, $pK_{ae} \simeq 18.0$—19.0. 1,5-Diphenylformazan is substantially more acidic ($pK_{ae} = 16.5 \pm 1.0$), and methyl substituents in the 1- and 5-aryl groups have the small but positive effect of lowering the acid strength. Triarylformazans exist substantially as the red intramolecularly hydrogen-bonded isomers, and are generally too weakly acidic for titration with sodium ethoxide.

Evidence for intramolecular hydrogen bonding when a 3-nitro-group is present, and also for the existence of tautomeric forms of 3-diphenylmethylformazans has been obtained.

FORMAZANS (1) have intense colours ($\varepsilon > 10^4$ mol^{-1} cm^{-1}) and it has been shown that the H atom on N-5 has very weakly acidic properties.[1–3] This work was initiated in an attempt to assess a number of formazans as potential acid–base indicators for titrations in liquid ammonia. Exploratory work indicated that, with a few exceptions, the colours of formazan solutions in water–organic solvent mixtures cannot be changed by mere addition of hydroxide ions, whereas many formazans in dry ethanolic solution undergo marked colour changes on addition of the more basic ethoxide ion. Thus the formazans, too weakly acidic to be titrated in aqueous media, can be titrated in the more basic ethanol. Preliminary experiments also showed that titrations were possible in methanolic solution, but that much higher concentrations of methoxide were required to effect the same degree of ionisation of the formazan molecule. That the formazans behave as monoprotic acids is evident from the formula[1] of bis-(3-methyl-1,5-diphenylformazanido)nickel and its crystal structure.[4]



$$\mathrm{Ar^1}\underset{1}{\mathrm{N}}{=}\underset{2}{\mathrm{N}}{-}\underset{3}{\mathrm{CR}}{=}\underset{4}{\mathrm{N}}{-}\underset{5}{\mathrm{N}}\mathrm{HAr^2}$$

(1)

Geometrical isomerism about the two double bonds in

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[1] H. M. N. H. Irving, J. B. Gill, and W. R. Cross, *J. Chem. Soc.*, 1960, 2087.

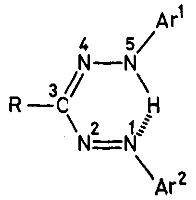
[2] G. A. Sereda, R. I. Ogloblina, V. N. Podchainova, and N. P. Bednyagina, *Zhur. analyt. Khim.*, 1968, **23**, 1220.

[3] H. M. N. H. Irving and C. F. Bell, *J. Chem. Soc.*, 1953, 3542; 1954, 4253.

[4] D. Dale, *J. Chem. Soc.* (*A*), 1967, 278.

the formazan nucleus (1) provides for four discrete structures.[5] The two with a *cis*-configuration (2) about the 3,4-bond are red in solution with an absorption band at *ca.* 490 nm. The yellow solutions of the two isomers with the *trans*-configuration (3) absorb at *ca.* 420 nm. It has been established [6] that the ν(N–H) bands observed in the i.r. between 3 200 and 3 300 cm^{-1} result from only the open yellow *trans*-isomers.

The 1,3,5-triarylformazans are stable in the red *cis*-form,[7] and absorb at the lower frequency, *ca.* 3 010 cm^{-1}, attributable to a modified N–H · · · N stretching vibration. Unfortunately this comparatively weak ν(NH) band is masked by the ν(CH) vibration region and is of little value in the examination of a wide variety of formazans. Thus formazans stable in the red form possess a *cis*-configuration about the 3,4-bond with the internally hydrogen-bonded structure (2) as the more stable arrangement. This is well supported by their physical properties, and by the similarity of the absorption spectra of the metal–formazan complexes to those of the parent ligand molecules.[1,8]



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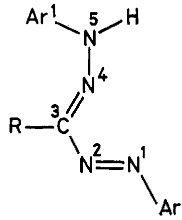

(3)

EXPERIMENTAL

Titrations.—The pK_{ae} values of titratable formazans were obtained by spectrophotometric titration with ethoxide solutions (K_{ae} is the dissociation constant of a formazan acid referred to the pH_{et} scale of ethanol whose autoprotolysis constant,[9] pK_{et}, is 19.14 at 298 K). Addition of ethoxide to formazan solutions caused replacement of the intense band at *ca.* 415—420 nm (due to the yellow isomer) by a more intense band at *ca.* 505—515 nm (due to the formazanide anion). The spectroscopic titrations gave good isosbestic points (for an example see Figure 1).

Beer–Lambert law plots for the undissociated formazans in ethanol provided evidence for the stability, or otherwise, of the various isomers in solution and also the means by which the concentration of undissociated yellow formazan isomer could be followed in a titration mixture. A set of absorption curves for a series of solutions, each of which contained the same concentration of formazan (*ca.* 2.5×10^{-5}M) at a different pH_{et} value was recorded. The pK_{ae} of each acid was determined from the equation $pK_{ae} = pH_{et} + \log([FH]/[F^-])$; pH_{et} was available from the known ethoxide concentration and the ionic product of ethanol.

Solutions of sodium ethoxide at *ca.* 0.2M concentration were the most suitable titrants. Freshly cut sodium (1.5 g) was dissolved in ethanol (400 ml). The resulting solution was diluted with ethanol to the desired concentration. Ethoxide solutions were freshly prepared for each titration and standardised against an aqueous solution of twice-crystallised sulphamic acid (a fresh solution was used for each standardisation). For each solution used in the spectrophotometric titrations a standard formazan solution in ethanol was diluted ten-fold by addition of a measured sample of standard ethoxide and diluent ethanol. Spectra were recorded as soon as possible after mixing with the appropriate ethoxide solution in the reference cell.

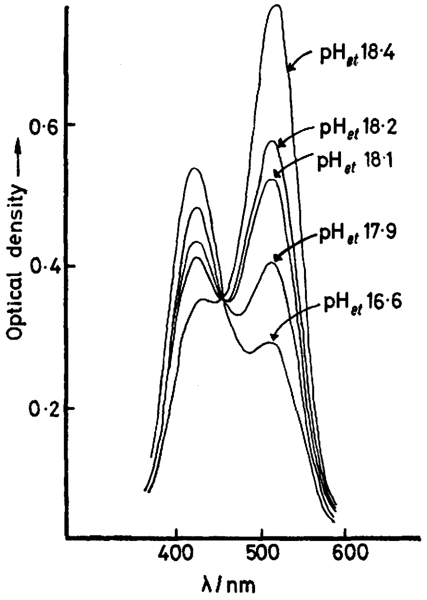

FIGURE 1 Spectroscopic titration of 3-methyl-1,5-diphenylformazan with 0.25M-sodium ethoxide in ethanol; [formazan] 2.40×10^{-5}M

The pK_{ae} value of a formazan was taken as the average of the results from its spectrophotometric titration. To ensure a small spread of results and minimal errors from the estimation of concentrations in anionic and molecular forms, [FH] and [F^-] must be approximately equal when pK_{ae} is similar in magnitude to pH_{et}. Although the method was most efficacious when pK_{ae} was similar to pH_{et}, this requirement imposed the serious limitation that the ionic strength of the background could not be held constant. Also with these concentration conditions and absorption band positions the overlap of the two absorption bands due to the undissociated and anionic forms was appreciable. Accordingly a manual curve analysis was carried out to estimate the contribution of the 505 nm band to the observed optical density of the 425 nm band, to determine the true concentration of undissociated formazan.

Table 1 shows results of two titrations of 3-methyl-1,5-diphenylformazan. The other titratable formazans were studied similarly. Results within a titration were found to be reproducible to within 0.5 pK_{ae} units and are accordingly quoted to within ±0.3 pK_{ae} units in Table 2.

Visible spectra of solutions were obtained with a Unicam SP 700A spectrophotometer, and i.r. spectra of all compounds (in KCl discs) were recorded between 2 000 and

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[5] R. Kuhn and D. Jerchel, *Chem. Ber.*, 1949, **82**, 515.

[6] A. Foffani, C. Pecile, and S. Ghersetti, *Tetrahedron Letters*, 1959, **11**, 16.

[7] G. Arnold and C. Schiele, *Spectrochim. Acta*, 1969, **25A**, 685.

[8] L. Hunter and C. B. Roberts, *J. Chem. Soc.*, 1941, 820.

[9] P. Danner, *J. Amer. Chem. Soc.*, 1922, **44**, 2832.

4 000 cm^{-1} with a Perkin-Elmer 457 grating spectrophotometer. Additional i.r. spectra were recorded for either hexachlorobutadiene mulls or solutions in carbon tetrachloride.

Dry ethanol was obtained by refluxing absolute ethanol over magnesium turnings for 12 h followed by immediate distillation in an apparatus protected from atmospheric moisture.

Two new formazans were prepared in this work; others were prepared by methods cited in Table 2.

3-*Diphenylmethyl*-1,5-*diphenylformazan*.— Diphenylacetaldehyde phenylhydrazone [from phenylhydrazine (100 mmol) and diphenylacetaldehyde (100 mmol) in ethanol (30 ml)] was dissolved in acetone (100 ml) and ethanol (100 ml). To this solution was slowly added at 0 °C a solution prepared from aniline (100 mmol), conc. hydrochloric acid (100 ml), water (25 ml), and sodium nitrite (100 mmol). The tarry product was recrystallised several times from ethanol to give a low yield of the *formazan* (Found: C, 79.2; H, 5.6; N, 14.2. $C_{26}H_{22}N_4$ requires C, 80.0; H, 5.6; N, 14.4%).

TABLE 1

Spectrophotometric titration data for 3-methyl-1,5-diphenylformazan with sodium ethoxide in ethanol

OD	OD$_{corr.}$	10^5[FH]/M	10^5[F$^-$]/M	log ([FH]/[F$^-$])	[NaOEt]/M	pH$_{et}$	pK_{ae}
Titration I							
0.35	0.27	1.03	1.37	−0.13	0.199	18.44	18.31
0.42	0.34	1.30	1.10	0.07	0.120	18.22	18.29
0.44	0.38	1.45	0.95	0.18	0.099	18.14	18.32
0.49	0.44	1.68	0.72	0.37	0.061	17.92	18.29
0.54	0.54	2.04	0.36	0.75	0.030	17.62	18.37
Standard solution:† formazan 2.40 × 10^{-4}M, ethoxide 0.25M							
Titration II							
0.35	0.19	0.70	1.41	−0.30	0.307	18.63	18.33
0.37	0.29	1.10	1.01	0.04	0.186	18.41	18.37
0.37	0.25	0.97	1.14	−0.07	0.154	18.33	18.26
0.45	0.45	1.71	0.40	0.63	0.046	17.80	18.43
Standard solution:† formazan 2.11 × 10^{-4}, ethoxide 0.34M							

† In preparation of the titration solutions a ten-fold dilution of standard solution was effected.

TABLE 2

Spectral and pK_{ae} data of substituted formazans in ethanol

Substituted Formazan				Band maxima					
3 R	1 Ar^1	5 Ar^2	Ref.	λ_1/nm *	λ_2/nm *	ν(N–H)/cm^{-1}	Colour of ethanolic solution	pK_{ae} (spectrophotometric titration)	pK_{ae} (colour change method)
Me	Ph	Ph	1, *a*	415 (2.62)		3 295ms	Yellow	18.3	18.4 ± 1.0
Et	Ph	Ph	5	420 (1.90)		3 270m	Yellow	18.6	18.4 ± 1.0
Cl	Ph	Ph	3	420 (2.77)		3 250mw	Yellow	18.3	18.5 ± 1.0
Me	*p*-MeC$_6$H$_4$	*p*-MeC$_6$H$_4$	1, *a*	425 (2.48)		3 240ms	Yellow	18.5	18.6 ± 1.0
m-NO$_2$·C$_6$H$_4$	Ph	Ph	*b*		490s, 540w	Absent	Red	19.1	
p-NO$_2$·C$_6$H$_4$	Ph	Ph	*b*	400s	490s	3 190w	Red		18.8 ± 1.0
H	Ph	Ph	1	405s	465s	Absent	Orange-yellow		16.5 ± 1.0
(Ph)$_2$CH	Ph	Ph			470	3 330w	Red		18.8 ± 1.0
CN	Ph	Ph		440 (2.11)	540w	3 220m	Yellow	Not titratable	
Ph	Ph	Ph	*c*		490s, 530w	Absent	Red		
p-MeC$_6$H$_4$	Ph	Ph	1		480s, 550w	Absent	Red		
NO$_2$	Ph	Ph	*d*		450 (21.4)	Absent	Red		

* For bands with no contribution to band intensities from other bands due to formazan isomers, values of $\log_{10} 10^{-4}$ ε/l mol^{-1} cm^{-1} are quoted in parentheses.

[a] M. Ragno and S. Bruno, *Gazzetta*, 1946, **76**, 485. [b] M. Busch and H. Pfeiffer, *Ber.*, 1926, **59**, 1162. [c] A. M. Mattison, C. O. Jensen, and R. A. Dutcher, *J. Amer. Chem. Soc.*, 1948, **70**, 1284. [d] F. Bamberger, *Ber.*, 1894, **27**, 155.

3-*Cyano*-1,5-*diphenylformazan*.—Potassium cyanoacetate was produced by refluxing methyl cyanoacetate (100 mmol) and potassium hydroxide (110 mmol) in ethanol for several hours. A diazonium chloride solution at 0 °C, prepared from aniline (200 mmol), conc. hydrochloric acid (50 ml), water (50 ml), and sodium nitrite (200 mmol), was made just basic with potassium hydroxide and added slowly to the basic ethanolic cyanoacetate (100 mmol). Recrystallisation of the precipitate from ethanol gave bronze *plates* (Found: C, 67.1; H, 4.4; N, 28.1. $C_{14}H_{11}N_5$ requires C, 67.6; H, 4.4; N, 28.1%).

DISCUSSION

The positions of maximum absorption listed in Table 2 show that some formazans are present entirely as the yellow *trans*-isomer, others as the red *cis*-form, and some as an equilibrium mixture of the two [(2) $\rightleftharpoons$ (3)]. The position of this equilibrium in solution [1] is solvent-dependent, as shown, for example, in Figure 2. The shoulder at *ca.* 480—500 nm on the higher wavelength side of the maximum indicates the presence of the red isomer. The proportion of red isomer is high in benzene (B) and carbon tetrachloride (D), less than 20% in pyridine (C), and very small in ethanol (A). Thus the choice of ethanol as the titration medium ensured that, for the first four members of Table 2, it was the yellow *trans*-isomer for which the pK_{ae} values were being determined.

The spectra of the corresponding red-pink formazanide anions showed sharply defined peaks in the 500—520 nm region with larger extinction coefficients (log ε 4.7—4.8) than those of the undissociated yellow formazan molecules.

The formazans stable only as their red isomers (the last group of Table 2) were not titratable even in very strong ethoxide solutions. It is thus clear that the formazan nucleus in the intramolecularly hydrogen-bonded form possesses little tendency to protonate even very basic species.

Solutions of formazans (1) in which R = alkyl, Cl, CN, or NO_2 showed absorption peaks at *ca.* 420 nm. The absence of intramolecular hydrogen bonding in 3-methyl-, 3-ethyl-, and 3-chloro-1,5-diphenylformazans was indicated by the medium intensity ν(N–H) vibrations at 3 295, 3 270, and 3 250 cm^{-1}, respectively.

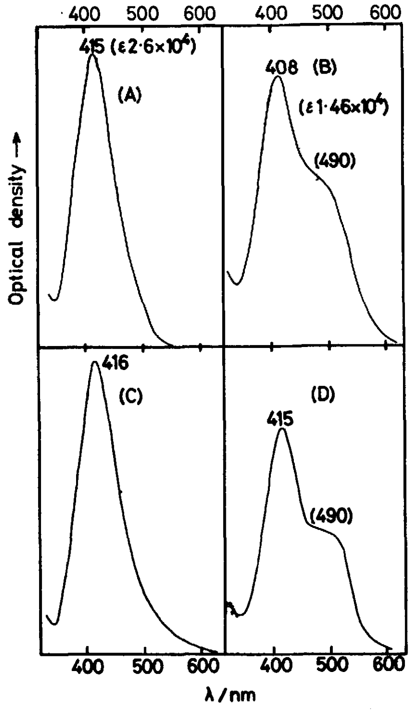


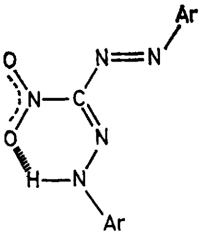
FIGURE 2 Visible absorption spectra of 3-methyl-1,5-diphenylformazan in (A) ethanol, (B) benzene, (C) pyridine, and (D) carbon tetrachloride

Not surprisingly, 1,5-diphenylformazan (1; $Ar^1 = Ar^2 = Ph$, R = H) behaved differently from the other members of the series. In ethanol, addition of ethoxide caused a striking colour change from yellow-orange to deep violet. In neutral ethanol two separate bands at 405 and 465 nm, with time-independent relative absorbances, indicated a stable equilibrium between yellow and red forms. As the pH_{et} value of these solutions was raised by addition of ethoxide, a band at 540 nm (due to the violet 1,5-diphenylformazanide) appeared, with concurrent disappearance of the band at 405 nm. The band due to the red isomer remained throughout the titration, indicating that it was the yellow *trans*-isomer which was being titrated. Determination of the pK_{ae} value by the method used for the other yellow formazan isomers was impossible because of the contribution to the intensity of the band at 405 nm from the band centred at 465 nm due to the red form. Also as the titration proceeded the titrated yellow form appeared to be continually replaced by the red form. The pK_{ae} value of this formazan was estimated by assuming that the colour change which occurred on addition of ethoxide ion would take place over about one unit of pH_{et}. (This is reasonable when applied to titrations with indicators in aqueous solution.) The concentration of ethoxide ion (0.44M) required to bring 1,5-diphenylformazan mid-way through its colour change corresponded to $pH_{et} = 16.5$. Accordingly we suggest a value of $pK_{ae} = 16.5 \pm 0.5$. The validity of this method of estimation was verified by the comparison of its results for 3-methyl-, 3-ethyl-, and 3-chloro-1,5-diphenylformazans with those obtained from spectrophotometric titrations as shown in Table 2.

The order of pK_{ae} values in the homologous 1,5-diphenylformazan series with R = H, Me, or Et follows the characteristic trend shown by the simple aliphatic carboxylic acids in aqueous solution. When the series is extended to include the 3-chloro-compound ($pK_{ae} = 18.3$), comparison with the comparatively strong chloroacetic acid ($pK_a = 2.91$) indicates that this formazan occupies an anomalous position. For aqueous solutions of carboxylic acids the effect is commonly attributed to the increasing electron donor characteristic of alkyl substituents and the corresponding loss of stability of the anion with respect to the neutral molecule, making the loss of a proton energetically less favourable. The anion of chloroacetic acid is stabilised with respect by the electron-withdrawing capacity of the chloro-substituent, acting as before through the orbitals of σ-symmetry to produce an acid much stronger than acetic acid. On the other hand, 3-methyl- and 3-chloro-1,5-diphenylformazans are of approximately equal strength for, in this case, the delocalised π-orbital system of the formazan nucleus may interact much more readily with orbitals of suitable symmetry on the substituent in the 3-position and so stabilise the neutral molecule with respect to its anion by means of a ' back-bonding ' effect.

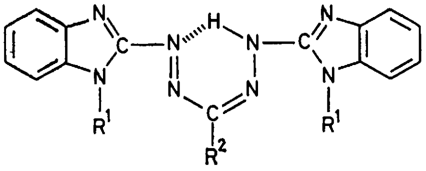
The availability of low-lying, antibonding π molecular orbitals of 3-NO_2 and -CN substituents can be used to account for the very weakly acidic character of the 3-cyano- and 3-nitro-1,5-diphenylformazans. 3-Cyano-1,5-diphenylformazan showed a medium intensity ν(NH) band at 3 220 cm^{-1} indicating that it exists in the yellow *trans*-form in ethanol. The visible spectrum showed a barely discernible shoulder in the 540 nm region (red *cis*-isomer) which had increased in intensity after the dilute solution had been left for 12 h. This suggests a high activation energy of transition between the red and the yellow isomers. No ν(N–H) band was observed for the 3-nitro-compound, and as the visible spectrum indicated the molecule to be in the yellow *trans*-form it is concluded that this formazan is stabilised in a molecular non-titratable form by intramolecular hydrogen bonding with the nitro-group (4).

It has been reported[10] that red rather than yellow isomers of 3-arylformazans are thermodynamically stable in ethanol. We detected no ν(N–H) bands in i.r. spectra of the four triarylformazans and conclude that these exist in the intramolecularly hydrogen-bonded form (2). The large difference in the intramolecular hydrogen-bond energies of 29.2 and 11.3 kJ mol^{-1} for 1,3,5-triphenyl- and 1,5-diphenyl-formazan has been attributed to conjugation by the 3-phenyl group with other groups in the molecule.[11] A more attractive alternative explanation lies in the absence of hydrogen bonding in the yellow *trans*-1,5-diphenylformazan and the corresponding partial contribution to the molecular heat of combustion by the intramolecular hydrogen bond of the red *cis*-isomer.



(4)

The intramolecularly hydrogen-bonded 1,3,5-triphenyl- and 3-*p*-chlorophenyl-1,5-diphenyl-formazans are such weak acids that anions were not detected. Although there was no apparent colour change when ethoxide was added to 3-*m*-nitrophenyl-1,5-diphenylformazan the band at 490 nm was shifted to higher wavelength with increasing pH$_{et}$. This probably indicates the formation of a new band attributable to formazanide anion; a concurrent decrease in intensity of a band at 310 nm supports this. Using the band at 310 nm, which obeyed the Beer–Lambert law, a pK_{ae} value of 19.1 was obtained.



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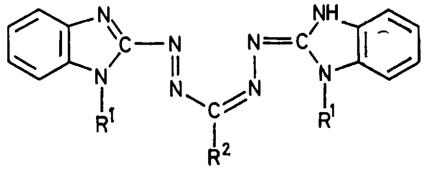


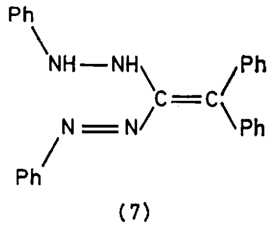
(6)

The two bands at 490 and 400 nm indicate that ethanolic solutions of 3-*p*-nitrophenyl-1,5-diphenylformazan contain an equilibrium mixture of red and yellow isomers. In contrast to the 3-*m*-nitrophenyl compound, a weak ν(NH) band at *ca.* 3 190 cm^{-1} indicates the presence of non-intramolecularly hydrogen-bonded *trans*-isomer. Spectrophotometric titration was therefore impossible; the method used for 1,5-diphenylformazan gave pK_{ae} = 18.8 ± 0.5.

The greater acidity of the 3-nitrophenylformazan relative to other triarylformazans can be accounted for by the greater degree of electron delocalisation allowed by the presence of the 3-nitro-group.

The influence on acidity of tolyl groups in the 1- and 5-positions was investigated. 3-Methyl-1,5-di-*p*-tolylformazan exhibited a sharp visible absorption band at 425 nm, and a strong ν(NH) band at *ca.* 3 240 cm^{-1}, confirming that this formazan exists in the yellow *trans*-form in ethanol. We consider our pK_{ae} value of 18.7 to have a small but significant difference from the value of 18.3 obtained for 3-methyl-1,5-diphenylformazan. In the only other acid-strength study on formazans to be reported, using members of the benzimidazole series (5; R^1 = aryl or alkyl, R^2 = alkyl group) in aqueous acetone Sereda *et al.*[2] obtained pK values between 8.4 and 10.5. The strongest formazan acid observed in our investigation, 1,5-diphenylformazan, might be expected to have a pK_a value of *ca.* 13 on the aqueous scale. The inclusion of benzimidazole substituents allows tautomerism between structures (5) and (6), and structure (6) will clearly possess different acid–base properties from those of the parent formazans.

We believe that tautomerism may also occur in 3-diphenylmethyl-1,5-diphenylformazan, which has a weak ν(N–H) band at *ca.* 3 330 cm^{-1}, a much higher frequency than those of the other corresponding ν(N–H) bands, and a single visible band at 470 nm, midway between the characteristic band positions of *cis*- and *trans*-isomers. Ethoxide causes the visible band to shift to 490 nm, a few nm less than the wavelength attributed to the formazanide anion. These anomalous observations could be attributed to the tautomeric form (7). The pK_{ae} value of 18.8, estimated from the concentration of ethoxide required to displace the visible band, would then correspond to the loss of one of the two NH protons of (7).



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