ACID-BASE PROPERTIES OF 1,3-DIPHENYL-5-(1*H*-TETRAZOL-2-YL)-FORMAZAN AND 1,3-DIPHENYL-5-(2*H*-1,2,4-TRIAZOL-3-YL)-FORMAZAN*

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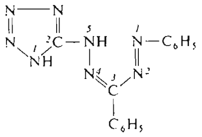
Two new compounds from the formazan series, *viz.* 1,3-diphenyl-5-(1*H*-tetrazol-2-yl)formazan and 1,3-diphenyl-5-(2*H*-1,2,4-triazol-3-yl)formazan, were prepared, and the dissociation constants and molar absorptivities of all of their acid-base species were determined spectrophotometrically employing the SPEKTFOT computer program.

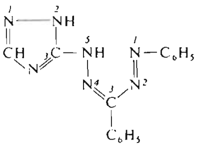
Heterocyclic azo derivatives are among organic reagents that have found wide application in analytical chemistry as metallochromic indicators[1] or as reagents for photometric and extraction-photometric determinations of various elements[1,2]. To such reagents belong also hetero-substituted formazans.

Among works dealing with the synthesis, structure, complexing properties, and analytical applications of formazans with heterocyclic substituents, there dominate the studies of two research groups: the Japanese group[3-9] is involved with the study of 1-hetaryl-3,5-diphenylformazans (hetaryl = thiazolyl, benzthiazolyl, selenazolyl, oxazolyl, pyridyl, nitropyridyl, *etc.*) as reagents suitable for the determination of Ni, Cu, Co, Zn, Cd, the Soviet group[10-14] deals with 1-benzazolyl- and 1,5-dibenzimidazolylformazans as reagents suited for photometric determinations of Cu, Ag, Ni, Zn, Pb, Hg, Cd, Tl.

The present work is concerned with the study of the acid-base properties of two hetarylformazans, *viz.* 1,3-diphenyl-5-(1*H*-tetrazol-2-yl)formazan (*I*) and 1,3-diphenyl-5-(2*H*-1,2,4-triazol-3-yl)formazan (*II*).



I-TEPF



II-TRPF

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EXPERIMENTAL

Chemicals and Solutions

The spectrophotometric measurements and the electrode calibrations were carried out using reagent grade chemicals (Lachema, Brno, and Merck, Darmstadt). The solutions were prepared with distilled water, deionized by passing it over an ion exchanger column (Seibold, Vienna); its conductivity after the deionization was $3\cdot3 \,.\, 10^{-6}$ S cm^{-1}. Ethanol was redistilled on a column with a variable reflux ratio, and its purity was checked spectrophotometrically[15].

Apparatus

The spectrophotometric measurements were performed on VSU 2, Spekol, and Specord UV VIS instruments (all Zeiss, Jena).

The hydrogen ion concentrations were measured on an OP-205 pH-meter (Radelkis, Budapest) fitted with a Metrohm A 20 glass electrode and a calomel reference electrode with saturated sodium chloride solution. The glass electrode was calibrated by potentiometric titration of an $HClO_4$ solution with an NaOH solution in 40% wt. ethanol. An E 436 Potentiograph (Metrohm, Herisau) equipped with an automatic recorder was employed for the titration. The titration data obtained were processed by the KALIBR program[16], and the calibration was checked prior to each measurement by employing phthalate buffer (0·05M hydrogenphthalate solution in 40% ethanol) with a known hydrogen ion concentration.

Preparation of 1,3-Diphenyl-5-(*1H*-tetrazol-2-yl)formazan (TEPF)

The preparation of TEPF proceeds in two steps[17]: diazotization of 5-aminotetrazole, and coupling of the formed diazonium salt with benzaldehyde phenylhydrazone, obtained by condensation of benzaldehyde with phenylhydrazine[18].

To a solution of 2·58 g (30 mmol) of 5-aminotetrazole, prepared according to[19], in 20 ml of 20% NaOH is added 1·75 g (26 mmol) of $NaNO_2$ dissolved in 20 ml of water containing 30 g of crushed ice. The mixture is cooled to 0°C and poured slowly into a constantly stirred mixture of 16 ml of concentrated HCl with 100 g of ice. The system is allowed to stand at 0°C for 20 min, and 20 g of $CH_3COONa.3\,H_2O$ is added.

5·85 g (30 mmol) of benzaldehyde phenylhydrazone is dissolved in 800 ml of ethanol and cooled to 0°C. To the stirred solution is added the solution of the diazonium salt. The red solution formed is allowed to stand for 12 h in cold, then filtered, and the filtrate is diluted with 400 ml of water. The TEPF separated is collected and dried on air. Yield 3·2 g of TEPF (36%).

The product is purified by dissolution in a small volume of ethanol and subsequent precipitation with water.

TEPF is a red crystalline powder, m.p. 154°C, well soluble in ethanol and sparingly soluble in water.

The purity of the product was checked by elemental analysis, thin layer chromatography, and titration with a copper(II) salt. For $C_{14}N_8H_{12}$ (292·3) calculated: 57·52% C, 4·14% H, 38·32% N; found: 57·69% C, 4·06% H, 38·63% N.

In a chromatographic treatment of TEPF in ethanolic solution on silica gel (Silufol UV 254, Kavalier) using n-heptane as eluting agent, most of the substance remained on the start, while a slight yellow spot travelled with the solvent (R_F 0·175).

Spectrophotometric titration (λ 590 nm) of a copper(II) salt solution with a solution of TEPF in 40% wt. ethanol, performed in the presence of acetate buffer (pH 5·9), showed that the product contained 99·1% TEPF.

Preparation of 1,3-Diphenyl-5-(2*H*-1,2,4-triazol-3-yl)formazan (TRPF)

This reagent is prepared by coupling of 1,2,4-triazole diazonium salt with benzaldehyde phenylhydrazone; 5-amino-1,2,4-triazole (Spolana, Neratovice) was used for the preparation of the former substance.

10 g (50 mmol) of benzaldehyde phenylhydrazone is dissolved in a hot mixture of 800 ml of ethanol and 30 ml of pyridine. After cooling, 5 g of $CH_3COONa.3\ H_2O$ is added.

4·2 g (50 mmol) of 3-amino-1,2,4-triazole is dissolved in a system of 20 ml of a water–ethanol mixture (3 : 1) and 10 ml of concentrated HCl and cooled down to −5°C, and a solution of 4 g (60 mmol) of $NaNO_2$ in 10 ml of water of the same temperature is added. The diazonium salt formed is added to the cooled solution of benzaldehyde phenylhydrazone, and the mixture is stirred for another 30 min. The dark-red solution formed is allowed to stand in cold for 12 h. The first precipitate is collected, and to the filtrate is added the same volume of water. The precipitate separated is filtered out after 24 hours' standing. Yield 2 g of TRPF (13·8%).

The product is dissolved in 100 ml of hot 50% vol. ethanol, the hot solution is filtered, and the filtrate is diluted with water in the ratio 1 : 1. The precipitate formed is allowed to stand for several hours and collected.

TRPF is a red crystalline powder, m.p. 109°C, well soluble in ethanol and insoluble in water.

For $C_{15}H_7H_{13}$ (291·3) calculated: 61·84% C, 4·50% H, 33·66% N; found: 62·27% C, 4·61% H, 32·34% N.

Similarly as in the preceding case, in the chromatography of an ethanolic solution of TRPF on silica gel the majority of the substance remained on the start, a yellow spot followed the solvent (R_F 0·175).

Spectrophotometric titration of a copper(II) salt with a solution of the reagent in 40% ethanol (λ 620 nm; pH 5·4) showed that the product contained 87·6% TRPF.

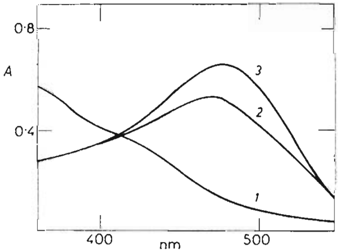


FIG. 1

Absorption curves of TEPF in 40% wt. ethanol, $c_L = 6·11 . 10^{-5}\ mol\ l^{-1}$, $I = 0·1$, $l = 1$ cm; pH: *1* 2·04, *2* 6·02, *3* 12·04

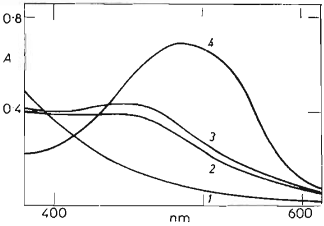


FIG. 2

Absorption curves of TRPF in 40% wt. ethanol, $c_L = 3·92\ m\ 10^{-5}\ mol\ l^{-1}$, I 0·1, $l = 1$ cm; pH *1* 1M-$HClO_4$, *2* 2·08, *3* 6·46, *4* 11·62

RESULTS

Absorption Spectra

The absorption curves of TEPF and TRPF in solutions in 40% wt. ethanol were studied in the range pH 2 to 13. The $A = f(\lambda)$ dependences at constant pH are shown in Figs 1 and 2. The pH values were chosen so that always one of the acid–base species predominated. The data characterizing the spectral features of the various species are given in Table I.

Dissociation Constants

For a study of the protonation equilibria of the reagents, suitable wavelengths were picked out based on the shape of their absorption curves for different pH values. At these wavelengths, the dependences of the absorbances on pH were determined and the dissociation constants of the reagents were calculated by employing the SPEKTFOT program[20]. The requisite initial parameter estimates for the processing were obtained by graphical and logarithmic analysis of the $A = f(\text{pH})$ curves at the wavelengths chosen. The results of the data processing are presented in Tables II–IV, the $\varepsilon = f(\lambda)$ dependence in the range of 400–600 nm for the various acid–base species are shown in Figs 3 and 4; this wavelength range was chosen with regard to the complexing equilibria of the reagents in question.

TABLE I

Parameters of the absorption spectra of the reagents in 40% wt. ethanol at 20°C, I 0·1

Species	pH	λ_{max} nm	ε_{max} l mol^{-1} cm^{-1}
	TEPF (λ_{iso} 410 nm)		
H_2L	<2·5	360	15 000
HL^-	6–13	465	13 000
L^{2-}	>13	475	14 000
	TRPF (λ_{iso} 395 and 420 nm)		
H_2L	< 2	370	12 000
HL^-	3–6	440	8 400
L^{2-}	>10	480	14 000

DISCUSSION

Preparation of the Reagents

The reagents are fairly easy to prepare if the requisite tetrazole and triazole amino derivatives are available. The two compounds, TEPF and TRPF, are formed on coupling of the diazonium salts of the corresponding heterocyclic amino derivatives with benzaldehyde phenylhydrazone. The diazotization takes place in aqueous solution acidified with hydrochloric acid, the coupling, in an aqueous–ethanolic solution in the presence of sodium acetate.

As the results of the chromatographic treatment indicate, the two reagents contain an impurity which in the conditions applied (n-heptane) travels, while the reagents remain on the start. We suggest that this impurity is triphenylformazan (TPF); this assumption has been verified by a chromatographic treatment of TPF in the same conditions: in mixtures of TPF with the reagents, the travelling component exhibited the same R_F value as the impurity in the preparations.

The possibility that TPF may form during the synthesis of heteryldiphenylformazans accomplished by coupling arylhydrazone with hetaryldiazonium salt has been pointed out in the paper[21]. The reaction pathway is probably such that azolyphenyl-

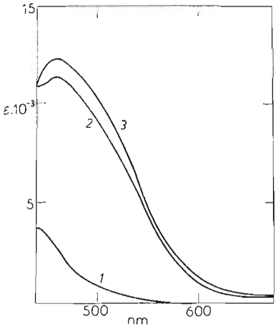


FIG. 3

Curves of the $\varepsilon = f(\lambda)$ dependences for the various acid–base species of TEPF. Species: 1 H_2L, 2 HL, 3 L

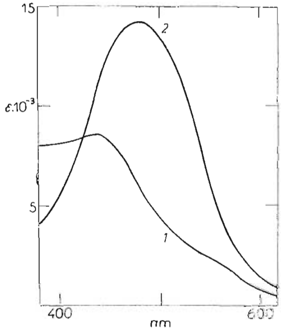


FIG. 4

Curves of the $\varepsilon = f(\lambda)$ dependences for the various acid–base species of TRPF. Species: 1 HL, 2 L

TABLE II

Dissociation constants of the reagents in 40% wt. ethanol at 20°C, *I* 0·1

Equilibrium	pK_a	Reagent concentration mol l^{-1}
TEPF (data from measurements at 7 wavelengths)		
$H_2L \rightleftarrows HL^- + H^+$	4·30 ± 0·13	2·08 . 10^{-5}
$HL^- \rightleftarrows L^{2-} + H^+$	11·57 ± 0·38	3·12 . 10^{-5}
TRPF (data from measurements at 9 wavelengths)		
$H_2L \rightleftarrows HL^-\ H^+$	~2	2·21 . 10^{-5}
$HL^- \rightleftarrows L^{2-} + H^+$	8·08 ± 0·18	2·85 . 10^{-5}

TABLE III

Molar absorptivities of the various acid–base species of TEPF in 40% wt. ethanol at 20°C, *I* 0·1

Species	Absorptivity, l mol^{-1} cm^{-1}, at the wavelength, nm						
	440	450	460	470	480	490	500
H_2L	3 670	3 640	2 750	2 040	1 580	1 330	1 110
HL^-	10 800	10 920	11 290	11 170	10 550	9 740	9 930
L^{2-}	10 200	12 040	12 230	12 160	11 500	11 000	10 850

TABLE IV

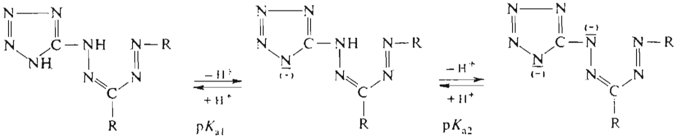
Molar absorptivities of the various acid-base species of TRPF in 40% wt. ethanol at 20°C, *I* 0·1

Species	Absorptivity, l mol^{-1} cm^{-1}, at the wavelength, nm								
	440	460	480	500	510	540	560	580	600
HL^-	8 520	7 600	5 800	4 160	3 250	2 740	2 090	1 500	730
L^{2-}	10 920	13 570	14 260	13 310	11 770	8 560	4 670	2 500	1 390

formazan is first formed, which in acid solution is not very stable, decomposing to yield benzenediazonium chloride, and the latter then takes part in the coupling with the unreacted benzaldehyde phenylhydrazone.

Acid-Base and Spectral Properties of the Reagents

The reagents in aqueous-ethanolic solutions act as dibasic acids; the dissociation reactions (*e.g.*, of TEPF) can be represented by the scheme



(H_2L) (HL^-) (L^{2-})

$R = C_6H_5$

SCHEME 1

The basicity of the heterocyclic nitrogen of the tetrazolyl derivative in position 1 exceeds that of the nitrogen of the triazolyl derivative in position 2; this is consistent with the higher basicity of tetrazole itself as compared with triazole itself (pK_{NH} for tetratole 4·9, for triazole 2·3).

Based on the overall protonation constants pertaining to the protonation of the heterocyclic nitrogen and of the formazan chain nitrogen, the trend of the properties of other analogous heteroformazans can be predicted. The protonation constant ($\log \beta_H = pK_1 + pK_2$) increases in the hetaryl series triazolyl ($\log \beta_H = 9{\cdot}5$) < < benzthiazolyl (10·2, ref.[3]) < thiazolyl (12·6, ref.[5]) < tetrazolyl (15·9) < pyridyl (17·2, ref.[3]). The stability of complexes of these heteryl derivatives with metal ions can be expected to increase in the same order.

REFERENCES

1. Anderson R. G., Nickless G.: Analyst (London) *92*, 207 (1968).
2. Shibata S.: in the book: *Chelates in Analytical Chemistry* (H. A. Flaschka, A. J. Barnard, jr, Eds), Vol. 4. M. Dekker, New York 1972.
3. Kiyakawa M., Kawase A.: Bunseki Kagaku *21*, 244 (1972).
4. Kawase A.: Bunseki Kagaku *16*, 1364 (1967).
5. Uchiuma A.: J. Chem. Soc. Jap., Pure Chem. Sect. *90*, 1133 (1969).
6. Uchiuma A.: Rep. Govt. Chem. Ind. Res. Inst. Tokyo *67*, 170 (1972).
7. Matsushima T., Kawase A.: Bunseki Kagaku *20*, 1310 (1971).

8. Uchiumi A., Iida H.: J. Chem. Soc. Jap., Pure Chem. Sect. *89*, 776 (1968).
9. Suenaga E.: Yakugakushi (Pharmacy) *79*, 803 (1959).
10. Padtschaynova V. N., Lomonosov S. A.: Zh. Anal. Khim. *19*, 1062 (1964).
11. Dubinina L. F., Padtschaynova V. N.: Zavod. Lab. *38*, 1322 (1972).
12. Padtschaynova V. N., Serebryanikova I. N.: Zh. Obshch. Khim. *44*, 618 (1974).
13. Segovskaya V. V., Ermakova M. I.: *Formazany*, p. 68. Trudy Inst. Khim. Akad. Nauk SSR 1974.
14. Ermakova M. I., Latos N. I.: *Formazany*, p. 102. Trudy Inst. Khim. Akad. Nauk SSSR 1974.
15. Šůcha L., Suchánek M.: This Journal *31*, 4539 (1966).
16. Suchánek M., Šůcha L.: Sb. Vys. Šk. Chemicko-Technol. Praze H *10*, 39 (1974).
17. Stiapnov V. P., Kreschina K. I., Skatchilova A. A.: Khim. Geterotsikl. Soedin. *11*, 1570 (1973).
18. Matson A., Jenson C., Duther R.: J. Amer. Chem. Soc. *70*, 1284 (1948).
19. Michina J. S., Herbst R. M.: J. Org. Chem. *15*, 1082 (1950).
20. Suchánek M., Šůcha L.: Sb. Vys. Šk. Chemicko-Technol. Praze H *13*, 41 (1978).
21. Segal L. M., Segal I. L.: Khim. Geterotsikl. Soedin. *8*, 1062 (1972).

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