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Derivatives of Δ^2-pyrazoline-products of 1,5-diaminotetrazole interaction with chalcone: Molecular structure and spectral properties

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Abstract

1,5-diaminotetrazole at conditions of its interaction with chalcones (1,3-diphenylpropenones) in hot DMF undergoes Dimroth rearrangement to 5-tetrazolylhydrazine, which results in formation of 1-(5-tetrazolyl)-3,5-diaryl-Δ^2-pyrazolines (**I**). Structure of the obtained products was confirmed by their parallel synthesis and X-ray structural analysis. Unusual fluorescence behavior of the tetrazolopyrazolynes in polar solvents was attributed to the dissociation of their highly acidic tetrazole N–H group. The last hypothesis was confirmed at the investigation of the protolytic interactions of **I** with tertiary amine.
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Keywords: 1,5-diaminotetrazole; Dimroth rearrangement; Δ^2-Pyrazolines; X-ray structural analysis; High stokes shift fluorescence; Excited state photodissociation

1. Introduction

Condensation of nitrogen-containing binucleophilic agents with α,β-unsaturated ketones is one of the most suitable synthetic pathways to five-, six- and seven-membered partially hydrogenated heterocyclic compounds-potential pharmaceutically active analogs of natural compounds. High regioselectivity of the discussed reaction owing to the pronounced difference in electrophilic parameters of carbonyl and β-carbon reaction centers is the most important advantage of this reaction, which allows to synthesize several hardly accessible compounds, over the widely known analogous reactions of β-diketones. Our interest to 1,5-diaminotetrazole as binucleophilic agent in the above mentioned condensation was stipulated by its possible tetrazolo-azido tautomerism and its structural transformation owing to the Dimroth rearrangement [1–3].

In our preliminary publication [4], we reported formation of fluorescent products in reaction of 1,5-diaminotetrazole with chalcones and made a hypothesis about the possible presence of Δ^2-pyrazoline ring in their molecules. The alternative molecular structure of tetrazolo[1,5-b] triazepines was proposed earlier to the products of the discussed reaction [5], however such a conclusion was not supported later by the data for chalcone reactions with several N-amino group containing vicinal diaminoimidazoles and diaminotriazoles [6–9]. Generally, 1,3,5-triaryl derivatives of Δ^2-pyrazoline belong to a class of highly effective organic luminophores with the intensive blue–green emission in the solid state and in the liquid solutions [10], while as we did not expected pronounced fluorescence ability of tetrazolo[1,5-b]triazepines. Taking into account the fact, that structural and spectral features of triaryl-Δ^2-pyrazolines with the electronodeficite heterocyclic moieties in position 1 were not described properly, in this paper we decided to focus our attention on the synthesized 1-(5-tetrazolyl)-3,5-diaryl-Δ^2-pyrazolines (**I**) [4].

2. Experimental

The investigated 1-(5-tetrazolyl)-3,5-diaryl-Δ^2-pyrazolines **Ia–i** were synthesized by two general schemes: at heating of equimolar amounts of 1,5-diaminotetrazole (**II**) with chalcones (1,3-diarylpropenones, **IIIa–d**) in DMF at 150 °C [1,5] or by the classical method for obtaining pyrazolines-at interaction of corresponding chalcones with 5-tetrazolohydrazine (Scheme 2, Table 1).

1,5-Diaminotetrazole (**II**) was synthesized at interaction of semicarbazide with NaN_3 and access amounts of NH_4Cl and yellow modification of PbO in DMF [11]. Thermal

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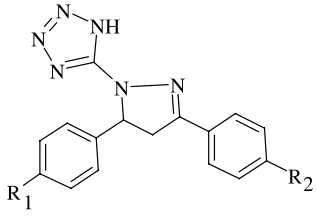
Table 1
Experimental physico-chemical parameters of the synthesized tertazolopyrazolines **Ia–i**



Compound	R_1	R_2	Molecular composition	Element analysis (found/calc., %)			M.P. °C[a]	Yield %
				C	H	N		
Ia	H	H	$C_{16}H_{14}N_6$	66.19	4.78	29.01	228–229[b]	60[c]
				66.04	4.86	28.95		39[d]
Ib	H	CH_3	$C_{17}H_{16}N_6$	67.06	5.19	27.51	211–213[e]	61[c]
				66.94	5.30	27.61		
Ic	H	OCH_3	$C_{17}H_{16}N_6O$	63.74	5.07	26.19	201–202	69[c]
				63.93	5.03	26.23		
Id	H	Br	$C_{16}H_{13}N_6Br$	51.87	3.46	22.58	236–237	51[c]
				52.05	3.55	22.76		43[d]
Ie	Br	H	$C_{16}H_{13}N_6Br$	51.89	3.40	22.53	223–224	41[d]
				52.05	3.55	22.76		
If	Br	OCH_3	$C_{17}H_{15}N_6BrO$	51.14	3.67	20.87	203–204	62[d]
				50.91	3.79	21.05		
Ig	Br	Br	$C_{16}H_{13}N_6Br_2$	42.88	2.78	18.49	232–234	36[d]
				42.69	2.70	18.75		
Ih	Cl	H	$C_{16}H_{13}N_6Cl$	59.17	4.14	25.62	224–225	49[d]
				58.95	4.03	25.88		
Ii	OCH_3	CH_3	$C_{18}H_{18}N_6O$	64.66	5.29	25.04	193–195	56[d]
				64.41	5.43	25.13		

[a] Uncorrected melting points.
[b] M.P. = 227 [5].
[c] This compound was synthesized at interaction of 1,5-diaminotetrazole with the corresponding 1,3-diarylpropenone-1.
[d] This compound was synthesized at interaction of 5-tetrazolylhydrazine with the corresponding 1,3-diarylpropenone-1.
[e] M.P. = 211 [5].

isomerization diaminotetrazole ↔ tetrazolohydrazine takes place at such conditions, this is the classical example of the Dimroth rearrangement [2].

5-Tetrazolohydrazine (**IV**) was obtained at the reaction of 5-aminotetrazole with aqueous $NaNO_2$ in diluted acetic acid, followed by the reduction of the formed 1,3-di(5-tetrazolyl)-triazene by $SnCl_2$ dihydrate in concentrated hydrochloric acid [12]. Then 5-tetrazolohdrazine water solution (contents of **IV** was detected by the quantitative precipitation of its benzalhydrazone from the small aliquot) was introduced into reaction with chalcones.

Interaction of 5-tetrazolylhydrazine with chalcones, general procedure: aqueous solution of **IV** (35 mmol) was added to chalcone (35 mmol) solution in 50 ml of ethanol. Reaction mixture was heated during 6.5 h, evaporated down to 2/3 of the initial volume and the residue was poured into the 100 ml of ice water. Precipitated solid was filtered, dried and recrystallized from benzene.

All the synthesized compounds were purified by the recrystallization from benzene (TLC control with the benzene/diethyl ether 3/2 as eluent).

Crystals of **Ic** suitable to X-ray structural analysis were obtained by the diffusion of diethyl ether vapor into the saturated benzene solution of **Ic**.

Compound **Ic**[1]—$C_{17}H_{16}N_6O$, $M_r = 320.35$; $a = 8.450(3)$; $b = 14.706(4)$; $c = 13.804(4)$ Å; $\beta = 101.70(2)°$; $V = 1679.7(9)$ Å^3; monoclinic crystals; space group $P2_1/c$; $Z = 4$; $d_{calc} = 1.338$ g/cm^3; $T = 293$ K; $F(000) = 712$. Elementary cell parameters and intensities of 4888 independent reflections ($R_{int} = 0.028$) were collected on Siemens-*P*3/PC automatic diffractometer (μ(Mo Kα) = 0.093 mm^{-1}, graphite monochromator, $\theta/2\theta$-scanning, $2\theta_{max} = 60°$).

The structure was solved by direct method with the use of SHELX97 software [13]. Hydrogen atoms positions were calculated geometrically and were refined within the 'riding' model with the fixed isotropic thermal corrections $U_{iso} = nU_{eq}$, determined by the neighboring non-hydrogen atom ($n = 1.5$ for methyl group hydrogens and $n = 1.2$ for all the other ones). Structure refinement on $(F_{hkl})^2$ with the full-matrix least squares method in the anisotropic approximation for non-hydrogen atoms were performed to $wR_2 = 0.147$ ($R_1 = 0.060$) by 2230 reflections with $F > 2\sigma(F)$, $S = 0.93$.

[1] CCDC 181907 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033.

Infrared spectra were measured on the Specord 75 IR spectrometer in the KBr pellets. NMR ^{1}H spectra in DMSO D_6 were taken on Varian 200 Mercury VX device.

Electronic absorption spectra were recorded on the HITACHI U3210 spectrophotometer. Fluorescence spectra and quantum yields were measured on the HITACHI F4010 spectrofluorimeter with quinine sulphate in 0.5 M H_2SO_4 as the quantum yield reference standard (ϕ_f=0.546 [14]).

The constants of protolytic equilibrium for compounds **Ia**, **Ic** and **Ih** in the ground state were calculated from spectrophotometic titration data by the nonlinear iterative least-squares method [15] using a specially designed program based on the Fletcher–Powell algorithm. The excited-state protolytic equilibrium constants were evaluated by a fluorimetric titration technique according to the procedure proposed by Melo et al. [16]. In this case, the data treatment procedure also employed the nonlinear least squares routine.

Semiempirical quantum-chemical calculations of the electron spectra and the excited state electron density redistribution of the studied compounds were made by INDO/S method [17] basing on the optimized molecular geometry obtained with semiempirical method AM1 [18].

3. Results and discussion

IR and NMR ^{1}H spectra were measured for all the synthesized compounds (Table 2). Absence of infrared absorption near 2200 cm^{-1} confirms out expectations that in the crystalline phase tetrazol moiety exist in the cyclic form and its possible transformation into azide does not take place. Absorption bands at 1630 cm^{-1} were attributed to C–C_{arom} and C=N bond stretching, while as the broad diffuse band at 3400 cm^{-1} corresponds to the H-bonded tetrazolic cycle N–H vibrations. Signals of aromatic protons at 6.90–7.70 ppm were present in the NMR ^{1}H spectra. Typical ABX-system signals were observed: two doublets of methylenic protons at 3.15–3.35 and 3.80–4.12 ppm (H_A, H_B) and double doublet at 5.35–5.57 ppm (H_X). Broad low-field singlet deuterium-exchangeable signals of tetrazolic proton (15.4–15.8 ppm, 1H) is present as well. Position of the last signal demonstrates high acidity of tetrazolic NH, comparable to that of intermediately strong carboxylic acids.

However, the spectral data of Table 2 were not completely sufficient for unambiguous identification of the nature of the products formed. Particularly, if we take into account the possibility of the ring-chain tautomerizm of 1,5-diaminotetrazole **II** and participation of any of its isomeric structures in the reaction with 1,3-diarylpropenones-1, formation of three alternative isomeric products should be considered: 5,7-diaryl-5,6-dihydro-4H-tetrazolo[1,5-b]-1,2,4-triazepin (**C**) (as it was reported in [5]), i.e. in analogy to aromatic *ortho*-diamines, and products A and B, which obtaining requires transformation of diamine **II** into its azide form followed by the Dimroth rearrangement prior the reaction with chalcone. At these conditions two different heterocyclic systems could be formed: seven-membered triazepine (**B**) and five-membered pyrazoline (**A**) (Scheme 1).

To determine the reaction pathway and to identify the structure of the formed products we have made an attempt to realize the alternative synthetic scheme and to obtain the required products by direct interaction of 5-tetrazolohydrazine **IV** with 1,3-diarylpropenones **IIIa**,**d–i** (Scheme 2). The synthesized compounds were identical to the earlier products **Ia**,**d–i** by all their physico-chemical and spectral parameters. Thus, formation of 5,7-diaryl-5,6-dihydro-4H-tetrazolo[1,5-b]-1,2,4-triazepins and results, reported in [5], should be disclaimed, owing to the irreversibility of transformation of 1,5-diamino-tetrazole into 5-tetrazolo-hydrazine in soft reactions conditions.

Formation of 6,8-diaryl-7,8-dihydro-4(**H**)-tetrazolo[5,1-*c*] triazepines B seems to us less probable, owing to the higher nucleophilic ability of the exo-hydrazinic group with respect to the endocyclic tetrazolic NH group, which make five-membered pyrazoline cycle closing more favorable compared to the seven-membered triazepine one. Another one: compounds IIIa-i demonstyrate presence of higly acidic group with NMR ^{1}H signal at 15-16 ppm. This fact corresponds better to the structure A with its tetrazolic NH proton in and not to structure B, which azepinic NH signal are expected to manifest itself at much higher field region.

Therefore, final arguments in favor of the formation of pyrazolyne cycle were obtained by the X-ray structural analysis on the example of compound **Ic**. Its molecular geometry and atoms numbering scheme are shown on Fig. 1, atom coordinates are presented in the Table 3.

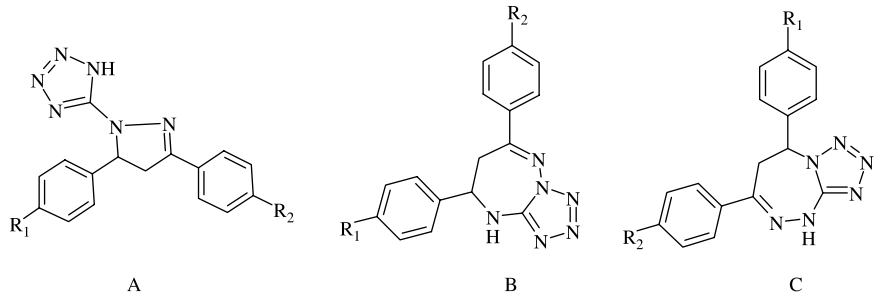
Pyrazoline ring of **Ic** is planar within 0.01 Å as well as the other cycles in this molecule. The most important part of the main chromophoric moiety of **Ic**, pyrazoline cycle and phenyl cycle in its position 3 are almost coplanar: the angle between their least-squares planes was found near 6°($\pm$0.2°). Tetrazole cycle forms an angle of 18°($\pm$0.2°) with the neighboring pyrazoline one, however, slight pyramidalization of the pyrazoline nitrogen atom in position 1 is the main reason of this (see valence angles C_1–N_5–N_6 117.70(14), C_1–N_5–C_2 123.46(15), N_6–N_5–C_2 114.31(14)). Aryl group in position 5 of the pyrazoline cycle is almost orthogonal to the rest of this molecule. As in the case of another triaryl-pyrazolines [19 and citation wherein], this moiety is not conjugated with the main chromophoric system of **Ic** and thus has no effect on its UV–vis and fluorescence spectra.

Generally, 1,3,5-tryarylpyrazolines are known as effective organic luminophores with blue–green emission in solid state and in solutions. This fact inspires our interest to the fluorescence properties of their newly synthesized tetrazole analogs.

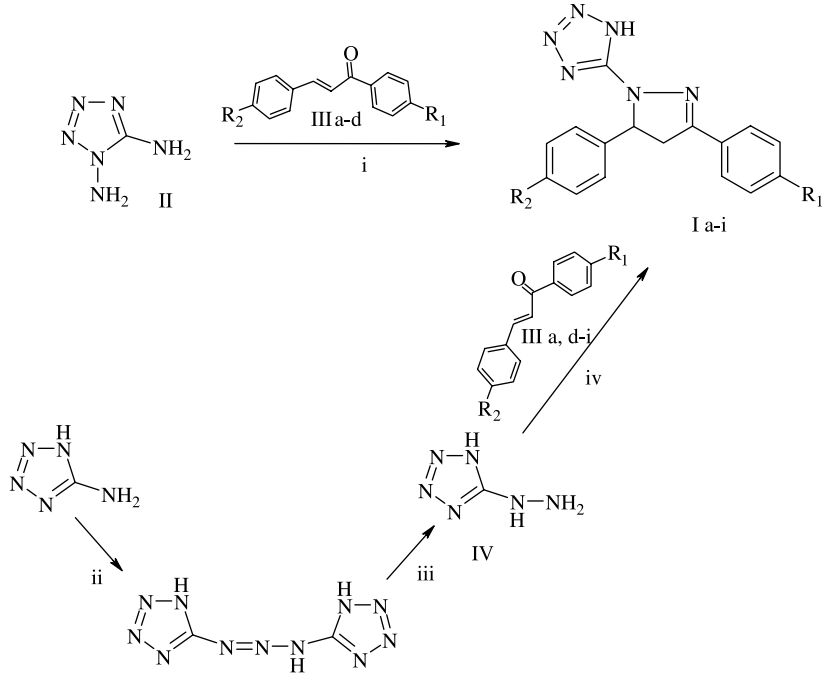
Substitution of phenyl moiety to tetrazole cycle in position 1 of 1,3,5-triphenylpyrazoline molecule leads to hypsochromic shift in its absorption spectrum from 358 nm [10] down to 308–314 nm (Table 4, toluene). The analogous behavior was observed for several other substituted pyrazolines with electron-accepting groups in one-position [20]. To our understanding this is the result of the electron influence of the introduced electron-withdrawing center onto the excited state electron density redistribution typical to this class of

Table 2
IR and NMR ^{1}H spectral data for tetrazolo-pyrazolynes **Ia–i**

Co mpound	IR spectra ν (cm^{-1})					NMR ^{1}H spectra δ (ppm), J (Hz)					
	C=C C=N	NH	ABX-system, 1H dd			J (ABX)			Aromatic protons	NH 1Hs	Other
Ia	1620	3414	3.19–3.31	3.90–4.11	5.43–5.56	−17.9	7.7	11.7	7.25–7.39 5H m, 7.43–7.53 3H m, 7.78–7.86 2H d (J=8.7)	15.7	–
Ib	1620	3427	3.19–3.29	3.92–4.12	5.40–5.51	−17.5	7.5	11.1	6.92–7.00 2H d (J=8.6) 7.11–7.24 4H, m 7.44–7.53 3H, m	15.4	2.20 3H, s. CH_3
Ic	1620	3426	3.16–3.24	3.89–4.09	5.36–5.48	−17.9	7.7	11.4	6.97–7.04 2H d (J=8.2), 7.13–7.27 4H m 7.46–7.57 3H m	15.6	3.77 3H, s. OCH_3
Id	1624	3427	3.22–3.34	3.92–4.09	5.39–5.53	−18.0	7.9	11.6	7.26–7.33 2H d (J=8.9) 7.43–7.50 3H m 7.60–7.69 2H d (J=8.5) 7.77–7.85 2H d (J=8.9)	15.7	–
Ie	1628	3431	3.22–3.34	3.92–4.10	5.44–5.56	−18.0	7.9	11.9	7.32–7.44 4H m 7.54–7.61 3H m 7.77–7.86 2H d (J=8.9)	15.5	–
If	1624	3428	3.17–3.31	3.88–4.06	5.37–5.51	−18.0	7.9	11.6	6.99–7.09 2H d (J=8.9) 7.25–7.34 2H d (J=8.2) 7.49–7.58 2H d (J=8.2) 7.70–7.79 2H d (J=8.9)	15.6	3.79 3H s OCH_3
Ig	1626	3434	3.21–3.36	3.89–4.08	5.42–5.57	−18.0	7.9	11.9	7.26–7.33 2H d (J=8.2) 7.49–7.57 2H d (J=8.9) 7.65–7.78 4H m	15.6	–
Ih	1622	3428	3.20–3.36	4.00–4.19	5.41–5.57	−18.0	7.6	11.2	7.35–7.43 2H d (J=8.5) 7.56–7.63 3H m 7.78–7.85 2H d (J=8.9) 8.11–8.20 2H d (J=8.9)	15.8	–
Ii	1618	3426	3.14–3.28	3.84–4.03	5.34–5.47	−17.7	7.3	11.6	6.99–7.06 2H d (J=8.5) 7.09–7.26 4H m 7.71–7.77 2H d (J=8.5)	15.5	2.25 3H s CH_3 3.75 3H s OCH_3



Scheme 1. Alternative structures, which could by considered as products of interaction of II with chalcones.



Scheme 2. Reagents and condition: (i) DMF 150 °C; (ii) $NaNO_2$, HOAc, 10 °C; (iii) $SnCl_2*2H_2O$, HCl, r.t.; (iv) C_2H_5OH, reflux.

luminescent compounds (Scheme 3). Appearance of the strong electron acceptor in pyrazolinic position 1 prevents removal of electron density from N-1 atom towards the benzene ring in position 3 giving rise to changes in optical parameters of the compounds on study. The analogous, however, less distinct hypsochromic effect should be observed at introduction of electron donor groups into phenyl-3.

The lowest singlet excited state electron density redistribution is shown on the above scheme in comparison to the ground state for the molecule of 1,3,5-triphenylpyrazoline according to our INDO/S calculations (thick arrow). Electron accepting (EA) substituent in phenyl-1 and electron donor (ED) ones in phenyl-3 prevent this charge transfer making it less effective and resulting in hypsochromic shifts in the absorption spectra (their influence onto electron density moving is shown by thin arrows).

High fluorescence quantum yields (0.6–0.8) are typical to tetrazolo-pyrazolines in toluene (Table 4). Definite deviations are observed to compounds with electron donor groups in phenyl-3. Such behavior could be attributed to the electronic effect of substituents pushing electron density in direction

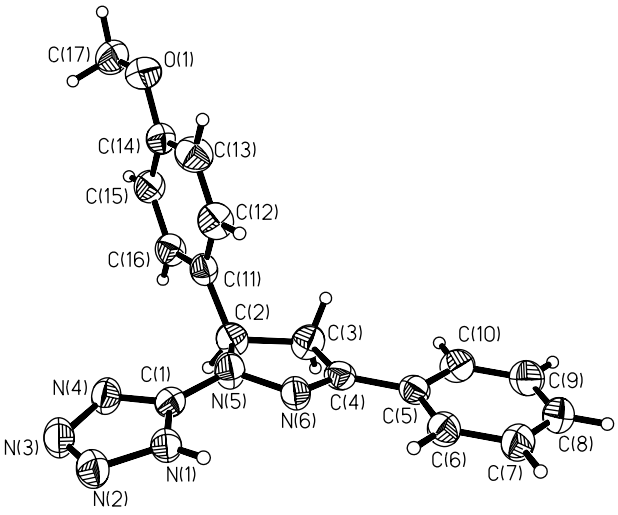


Fig. 1. X-ray molecular structure, scheme of atom numbering and thermal vibrations ellipsoids (at 50% probability) for compound Ic.

Table 3
Atom coordinates (Å) and equivalent isotropic displacement parameters (Å^2) for compound **Ic**

Atom	*X*	*y*	*Z*	U_{eq}
N1	1.02559(18)	0.14148(10)	0.73191(11)	0.0386(4)
N2	1.1251(2)	0.18162(12)	0.67876(12)	0.0472(4)
N3	1.1484(2)	0.26357(12)	0.71132(13)	0.0494(4)
N4	1.0660(2)	0.27997(10)	0.78522(12)	0.0439(4)
N5	0.8967(2)	0.18719(10)	0.86207(12)	0.0442(4)
N6	0.85566(19)	0.09787(10)	0.87801(12)	0.0390(4)
O1	0.43990(17)	0.53693(11)	0.83150(12)	0.0581(4)
C1	0.9932(2)	0.20225(11)	0.79655(14)	0.0363(4)
C2	0.8854(2)	0.24997(13)	0.94427(14)	0.0417(5)
C3	0.8218(3)	0.18387(13)	1.01485(15)	0.0463(5)
C4	0.8108(2)	0.09429(12)	0.96173(14)	0.0364(4)
C5	0.7547(2)	0.00928(12)	0.99860(13)	0.0362(4)
C6	0.7601(2)	−0.07160(13)	0.94761(15)	0.0429(5)
C7	0.7054(3)	−0.15144(14)	0.98166(17)	0.0496(5)
C8	0.6439(3)	−0.15150(15)	1.06696(17)	0.0520(5)
C9	0.6378(3)	−0.07245(15)	1.11806(16)	0.0527(6)
C10	0.6936(2)	0.00831(14)	1.08514(14)	0.0460(5)
C11	0.7744(2)	0.32870(12)	0.91042(13)	0.0373(4)
C12	0.6310(2)	0.31687(14)	0.84160(15)	0.0466(5)
C13	0.5237(3)	0.38726(15)	0.81698(16)	0.0516(5)
C14	0.5575(2)	0.47192(13)	0.86003(15)	0.0430(5)
C15	0.6996(2)	0.48593(13)	0.92710(16)	0.0451(5)
C16	0.8073(2)	0.41390(13)	0.95179(15)	0.0423(5)
C17	0.4679(3)	0.62565(15)	0.8733(2)	0.0618(6)
H1N	0.9899	0.0866	0.7250	0.046
H2	0.9931	0.2722	0.9753	0.050
H3A	0.8961	0.1803	1.0783	0.056
H3B	0.7167	0.2029	1.0254	0.056
H6	0.8011	−0.0720	0.8899	0.052
H7	0.7099	−0.2053	0.9471	0.060
H8	0.6065	−0.2054	1.0897	0.062
H9	0.5960	−0.0728	1.1754	0.063
H10	0.6901	0.0617	1.1207	0.055
H12	0.6075	0.2604	0.8118	0.056
H13	0.4279	0.3780	0.7712	0.062
H15	0.7236	0.5429	0.9556	0.054
H16	0.9035	0.4234	0.9971	0.051
H17A	0.5650	0.6502	0.8579	0.093
H17B	0.4790	0.6220	0.9438	0.093
H17C	0.3783	0.6644	0.8464	0.093

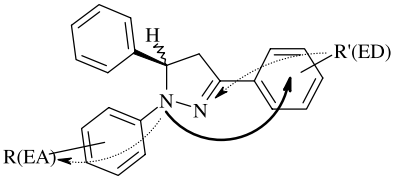
opposite to the main excited state charge redistribution in these molecules. Fluorescence Stokes shifts in toluene are slightly larger than expected 'normal' values of 3000–5000 cm^{-1}. However, the observed enlarged $\Delta\nu_{ST}$ in the range of 6000 cm^{-1} could be explained by the possible excited state planarization [21–23] of the main chromophoric unit, which includes tetrazole, pyrazoline and benzene cycles. In particularly, pyramidalized pyrazolinic nitrogen atom in position 1 could change its conformation to more flattened one.

Interesting changes in spectral properties were detected in polar, and, especially, in proton-donating solvents. Having five potentially nucleophilic nitrogen atoms and one rather acidic N–H group in their molecules, tetrazolo-pyrazolynes are able to form multiple hydrogen bonds with solvent molecules. And indeed, in methanol practically all the compounds on study demonstrate hypsochromic shifts in their absorption spectra (Table 4). These changes could be explained by the formation of H-bonds with tetrazolic nitrogens, which make the heterocycle more electron accepting, lowering the main intramolecular excited state charge transfer to the phenyl-3 and thus, shifts the absorption of tetrazolo-pyrazlines further to the short wavelengths. Another hydrogen bonding with the participation of pyrazolinic N-2 atom should be considered as well, because the spectral effect of such interaction might be the same.

In contrast to the absorption spectra, significant red shift was observed for the emission bands of tetrazolo-pyrazolines in methanol. This results in the increase of the Stokes shifts up to 8500–9000 cm^{-1}. At the same time, fluorescence intensity decreases significantly: quantum yields in this solvent did not exceed 0.1. Moreover, in aprotonic polar acetonitrile we observed two-banded emission spectra with positions of short-wavelength bands close to that in toluene, while as the long-wavelength ones were located in the spectral region typical to that of methanol solutions. Fig. 2 demonstrates that fluorescence spectrum of **Ia** in acetonitrile (**A**) could be presented as practically the superposition of the emission bands in toluene (T) and in methanol (M): (**A**–M) ~ T.

Table 4
UV/vis spectral and fluorescent properties of tetrazolo-pyrazolynes **Ia–i**

Com-pound	Solvent	λ_a, nm (ν_a cm^{-1})	ε_a	λ_f, nm (ν_f cm^{-1})	$\Delta\nu_{ST}$, cm^{-1}	ϕ_f
Ia	Toluene	314 (31840)	–	388 (25800)	6040	0.82
	methanol	309 (32360)	18200	425 (23520)	8840	0.07
Ib	Methanol	309 (32360)	18500	422 (23700)	8660	0.08
Ic	Toluene	315 (31760)	–	390 (25660)	6100	0.56
	methanol	312 (32050)	18800	423 (23640)	8410	0.08
Id	Toluene	314 (31840)	–	387 (25860)	5980	0.69
	methanol	312 (32050)	18000	431 (23200)	8850	0.08
Ie	Methanol	308 (32470)	18300	433 (23090)	9380	0.06
If	Toluene	315 (31780)	–	391 (25560)	6220	0.60
	methanol	313 (31950)	18800	435 (22990)	8960	0.06
Ig	Methanol	314 (31840)	18200	435 (22990)	8850	0.08
Ih	Toluene	314 (31880)	–	387 (25840)	6040	0.71
	methanol	314 (31840)	18900	429 (23310)	8530	0.07
Ii	Toluene	316 (31660)	–	391 (25560)	6100	0.79
	methanol	312 (32050)	18000	425 (23530)	8520	0.08



Scheme 3. The main excited state electron density redistribution in the molecule of 1,3,5-triarylpyrazolyne and its deterioration by the substituents in side phenyl moieties.

This abnormal spectral behavior needs justification, and first we made series of quantum-chemical calculations in our attempt to understand the reasons for the observed abnormal spectral properties of tetrazolo-pyrazolines in polar solvents.

Tetrazolic N–H group demonstrate rather high proton mobility in the studied compounds: its IR frequencies at 3410–3430 cm^{-1} and NMR ^1H signal positions at 15.5–15.7 ppm are in line with the above statement. Acidic properties of tetrazolic cycle in the studied molecules were checked also at our experiments on titration of tetrazolo-pyrazolines in acetonitrile by strong organic base-triethylamine (Fig. 3). As an example we have checked protolytic interaction of three compounds belonging to the studied series: unsubstituted molecule (**Ia**, pK 4.02 ± 0.03), its Cl–(**Ih**, pK 4.37 ± 0.02) and -OCH_3 (**Ic**, pK 3.52 ± 0.04) derivatives.

Thus, we had to check the hypothesis, that the anomalous fluorescence behavior of tetrazolo-pyrazolines in polar solvents may be determined with the excited state N–H photodissociation. The latter could be of two types: intermolecular, when proton is transferred to the neighboring solvent molecule, and intramolecular, when proton moves to

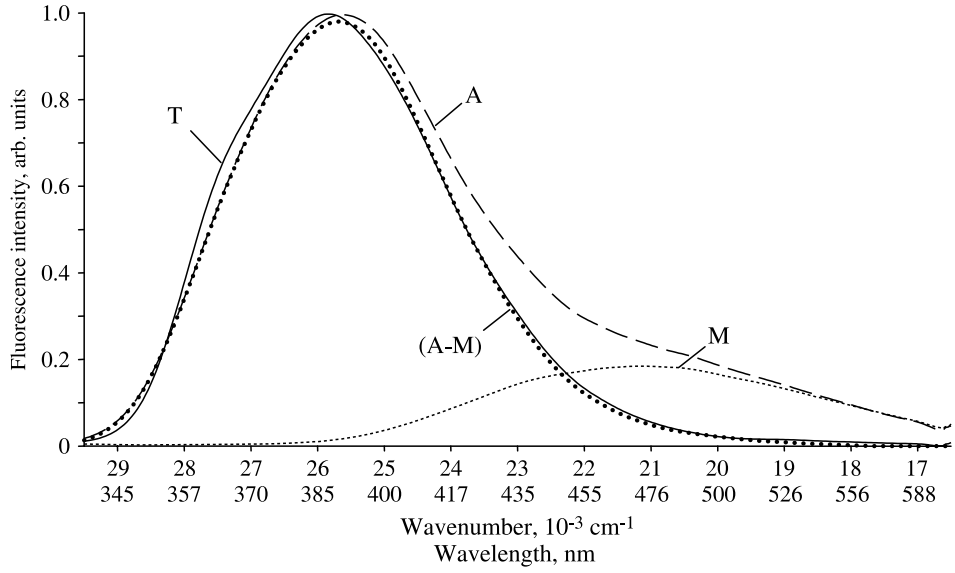


Fig. 2. Fluorescence spectra of compound **Ia** in toluene (T), acetonitrile (A) and methanol (M). Difference of the spectra in acetonitrile and methanol (A–M) is close in shape and in position to the spectrum in toluene.

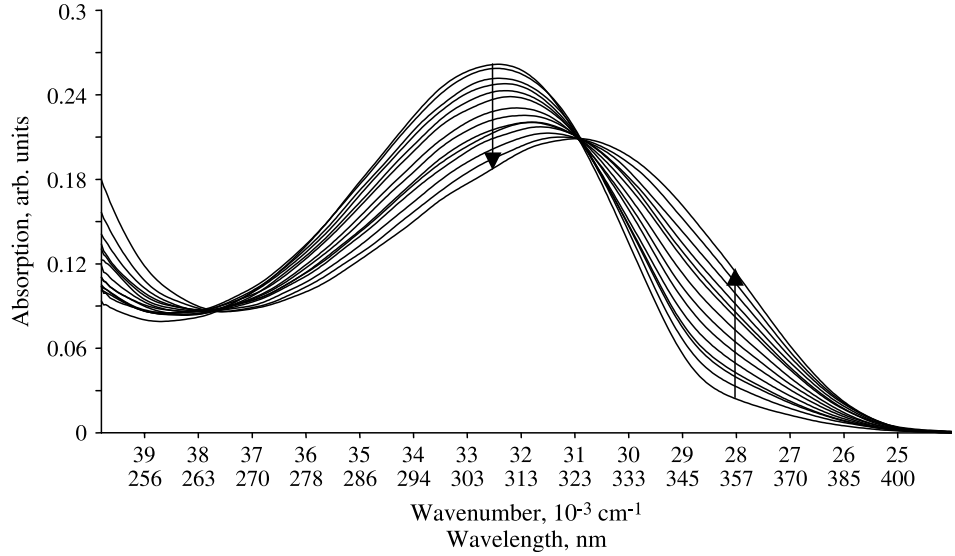


Fig. 3. Spectrophotometric titration by triethylamine (0, 4.10^{-6}–0.02 Mol/dm^3) of the tetrazolo-pyrazoline **Ia** in acetonitrile.

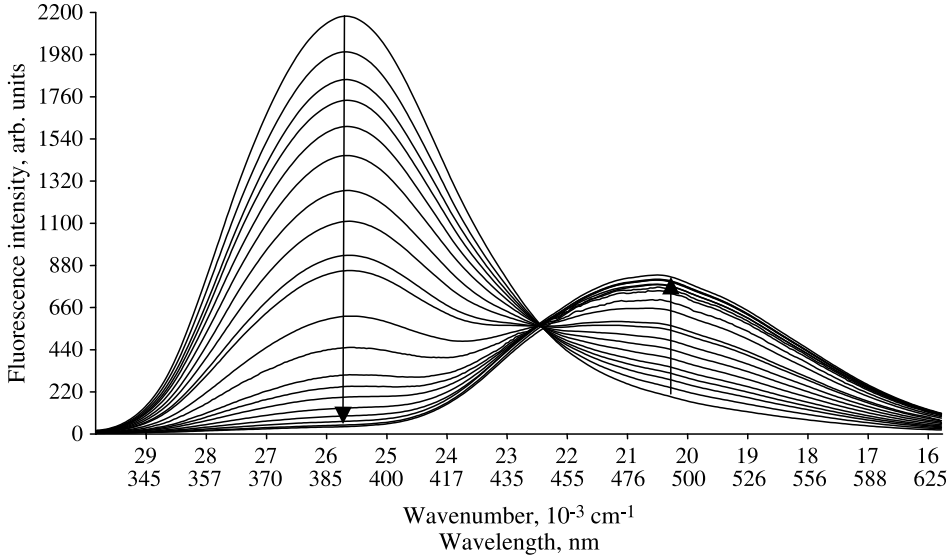


Fig. 4. Fluorimetric titration by triethylamine (0, 4.10^{-6}–0.02 Mol/dm^3) of the tetrazolo-pyrazoline **Ia** in acetonitrile.

the closest basic center of the same molecule-nitrogen atom in position 2 of pyrazoline cycle.

Our X-ray structural experiments reported the distance between the above mentioned acidic (N_1–H) and basic (N_6) centers, $r_{H-N} \sim 2.6$ Å. Thus, we have to consider the intramolecular H-bond in the studied molecules should not be strong. According to our INDO/S calculations, in S_1 -state N–H group should increase its acidity ($\Delta q_N = 0.01$ e), while as pyrazolinic N-2 atom should become more basic ($\Delta q_N = 0.06$ e), however the above mentioned changes are not very high. If the intramolecular proton phototransfer would be realized at the electronic excitation, the energy of the lowest singlet excited state should decrease down to ~1000 nm (AM1 + INDO/S modeling data), which could not be observed on our spectrometers. Moreover, such a low energy gap between the ground and the excited states get rise the effective internal conversion [24,25], which concur with fluorescence emission and makes the latter nearly impossible.

Analogous fluorimetric titration with triethylamine was made for the above mentioned tetrazolo-pyrazolines in acetonitrile (Fig. 4). Fine isoemissive points evidenced about the absence of any other equilibria except the main one-dissociation of N–H group. The determined pK values were close to that of spectrophotometric titration (pK_{fl} 4.00 ± 0.02, 4.42 ± 0.04 and 3.53 ± 0.03 for **Ia**, **Ih** and **Ic** correspondently), thus we have to make a conclusion that changes in the emission spectra presented on Fig. 4 are completely determined by the ground state protolytic interactions of tetrazolo-pyrazolines and triethylamine.

4. Conclusion

1,5-diaminotetrazole at conditions of its interaction with chalcones (1,3-diphenylpropenones) in hot DMF undergoes Dimroth rearrangement to 5-tetrazolylhydrazone, which results in formation of 1-(5-tetrazolyl)-3,5-diaryl-Δ^2-pyrazolines (**I**). Structure of the obtained products was confirmed by their parallel synthesis and X-ray structural analysis (on the example of **Ic**). Unusual fluorescence behavior of the tetrazolopyrazolines in polar solvents was attributed to the dissociation of their highly acidic tetrazole N–H group. The last hypothesis was confirmed at the investigation of the protolytic interactions of **I** with tertiary amine.

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