Association of anions of phenolsulfonephthalein and its alkyl-substituted derivatives with single-charged cations of polymethines

S. A. Shapovalov

V. N. Karazin Kharkov National University,
4 pl. Svobody, 61077 Kharkov, Ukraine.
Fax: +38 (057) 707 5130. E-mail: serghey.a.shapovalov@univer.kharkov.ua

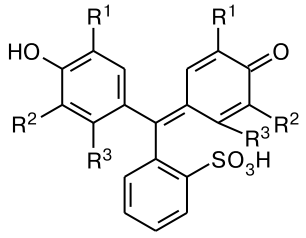
The interaction of single- and double-charged anions (HAn^-, An^{2-}) of sulfonephthaleins (phenolsulfonephthaleins and its alkyl-substituted derivatives, *viz.*, *o*-cresolsulfonephthalein and thymolsulfonephthalein) with single-charged cations (Ct^+) of polymethines (pinacyanol, quinaldine red) was studied. The interaction in an aqueous solution affords heteroassociates of stoichiometric composition $(Ct^+)\cdot HAn^-$ and $(Ct^+)_2\cdot An^{2-}$. The association constants were estimated from the spectrophotometric data. The enthalpies of formation of dye and heteroassociate ions were calculated and the most probable structure of the heteroassociates was determined using the semiempirical methods.

Key words: sulfonephthaleins, heteroassociation, spectrophotometry, aqueous solution, association constant, enthalpy of formation.

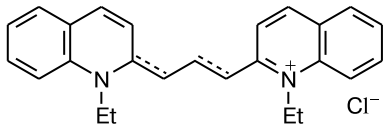
It is known[1—3] that cation-anionic interactions between ions of dyes are accompanied by a substantial change in light absorption of the solution. Association in aqueous solutions is of special interest, since it is water where protolytic and aggregative forms of dyes exhibit unique properties.[1,4] This completely concerns sulfonephthalein dyes. Among them phenolsulfonephthalein (PS) and its alkyl-substituted derivatives, *o*-cresolsulfonephthalein (CS) and thymolsulfonephthalein (TS), attract attention from the viewpoint of their ability to ion association. The high-sensitive method developed for the detection of vitamin B_1 is based on the formation of a heteroassociate between PS and the vitamin[5]; the spectral fiber pH-sensor of cells and biological tissues was produced.[6] The alkyl-substituted derivatives are characterized by the formation of ion pairs with organic counterions. They are sensitive to the content of a number of simple ions (Pb^{2+}, Cd^{2+},[7] H^+,[8] SO_4^{2-}, PO_4^{3-} (see Ref. 9)) and complicated polyfunctional organic molecules (proteins[10]) in polymer matrices[8] and in solutions.[7,9,11,12] For example, spectrophotometric determination of erythromycin is possible due to its association with TS,[11] whereas sulfate ion is indicated in an acidic medium due to the formation of an ion pair between CS and squaramide.[12] It was shown that the use of heteroassociates is promising for the development of high-sensitive methods for determination of ionic surfactants in aqueous solutions.[13—15]

An analysis of the published data showed the necessity of more detailed investigation of cation-anionic interactions with the formation of associates including anions (HAn^-, An^{2-}) of the dyes considered. The facts of interaction of PS and its alkyl-substituted derivatives with single-charged cationic polymethines (Ct^+) have been mentioned earlier.[13,16] However, the most probable structure of the associates and their energy characteristics, in particular, enthalpy of formation $\Delta_f H°$, were not discussed.

In the present report, using the results of spectrophotometric measurements and quantum chemical calculations, we consider the cation-anionic interactions resulting in the formation of stoichiometric associates of single- and double-charged anions of sulfonephthaleins (SP) with single-charged cations of pinacyanol (PNC^+) and quinaldine red (QR^+) and discuss the energy characteristics and



SP



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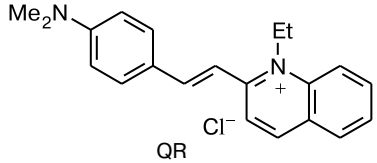

QR

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the probable structure of associates $Ct^+—HAn^-$ and $Ct^+—An^{2-}$. Note that polymethine cations Ct^+ are successfully used as "standard" ions in studying association processes of polyatomic species.[1—3,16,17]

Experimental

Sulfonephthalein disodium salts (reagent grade) and pinacyanol and quinaldine red chlorides (Sigma) were used. Purity of each dye was checked spectrophotometrically by the known values of molar absorption coefficient (ε_{max}/L mol^{-1} cm^{-1}) at the absorption band maximum (λ_{max}) of the most intensely colored protolytic form. Acidity of the medium was created by phosphate, borate, or acetic-acetate buffer solution and by additives of HCl or NaOH. It was found in additional experiments that the components of the buffer solutions used exert no noticeable effect on the studied heteroassociation processes. The ionic strength (I) of photometered solutions did not exceed 0.004 mol L^{-1}. The values of pH were monitored using a glass electrode. The calculations of equilibrium association constants (K_{as}) were based on the numerical values of absorbance, which were checked to the correspondence to the Bouguer—Lambert—Beer law. The absorption spectra were measured at room temperature immediately after preparation of photometered solutions on Hitachi-U3210 or SF-46 spectrophotometers with an inaccuracy of λ ±0.5 nm.

The geometric optimization of dye ions and their associates was performed by the AM1 (Austin Model 1) and PM3 (Parameterized Model 3) semiempirical methods in the framework of the MOPAC 2000 program package (Molecular Orbital PACkage). Note that the use of nonempirical methods, for example, Hartree—Fock, implies the necessity to specify nuclear coordinates of the molecule and the number of electrons and to choose the basis set of the calculation. The AM1 and PM3 methods work much more rapidly than the nonempirical methods and, which is the main, in the context of the problems solved in this study (determination of the geometry of polyatomic species and their $\Delta_f H°$) they give more reliable results. Their principal distinction from the nonempirical methods is the complete or partial rejection of calculations of one- and two-electron integrals appearing in the Hartree—Fock method. The approximate operator, whose elements are obtained from empirical data, is used instead of the precise operator. The differences in methods of choosing parameters, which are selected for both particular atoms and their pairs, and the introduction of various approximations (the approximation of zero-point differential overlapping is introduced for two-electron Coulomb and exchange integrals; only valent electrons are considered: it is believed that electrons of atomic cages only screen nuclei; only atomic orbitals with the principal quantum number corresponding to the highest electron-occupied orbitals of isolated atoms (minimal basis set) are taken into account in molecular orbitals, and several others) resulted in the creation of calculated modifications.[18] The AM1 and PM3 methods take into account a considerably greater number of parameters than other methods consider (for AM1 the parameters were optimized over 100 molecules, from 7 to 21 parameter per element; for PM3, over 657 molecules, 18 parameters per element). The values of $\Delta_f H°$ were calculated for the standard conditions.

In an aqueous solutions the cationic dyes exist as a single-charged cation (Ct^+). In strongly acidic and strongly alkaline media they are noticeably decolorized due to the formation of species HCt^{2+} and CtOH, respectively. Sulfonephthalein molecules dissociate stepwise as tribasic acids

$$H_3An^+ \rightleftharpoons H_2An^0 \rightleftharpoons HAn^- \rightleftharpoons An^{2-}.$$

The absorption bands of protolytic forms are well resolvable spectrally. Various anions are most intensely colored, especially An^{2-}. This fact favors the experimental study of ionic association of dyes in the region of very low (≥1·10^{-6} mol L^{-1}) concentrations of species. The substantial differences between the values of pK_{a1} and pK_{a2} (Table 1; the characteristics of sulfonephthaleins are presented by the data[19,20] for pinacyanol and quinaldine red, see Refs 19 and 21—23) make it possible to create such an acidity of the solution at which can exist only the anionic form interacting with the cationic dye.

Table 1. Spectral protolytic characteristics of the dyes[a]

Dye	Substituents, name	pK_{a1}[b]	pK_{a2}	λ_{max}[c]/nm (ε_{max}/L mol^{-1} cm^{-1})
	Sulfonephthaleins			
Phenolsulfonephthalein (PS)	$R^1 = R^2 = R^3 = H$	1.03	8.00	430 (2.4·10^4)/558 (6.2·10^4)
o-Cresolsulfonephthalein (CS)	$R^1 = R^3 = H$, $R^2 = Me$	1.05	8.46	433 (2.4·10^4)/572 (6.9·10^4)
Thymolsulfonephthalein (TS)	$R^1 = Pr^i$, $R^2 = H$, $R^3 = Me$	1.50	9.20	438 (1.45·10^4)/537 (2.8·10^4)
	Polymethines			
Pinacyanol (PNC)	1-Ethyl-2-[3-(1-ethyl-1*H*-quinolin-2-ylidene)propenyl] quinolinium	2.63	—	600, α-band (1.2·10^5); 550, β-band; 510, γ-band
Quinaldine red (QR)	2-[2-(4-Dimethylamino)phenyl]ethenyl-1-ethyl quinolinium	3.50	—	528 (3.1·10^4)

[a] The inaccuracy of pK_a is ±(0.03—0.08), that of λ_{max} is ±1 nm, and that ε_{max} is ±500 L mol^{-1} cm^{-1}.
[b] The values of pK_{a1} for PNC and QR refer to the dissociation of the HCt^{2+} cation.
[c] The values for HAn^-/An^{2-} in the case of sulfonephthaleins and for Ct^+ in the case of polymethines are indicated.

Results and Discussion

Association of Ct^+ with HAn^- and An^{2-}. The interpretation of spectral changes in the framework of the equilibrium approach (the use of the law of acting masses for determination of K_{as}) implies that the main law of light absorption by the protolytic forms of interacting dyes is fulfilled. It was spectrophotometrically found that in the studied regions of dye concentrations the linear equations of regressions of the law have the form presented in Table 2. The linear dependence of the absorbance on the content of the dye (C/mol L^{-1}) in solution $A_\lambda = B + kC$ is satisfactorily fulfilled in rather wide ranges of the dye concentrations. As follows from Table 2, the values of free terms of regressions B is random zero ($B < s_B$) and, therefore, $A_\lambda = kC$. It is noteworthy that the correlation coefficient almost coincides with unity. This suggests that PS and QR are not almost dimerized in the indicated concentration ranges. On the contrary, for PNC the main law of light absorption is fulfilled at low concentrations, because this polymethine is prone to self-association in water (the logarithm of dimerization constant of Ct^+ is equal to 4.79±0.06).[23] The transformation of the monomer into the dimer is manifested as a sharp weakening of the absorption of the α-band and an increase in the β-band intensity (see Table 1).

When studying the interaction of HAn^- or An^{2-} with Ct^+, it is necessary to fulfill such an acidity of the medium which would provide the coexistence of the corresponding ionic forms only (in the opposite case, the interpretation of spectral changes is impeded because of possible interactions involving other species as well). In order to reveal the optimal conditions of association, we calculated the fraction contents of the studied species with allowance for the above listed protolytic processes. For instance, it follows from the example shown in Fig. 1 that the interaction of cation QR^+ with anion PS^- can reasonably be studied at pH 4.0—6.0, that of cation PNC^+ with the same anion should be studied at pH 4.5—6.0, and the interaction of the polymethine cations with PS^{2-} should be studied at pH ≥ 9.0.

An analysis of changes in the electronic absorption spectra of mixtures of Ct^+ with HAn^- and Ct^+ with An^{2-} suggests that the spectral bands are not additive: the absorption intensity of a mixture of interacting counterions is systematically lower than the total light absorption of individual ions of the dyes. The characteristic indication of association is also a substantial decrease in the absorption intensity, which is distinctly observed as increasing amounts of PS are added to the unchanged amount of polymethine.

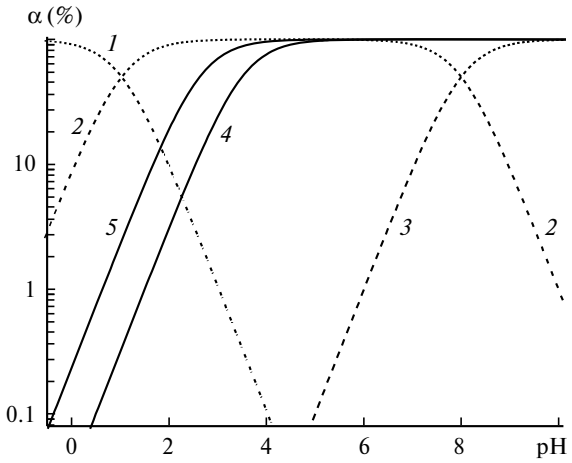


Fig. 1. Fraction content (α) of protolytic forms of phenolsulfonephthalein (*1*, H_2An; *2*, HAn^-; *3*, An^{2-}) and cations Ct^+ of pinacyanol (*4*) and quinaldine red (*5*) at various pH of an aqueous solution (ionic strength (I) → 0).

As an example let us consider in more detail the interaction of the double-charged anion PS^{2-} with cation PNC^+. Their absorption bands are almost superimposed (see λ_{max} in Table 1). The absorbance of the solution (A) increases along the whole scale of absorption frequencies with an increase in the PS concentration in the mixture (Fig. 2), if A is measured relative to water. In this case, the spectral shifts that occur are "masked" by the total absorption of the colored species.

A different pattern is observed if the values of A are measured relative to a solution of PS taken in the same concentration (it is reasonable to use the component, whose concentration is specified variable as a reference sample). In similar cases (Fig. 3), a decrease in A is observed. This indicates that a new compound appears in the

Table 2. Linear regression equations of the form $A_\lambda = B + kC$ for various ions*

Ion	C/mol L^{-1}	n	λ/nm	B	s_B	$k \cdot 10^{-4}$	s_k	r	s_r
PS^{2-}	$2 \cdot 10^{-6}$—$8 \cdot 10^{-5}$	11	558	0.00944	0.015	6.76	322	0.9999	0.0054
CS^{2-}	$5.0 \cdot 10^{-6}$—$1.0 \cdot 10^{-4}$	9	572	−0.0140	0.0038	6.86	116	0.9997	0.0022
TS^{2-}	$5.0 \cdot 10^{-6}$—$2.5 \cdot 10^{-4}$	10	537	0.0055	0.0068	2.88	165	0.9998	0.0018
QR^+	$1 \cdot 10^{-6}$—$1 \cdot 10^{-4}$	9	528	−0.0038	0.016	3.37	324	0.9996	0.033

* The values of s_B, s_k, and s_r are standard deviations of the free term of regression B, angular coefficient k, and correlation coefficient r, respectively. The value of n corresponds to the sampling volume of the initial molar concentration of the ion (C).

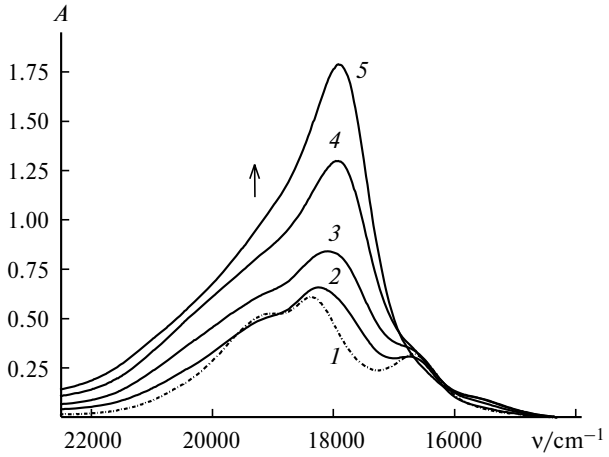


Fig. 2. Change in light absorption of pinacyanol ($4.85 \cdot 10^{-5}$ mol L^{-1}) upon the addition of phenolsulfonephthalein in a concentration of 0 (*1*), $2.5 \cdot 10^{-5}$ (*2*), $5.0 \cdot 10^{-5}$ (*3*), $7.5 \cdot 10^{-5}$ (*4*), and $1.0 \cdot 10^{-4}$ mol L^{-1} (*5*). Absorbing layer thickness 0.20 cm, pH 9.2, water as a reference solution. Hereinafter directions of spectral shifts are indicated by arrows.

solution (if no associate is formed, then for different PS concentrations in the mixture the contour of the absorption band would be retained almost unchanged and would coincide with curve *1* in Fig. 2). Note that for the α- and β-bands hypsochromic shifts are observed already at the concentrations of the anion comparable with the concentration of polymethine (see Fig. 3, spectra *2*—*5*).

An analysis of spectral changes (the presence of isosbestic points, local regions of absorbance saturation at a series of values of λ) in all systems shows that the cation and associate formed are in equilibrium

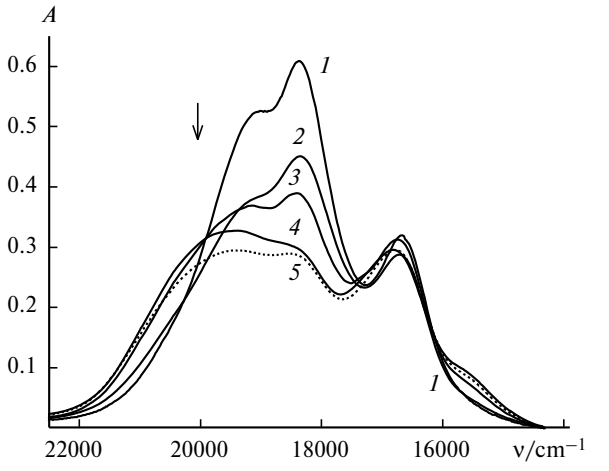


Fig. 3. Change in light absorption of pinacyanol ($4.85 \cdot 10^{-5}$ mol L^{-1}) upon the addition of phenolsulfonephthalein in a concentration of 0 (*1*), $2.5 \cdot 10^{-5}$ (*2*), $5.0 \cdot 10^{-5}$ (*3*), $7.5 \cdot 10^{-5}$ (*4*), and $1.0 \cdot 10^{-4}$ mol L^{-1} (*5*). Absorbing layer thickness 0.20 cm, pH 9.2, water (*1*) and solutions of sulfonephthalein in the corresponding concentrations (*2*—*5*) as reference solutions.

$$Ct^+ + HAn^- \rightleftharpoons Ct^+ \cdot HAn^-,$$

$$2\,Ct^+ + An^{2-} \rightleftharpoons (Ct^+)_2 \cdot An^{2-}.$$

The value of equilibrium constant K_{as}, determined by the law of acting masses as $K_{as} = [Ct^+ \cdot HAn^-] \cdot [Ct^+]^{-1} \cdot [HAn^-]^{-1}$ and $K_{as} = [(Ct^+)_2 \cdot An^{2-}] \cdot [Ct^+]^{-2} \cdot [An^{2-}]^{-1}$, is a measure of stability of associates (spectrophotometrically determined equilibrium molar concentrations of the corresponding species are given in brackets). Since the ionic strength of solutions I did not exceed 0.004 mol L^{-1}, the values of K_{as} (Table 3; K_{as} was calculated by analogy with Refs 3 and 16; for the data for PS, see Ref. 24) do not numerically differ from the thermodynamic values expressed not through equilibrium concentrations but through activities of the species. Note that blur appears and the color somewhat changes in more concentrated solutions of dye mixtures. These properties indicate the formation of compounds with more complicated stoichiometry and, probably, poorly soluble aggregates of various composition.

It follows from Table 3 that PNC associates are noticeably more stable than QR associates. One of the reasons for this is an increase in the fraction of hydrophobic interactions in pinacyanol associates. The hydrophobic contribution of the quinoline fragment in a PNC molecule is more significant, most likely, than the contribution of the *N*,*N*-dimethylaniline fragment in a QR molecule. In addition, the enhancement of association is favored by dispersion interactions appeared, to a considerable extent, for developed π-electron systems.[1,3] They are more typical of the cation PNC^+ due to specific features of the structure.

Structure and energy of the associates. It is known[1,25,26] that dyes with the flattened shape of the molecule are characterized to a greater extent by association. However, anions of the sulfonephthaleins considered are not planar π-electron systems. As follows from the values of K_{as}, the interaction between Ct^+ and anions is appreciable. Using quantum chemical calculations, we revealed the energy states (enthalpies of formation $\Delta_f H°$) for each counterion and associate and determined their most probable structure. The AM1 semiempirical method as one of extended MNDO methods and the PM3 method were used for the

Table 3. Values of $\log K_{as}$ for the sulfonephthalein associates with PNC and QR

Sulfonephthalein	$\log K_{as}$			
	PNC^+		QR^+	
	$Ct^+ \cdot HAn^-$	$(Ct^+)_2 \cdot An^{2-}$	$Ct^+ \cdot HAn^-$	$(Ct^+)_2 \cdot An^{2-}$
PS	5.83±0.10	11.81±0.10	5.13±0.09	8.64±0.09
CS	4.59±0.03	10.96±0.10	4.00±0.10	6.10±0.10
TS	5.29±0.05	11.00±0.10	4.10±0.10	5.90±0.10

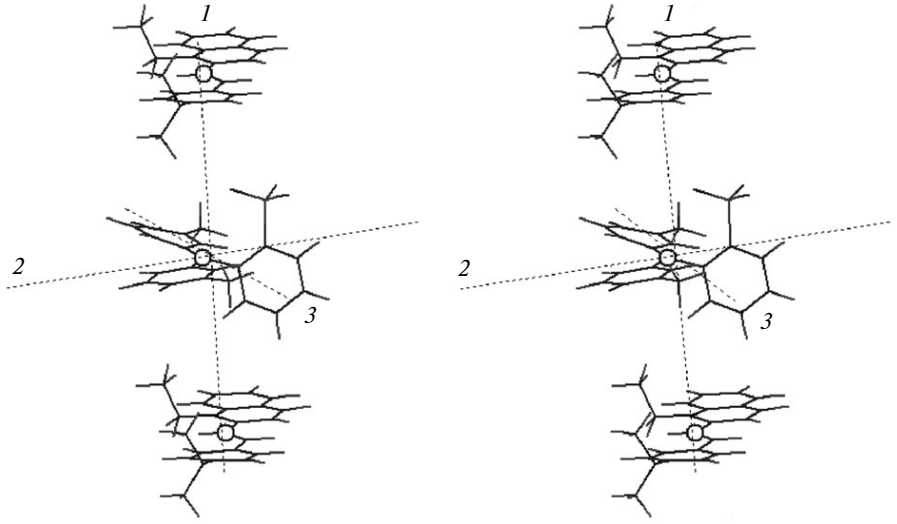
estimation of $\Delta_f H^\circ$ of ions and heteroassociates.[27,28] Parametrization of these methods was performed in such a way that the experimental values of $\Delta_f H^\circ$ of organic compounds would be best reproduced (for example, the average inaccuracy of the AM1 method for the calculation of $\Delta_f H^\circ$ is 25 kJ mol^{-1}).[27] It should be mentioned that similar nonempirical calculations result in inaccuracies for $\Delta_f H^\circ$ exceeding 100 kJ mol^{-1} even for small molecules. As the number of atoms in a molecule increases, inaccuracies in calculation of $\Delta_f H^\circ$ increase more and become systematic.[29] The two methods are used because of the wish to achieve higher reliability of the absolute values of $\Delta_f H^\circ$ and of the necessity to reduce to minimum the systematic inaccuracy in observation of the run of changing $\Delta_f H^\circ$ for the associates of related composition.

The convergence gradient of consecutive iterations (RMS-gradient (root-mean-square value), the local energy minimum of the structure was considered achieved when it was equal to zero) decreased from 4.2 to 0.04 kJ mol^{-1}. The data presented in Table 4 indicate satisfactory convergence of the results obtained by each calculation method. The variation range of $\Delta_f H^\circ$ does not exceed 20 kJ mol^{-1} (anion PS^-, AM1 method) and 26 kJ mol^{-1} (anion CS^-, PM3 method). A comparison of the absolute values of $\Delta_f H^\circ$ calculated by two semiempirical methods (hereinafter the most negative values were accepted as the final values of $\Delta_f H^\circ$ shows that the differences in them can hardly be considered principal in the context of the stated problems. So, a maximum divergence of the results of AM1 and PM3 calculations is 44 kJ mol^{-1} (for ion PS^{2-}).

We tested six—seven various starting mutual arrangements of counterions (each of the counterions was preliminarily geometrically optimized) during geometrical optimization of the associate structures to find the global energy minimum. The least minimum was chosen from the obtained set of energy (so-called local) minima, and the energy of this structure was taken to be corresponding to the global minimum. Then the additional geometrical optimization of the associate structure was performed by decreasing the values of RMS-gradient, as a rule, from 0.1 to $5.0 \cdot 10^{-3}$—$1.0 \cdot 10^{-4}$ kJ mol^{-1}, which decreased $\Delta_f H^\circ$. Completion of structure optimization was established by the absence of changing $\Delta_f H^\circ$ with a change in RMS (slope regions of the dependences). Figure 4 exemplifies the changes in $\Delta_f H^\circ$ at different values of RMS-gradient for the QR heteroassociates. Table 5 presents the course of consecutive geometrical optimization of the heteroassociate $(PNC^+)_2 \cdot TS^{2-}$ (anion in the center; stereoimages are given in Fig. 4 for clarity; the position of the anion relative to the observer is conventionally fixed). As follows from the data in Fig. 4 and Table 5, geometry optimization of the structure depends substantially on the values of RMS; however, the optimization is almost completed already at 0.01 kJ mol^{-1} and is accompanied by the shortening of the distance between the counterions and by a noticeable for-

Table 4. Variation scatter of values of $\Delta_f H^\circ$ for ions of the dyes

Ion	$\Delta_f H^\circ$/kJ mol^{-1}	
	AM1	PM3
PS^-	−(556—576)	−(575—586)
PS^{2-}	−(479—492)	−(534—536)
CS^-	−(647—661)	−(656—682)
CS^{2-}	−(569—570)	−(597—606)
TS^-	−(730—746)	−(746—763)
TS^{2-}	−(667—671)	−(702—712)
PNC^+	1076—1073	980—968
QR^+	989—984	918—912



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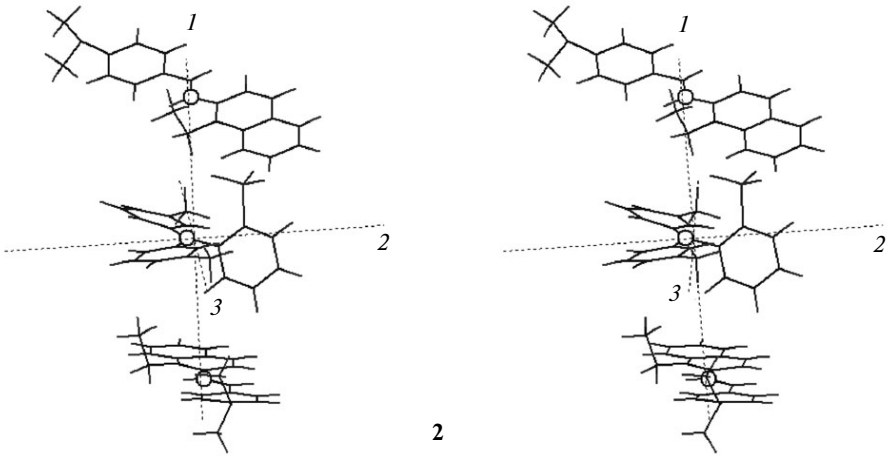

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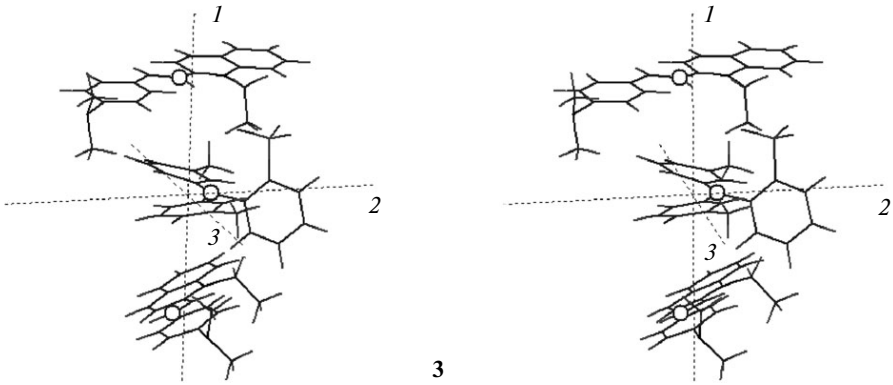

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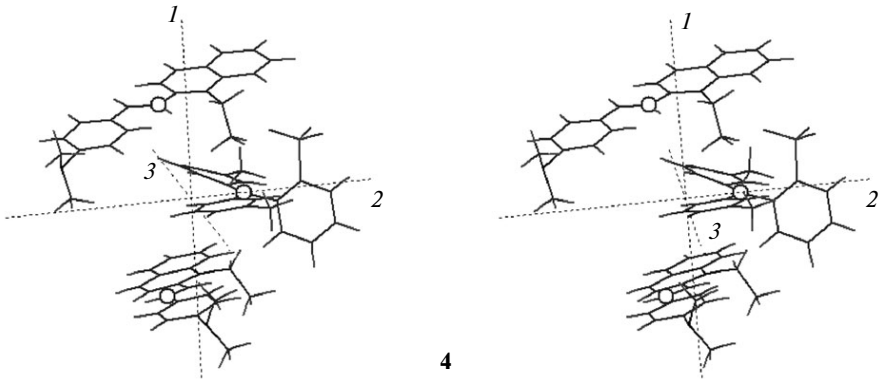

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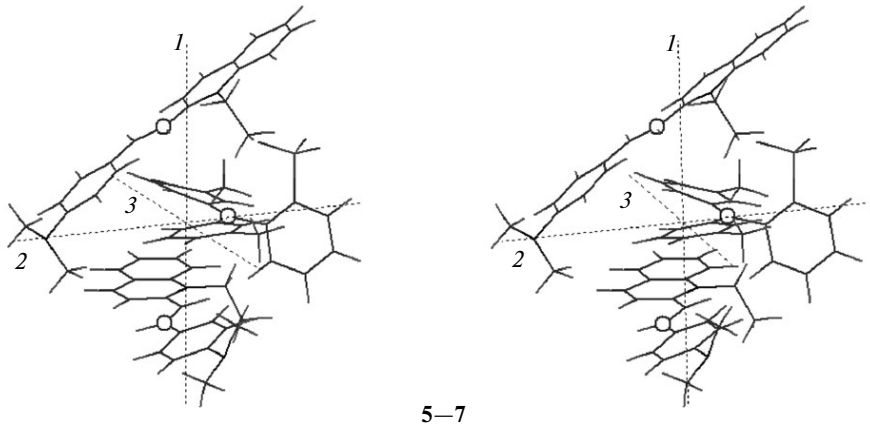

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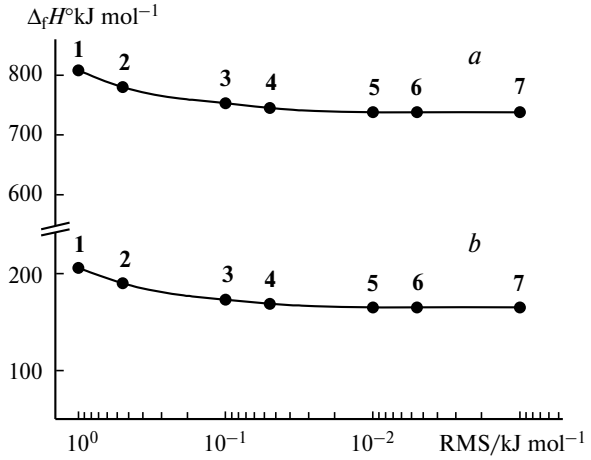

Fig. 4. Changes in values of $\Delta_f H°$ calculated by the AM1 method for quinaldine red heteroassociates with double- (*a*) and single-charged (*b*) cresolsulfonephthalein anions at various specified values of RMS-gradient; digits in curve *a* correspond to structures **1**—**7**, where **1** is the starting position of geometric optimization and **7** is the final position.

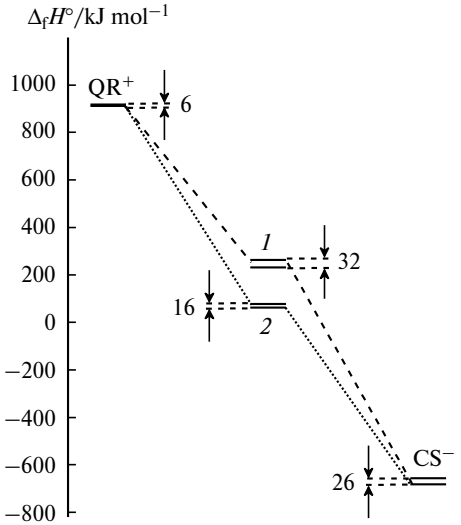

Fig. 5. Values of $\Delta_f H°$ (PM3 method) of quinaldine red (QR^+) and cresolsulfonephthalein (CS^-) ions and the algebraic sum of $\Delta_f H°$ of these ions (*1*) and $\Delta_f H°$ of the $QR^+ \cdot CS^-$ associate (*2*). Here and in Fig. 6 digits at arrows designate the variation range of $\Delta_f H°$/kJ mol^{-1} for the corresponding species.

mation of the planes of the π-electron systems of the polymethine cation.

Figures 5 and 6 exemplify the energy characteristics of ions of the CS and TS dyes and heteroassociates. In Fig. 5, $\Delta_f H°$ = 918—912 and −(656—682) kJ mol^{-1} correspond to ions QR^+ and CS^-, respectively (PM3 method, see Table 4). Their algebraic sum is Σ = (918 − 656)—(912 − 682) = = 262—230 kJ mol^{-1} (energy level *1*) exceeds $\Delta_f H°$ = = 77—62 kJ mol^{-1} of associate $QR^+ \cdot CS^-$ (level *2*) by (262 − 62)—(230 − 77) = 200—153 kJ mol^{-1}. Similarly, in Fig. 6 ions PNC^+ and TS^{2-} are characterized by the values $\Delta_f H°$ = 1076—1073 kJ mol^{-1} and −(667—671) kJ mol^{-1} (method AM1, see Table 4); in this case, two cations PNC^+ has an energy of 2152—2146 kJ mol^{-1}. The algebraic sum for the counterions is Σ = (2152 − 667)—(2146 − 671) = = 1485—1475 kJ mol^{-1} (level *1*). Since $\Delta_f H°$ of heteroassociate $(PNC^+)_2 \cdot TS^{2-}$ was found to be 844—822 kJ mol^{-1} (level *2*), the algebraic sum of the energy of the counterions exceeds $\Delta_f H°$ of the heteroassociate (in fact, the difference Σ − $\Delta_f H°$) by 663—631 kJ mol^{-1}. The relative inaccuracy of the difference Σ − $\Delta_f H°$ for the system QR^+—CS^- is (200 − 153) · 100%/200 = 23.5%, and that for the system PNC^+—TS^{2-} is (663 − 631) · 100%/663 = 5%.

The values of Σ, $\Delta_f H°$, and Σ − $\Delta_f H°$ for other associates were calculated by the same way and these data are listed in Table 6.

Table 5. Geometric optimization of the associate $(PNC^+)_2 \cdot TS^{2-}$ by the AM1 method (see Fig. 4)

Structure	*d**/Å		α/deg
	A	*B*	
1	7.8	7.8	~180
2	8.0	7.6	158
3	6.7	6.3	143
4	5.1	5.3	131
5—7	4.7	4.8	110

* Distance between the marked atoms: upper and medium (*A*); medium and bottom (*B*).

** Central angle with the vertex at the marked carbon atom of the anion.

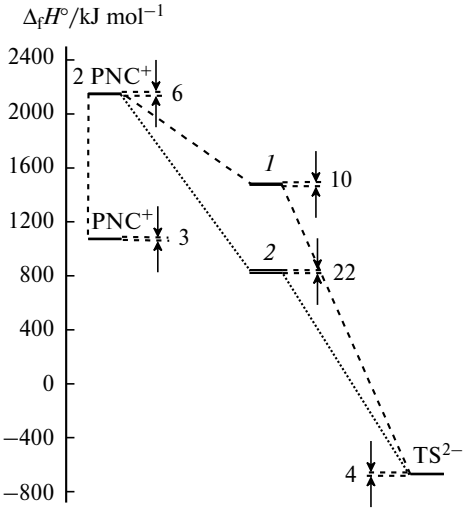

Fig. 6. Values of $\Delta_f H°$ (PM3 method) of pinacyanol (PNC^+) and thymolsulfonephthalein (TS^{2-}) ions and the algebraic sum of $\Delta_f H°$ of these ions (*1*) and $\Delta_f H°$ of the $(PNC^+)_2 \cdot TS^{2-}$ associate (*2*).

Table 6. Energy characteristics of the heteroassociates

Heteroassociate	AM1			PM3		
	Σ^a	$\Delta_f H°$	ρ^b (%)	Σ^a	$\Delta_f H°$	ρ^b (%)
	kJ mol^{-1}			kJ mol^{-1}		
Pinacyanol heteroassociates						
$PNC^+ \cdot PS^{--}$	497	344	19	382	134	9
$PNC^+ \cdot CS^-$	413	261	21	287	104	36
$PNC^+ \cdot TS^-$	327	170	17	205	24	24
$(PNC^+)_2 \cdot PS^{2-}$	1654	979	6	1400	688	7
$(PNC^+)_2 \cdot CS^{2-}$	1577	908	6	1331	630	18
$(PNC^+)_2 \cdot TS^{2-}$	1476	822	5	1225	514	10
Quinaldine red heteroassociates						
$QR^+ \cdot PS^-$	407	258	16	326	122	8
$QR^+ \cdot CS^-$	323	165	12	230	62	23
$QR^+ \cdot TS^-$	238	87	26	149	–45	25
$(QR^+)_2 \cdot PS^{2-}$	1475	757	5	1288	518	4
$(QR^+)_2 \cdot CS^{2-}$	1398	738	5	1219	476	7
$(QR^+)_2 \cdot TS^{2-}$	1297	625	5	1113	375	20

[a] Σ is the algebraic sum of $\Delta_f H°$ of the corresponding ions in the associate defined as $\Sigma = i\Delta_f H°(Ct) + \Delta_f H°(An)$, where i is the number of cations in the associate composition.
[b] Relative inaccuracy of $\Sigma - \Delta_f H°$. The values of Σ were calculated using $\Delta_f H°$ of the dye ions (see Table 4).

An analysis of the obtained data suggest the following. Since the error of the calculated value of $\Sigma - \Delta_f H°$ does not substantially exceed the mentioned average inaccuracy of the method of calculation of $\Delta_f H°$, we may assert that the association is energetically favorable. The energy gain achieves 150—250 kJ mol^{-1} (for associates of single-charged sulfonephthaleins) and 650—770 kJ mol^{-1} (for double-charged sulfonephthaleins). The data in Table 6, as well as the data in Table 3, indicate higher stability of the PNC associates.

Changes in $\Delta_f H°$ (vacuum) and K_{as} (solution) do not necessarily correspond to each other, since semiempirical calculations cannot take into account several interactions (for example, hydrophobic interactions characteristic of bulky polyatomic counterions of dyes[1,30]). Nevertheless, in spite of systematically lower values of $\Delta_f H°$ calculated by the PM3 method, approximately the same run of changing $\Delta_f H°$ is observed (hereinafter approximated values are given in parentheses, AM1/PM3) as in the case of K_{as}, for both pinacyanol associates

$$PNC^+ \cdot TS^- (170/24) < PNC^+ \cdot CS^- (261/104) < PNC^+ \cdot PS^- (344/134),$$

$$(PNC^+)_2 \cdot TS^{2-} (822/514) < (PNC^+)_2 \cdot CS^{2-} (908/630) < (PNC^+)_2 \cdot PS^{2-} (979/688),$$

and associates of quinaldine red

$$QR^+ \cdot TS^- (87/-45) < QR^+ \cdot CS^- (165/62) < QR^+ \cdot PS^- (258/122),$$

$$(QR^+)_2 \cdot TS^{2-} (625/375) < (QR^+)_2 \cdot CS^{2-} (738/476) < (QR^+)_2 \cdot PS^{2-} (757/518).$$

It follows from the quantum chemical calculations (by analogy to the data of Table 5) that the distance between the dyes in the associates of CS and TS anions is longer than that in the PS associates. Alkyl substituents prevent mutual approaching of the counterions. As a result, dispersion interactions are weakened, being a significant factor of association of association of polyatomic species,[16,30] and the CS and TS associates are less stable than those of PS.

It was found in special study than the introduction of bromine atoms into the sulfonephthalein structure enhances the cation-anionic interactions. For instance, the calculations show that $\Delta_f H°$ of the associates of single-charged 5,5′-dibromo-*o*-cresolsulfonephthalein is 312/202 kJ mol^{-1} for cation PNC^+, 219/107 kJ mol^{-1} for cation QR^+, and 928/703 and 747/525 kJ mol^{-1} for the double-charged anion, respectively. These values are systematically higher than $\Delta_f H°$ presented in Table 6 for the cresolsulfonephthalein anions containing no bromine. A similar situation is observed for associates of the anion of brominated thymolsulfonephthalein, *viz.*, 3,3′-dibromothymolsulfonephthalein. For its single-charged anion and cation PNC^+ $\Delta_f H°$ is 240/105 kJ mol^{-1}, for cation QR^+ 147/81 kJ mol^{-1}, and for the double-charged anion 858/527 and 703/406 kJ mol^{-1}, respectively. It is most likely that the bromine atoms are arranged in the plane of the benzene rings and exert almost no effect on the geometry of sulfonephthaleins but significantly enhance the hydrophobic component of intermolecular interactions.

The results obtained also indicate that processes of dye association are accompanied by rather complex combination of various interactions, including dispersion and π-electron interactions, the study of which implies a comparison of results of spectral measurements with computer simulation data.

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