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Solvatochromism of Heteroaromatic Compounds: XXI.[1] Ion Pairs of 4-Nitropyrazolide Anion

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Abstract — The solvatochromism of the long-wave UV absorption band of the contact ion pairs of the 4-nitropyrazolide anion with alkali metal cations in aprotic protophilic solvents with $\varepsilon \leq 24$ was studied and quantitatively described using the Kamlet–Taft empirical solvent parameters. Of two possible types of tight ion pairs differing in the murtual arrangement of the counterions, the solvent stabilizes the pair in which the cation is located in the σ plane of the anion in the vicinity of its nitrogen atoms. Among the factors affecting the quantitative characterisitcs of the solvatochromism of such ion pairs, the major factors are the polarity/polarizability of the solvent and the capability of its molecules for coordination with cations. The peripheral specific solvation of the cation in an ion pair stabilizes its Franck–Condon excited state relative to the ground electronic state. In the quantitative respect, this effect is similar to that characteristic of solvation H complexes.

It is known [2] that organometallic compounds can exist in solution in the form of tight and loose ion pairs. The position of the equilibrium between them depends on their structural features and external conditions.

Tight ion pairs $\{[A^-M^+]\}$ are also often termed contact ion pairs. Loose ion pairs are subdivided into solvation-separated ion pairs $\{[A^-//M^+]\}$ and ion pairs involving a solvent $\{[A^-SN^+]\}$ [2]. As compared to contact ion pairs, loose ion pairs are much more similar in positions of the UV absorption maxima to free ions generated in solvents with a strong dissociative power. Therefore, transformation of $[A^-//M^+]$ into $[A^-M^+]$ is, as a rule, accompanied by a pronounced spectral shift (ion-pair effect). The shift of the absorption maximum in going from a free ion to a contact ion pair is determined by the extent to which the ground and excited states of this pair are stabilized by the solvent and by the field of the cation.

In the case of aromatic amines in ether solvents, the transition $[A^-//M^+] \rightarrow [A^-M^+]$ is facilitated in solvents with a low dielectric permittivity ε, at elevated temperatures, with large cations, and with anions in which the negative charge is delocalized (see [3, 4] and references therein). These observations suggest the prevailing role of cation solvation. It is noted [3, 4] that, at similar physical characteristics of solvents, the position of the equilibrium $[A^-//M^+] \rightleftarrows [A^-M^+]$ is sensitive to the chemical structure of the solvent molecules. For example, in 1,2-dimethoxyethane, contact ion pairs of carbanions are less stable than in tetrahydrofuran [4], which allowed a conclusion that the mechanism of cation solvation is chiefly specific.

In heteroatomic and heteroaromatic anions, the degree of localization of the excess negative charge on the heteroatom is the major, and maybe even decisive, factor. The pattern with such ion pairs principally differs from that observed with carbanionic ion pairs. Contact ion pairs of such anions were detected even at very low temperatures and in highly polar solvents (e.g., dimethylformamide) [5–7]. The relative stability of ion pairs is also influenced by the specific solvation of the anion [5].

On the whole, formation of a contact ion pair in an aprotic protophilic medium can be considered as an exchange between the anion and solvent molecules in the first solvation sphere of the cation [8]. When the solvent is a weaker electron donor than the anion, the probability of formation ot $[A^-M^+]$ pairs is high, and vice versa. Under equal other conditions, the transformation $[A^-//M^+] \rightarrow [A^-M^+]$ will be hindered if the solvent can specifically solvate the anion. Since amphiprotic solvents can coordinate with both counterions, formation of contact ion pairs containing a heteroaromatic anion will be more probable in aprotic protophilic solvents than in amphiprotic solvents with the same dissociative power.

The above-mentioned papers also discussed the effect of the peripheral solvation of the cation in a

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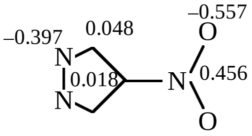
[1] For communication XX, see [1].

contact ion pair on its UV spectrum. This effect is qualitatively explained in terms of a hypothesis that the positive charge of the cation in [A^-M^+] is dissipated upon coordination of the cation with the solvent molecule, which affects the electric field produced by the cation. However, the extent of this effect is still unclear. It is also unclear whether this effect depends on particular counterions and especially on the structure of contact ion pairs of heteroaromatic anions with the highly localized charge.

Here we report and discuss the structure of contact ion pairs of the 4-nitropyrazolide anion with alkali metal cations (M^+) in aprotic protophilic solvents. The conclusions are based on the experimental data on the solvatochromism of the long-wave UV absorption band ($\nu^{\pm}_{\max}$). Analysis shows that the tight ion pairs under consideration exist in a wide range of the dielectric permittivities of the solvent (ε 7–24).

Theoretical data on the structure of contact ion pairs. The total Mulliken charge distribution on heavy atoms of the 4-nitropyrazolide anion (Scheme 1), obtained by *ab initio* (HF/6-31G*) calculations, shows that the excess electron density in its ground state is mainly localized on the N and O heteroatoms.

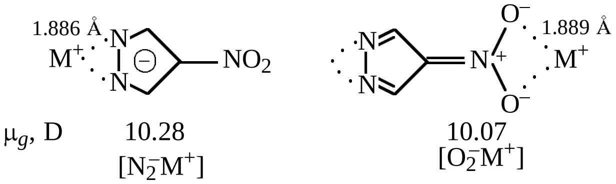
Scheme 1.



Thus, when interpreting the ion-pair effect in the UV spectrum, it is necessary to take into account possible formation of two species differing in the mutual arrangement of the counterions, namely, of the ion pairs denoted in Scheme 2 as [$N_2^-M^+$] and [$O_2^-M^+$]. When the cation is arranged beyond the horizontal symmetry plane of the mesomeric 4-nitropyrazolide anion, the contact ion pairs become unstable (the calculations were performed for Li^+) and transform into one of the structures shown in Scheme 2. This fact should result in that the influence of the size of the alkali metal ion, located in the σ plane of the contact ion pair, on the energy of the $\pi \rightarrow \pi^*$ electronic transitions will be considerably weaker as compared to aromatic carbanions or phenolate ions. This conclusion can be readily checked spectroscopically.

Both ion pairs are symmetrical and are characterized by approximately equal distances between M^+ and the donor atoms (N or O; in Scheme 2 and further, the theoretical results are given for the tight pairs with lithium cations, unless otherwise indicated). Nevertheless, the ion pair [$N_2^-M^+$] is considerably more stable (by 7.7 kcal mol^{-1}) in the isolated state.

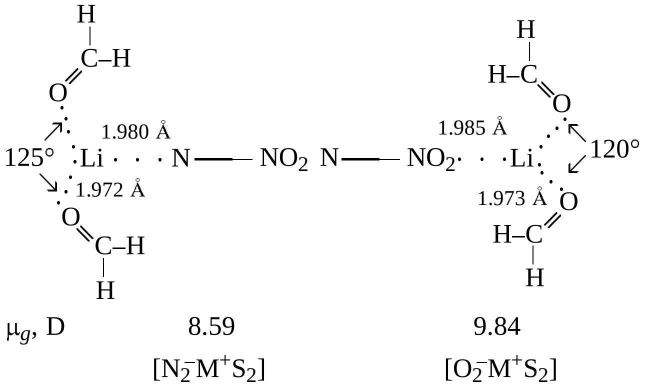
Scheme 2.



Simulation of the selective specific solvation of the cation in the contact ion pairs by calculation of the square-planar solvation complexes [$N_2^-M^+$] or [$O_2^-M^+$] with two formaldehyde molecules gave certain results.

First, such complexes are unstable, and full optimization of their geometry leads to the structures shown in Scheme 3. Second, the bond between the counterions in the contact ion pair upon peripheral solvation of the cation becomes weaker: The equilibrium Li–N or Li–O distances increase by ~0.11 Å. Thus, we can conclude that the effect exerted by selective solvation of the cation in contact ion pairs is formally equivalent to an increase in its ionic radius (HF/6-31G*, [$N_2^-M^+$], $l_{M–N}$: Li^+ 1.866, Na^+ 2.213, K^+ 2.581 Å). This conclusion can also be checked experimentally. Third, the relative stability of the specifically solvated contact ion pairs [$N_2^-M^+S_2$] and [$O_2^-M^+S_2$] remains approximately the same as without solvation: The ion pair [$N_2^-Li^+(H_2CO)_2$] is more favorable energetically by 7.5 kcal mol^{-1}. As the isomeric contact ion pairs shown in Schemes 2 and 3 differ in the ground-state dipole moments insignificantly, the solvation complexes [$N_2^-M^+S_2$] should undoubtedly remain preferable in aprotic protophilic solvents (solvation with a block of molecules).

Scheme 3.



Factors favoring elucidation of the structure of the contact ion pair in solution. There are three types of properties of contact ion pairs containing nitrogen and oxygen atoms in which the difference between the isomeric structures is sufficiently pronounced to identify the structure in solution.

The first such property deserves special mentioning. The 4-nitropyrazolide anion in the contact ion pair $[O_2^-M^+S_2]$ does not lose the capability for formation of H complexes with an amphiprotic solvent via N atoms. In this respect, such an ion pair should be similar to the free anion. The solvatochromism of the long-wave absorption band in the UV spectrum of the 4-nitropyrazolide anion was studied in [9] using solvents with a high dissociative power; it is described by Eq. (1):

$$\nu^{-}_{\max} = (31180 \pm 220) + (1420 \pm 70)\alpha - (1370 \pm 220)\pi^*; \quad (1)$$

$$R\ 0.985,\ sd\ 90,\ n\ 8.$$

Its free term corresponds to $\nu^{-}_{\max}$ in a fully inert medium ($\sigma = \pi^* = 0$); α and π^* are Kamlet–Taft empirical solvent parameters [10, 11]: α characterizes the capability of solvent molecules to act as hydrogen bond donors in an H complex with a solute, and π^*, the capability of the solvent to stabilize dipolar molecules or ions. It follows from Eq. (1) and data from [9] that the specific solvation contributes by more than a half to the shift of an electronic absorption band of a free anion in solution. Unfortunately, because of a number of factors, we failed to use this feature of contact ion pairs of the 4-nitropyrazolide anion for identifying their structure. Firstly, in amphiprotic solvents that are hydrogen bond donors, the solvatochromism of the long-wave absorption band is pronounced very weakly (Table 1). Therefore, in a relatively narrow range of parameters for alcohols it is impossible to obtain an equation describing the solvatochromism with a satisfactory correlation coefficient. Secondly, in such solvents the ion-pair effect is manifested weakly or is absent at all (Tables 1, 2), suggesting the occurrence of the labile equilibrium $[A^-M^+] \rightleftarrows [A^-//M^+]$. The same is suggested by a certain shift of the absorption maximum of sodium 4-nitropyrazolide in solutions with $\varepsilon < 13.5$ (nos. 1–3 and 10, Tables 1 and 2) toward higher frequencies relative to the free anion. Thirdly, in amphiprotic solvents with $\varepsilon > 13.5$, and also in *tert*-butyl and *iso*-amyl alcohols (nos. 4–9 and 11, Tables 1 and 2), the absorption band of the ion pair is slightly shifted in the opposite direction (bathochromically) relative to the free anion. This is most probably due to the fact that the specific solvation of the anion in the contact ion pair initiates the cationotropic transformation $[N_2^-M^+S_2] \rightleftarrows [O_2^-M^+S_2]$. The same is suggested by the results of the HF/6-31G* calculations of the ion pairs $[N_2^-Li^+]$ and $[O_2^-Li^+]$ solvated by four water molecules. Two of them interact with the lithium cation, and the other two, either with the oxygen atoms of the nitro group or with the nitrogen atoms of the five-membered ring. According to the *ab initio* calculations, the ion pair $[N_2^-Li^+](H_2O)_4$ is energetically preferable by 4.2 kcal mol^{-1}. Comparison with the isolated ion pairs (ΔE 7.7 kcal mol^{-1}) shows that the energy gap between the isomeric ion pairs appreciably decreases upon specific solvation of the nitrogen atoms of the heteroring, i.e., in amphiprotic solvents the equilibrium shifts toward the contact ion pair with the counterion localized in the vicinity of the oxygen

Table 1. Solvatochromism of the long-wave absorption band in the UV spectrum of sodium 4-nitropyrazolide in amphiprotic solvents

Solvent no.	Solvent	Kamlet–Taft parameters[a]			Ion pair, $\nu^{\pm}_{\max}$, cm^{-1}	Free ion,[b] $\nu^{-}_{\max}$, cm^{-1} (±90)
		α	β	π^*		
1	1-Octanol	0.62	0.97	0.37	31 850	31 550
2	1-Heptanol	0.64	0.96	0.39	31 600	31 550
3	1-Hexanol	0.67	0.94	0.41	31 700	31 550
4	*tert*-Butyl alcohol	0.68	1.01	0.41	31 450	31 600
5	1-Pentanol	0.70	0.92	0.44	31 400	31 550
6	2-Propanol	0.76	0.95	0.48	31 050	31 600
7	*iso*-Amyl alcohol	0.78	0.90	0.45	31 250	31 650
8	1-Propanol	0.78	0.83	0.52	31 250	31 600
9	1-Butanol	0.79	0.88	0.47	31 250	31 650
10	Benzyl alcohol	0.80	0.50	0.98	31 200	30 950
11	Ethanol	0.83	0.77	0.54	31300	31 600

[a] The solvatochromic parameters were taken from [10, 11]. [b] The position of the absorption maximum in the UV spectrum of the free anion was estimated by Eq. (1).

Table 2. Solvatochromism of alkali metal 4-nitropyrazolides (ν_{max}, cm^{-1}) in amphiprotic solvents

Solvent[a]	ε[b]	Counterion				
		Li^+	Na^+	K^+	Rb^+	Cs^+
1-Octanol	10.3[c]	31 750	31 850	31 950	31 950	31 850
tert-Butyl alcohol	12.5	31 550	31 450	31 650	31 650	31 600
1-Hexanol	12.5[c]	31 650	31 700	31 750	31 700	
Benzyl alcohol	13.1	31 350	31 200	31 200	31 100	31 150
1-Pentanol	13.9	31 450	31 450	31 400	31 400	31 400
1-Butanol	17.5	31 250	31 250	31 300	31 300	31 300
1-Propanol	20.5	31 250	31 250	31 250	31 300	31 250
Ethanol	24.6	31 350	31 300	31 250	31 300	31 300

[a] The solvatochromic parameters and UV absorption maxima for the free anion in alcohols are given in Table 1. [b] The dielectric permittivities of solvents are taken from [2]. [c] Data of [12].

atoms of the nitro group. In other words, in amphiprotic solvents with $\varepsilon < 24$, a complex labile equilibrium $[N_2^-M^+]_s \rightleftarrows [O_2^-M^+]_s \rightleftarrows [A^-M^+]$ is apparently realized.

The second specific feature is as follows. The *ab initio* calculations of ion pairs with Li^+ show that localization of the cation at the nitrogen or oxygen atoms affects the energies of the $\pi \rightarrow \pi^*$ transitions differently (Table 3). In the contact ion pair $[N_2^-M^+]$, the intramolecular charge-transfer transition (the most intense among the transitions given in Table 3) is shifted toward higher wave numbers relative to the free ion, and in the ion pair $[O_2^-M^+]$, to lower wave numbers. Specific solvation of the cation in both ion pairs with formaldehyde leads to a minor red shift of the intramolecular charge-transfer transition. Hence, comparison of the spectrum of the ion pair in aprotic protophilic solvent with the spectrum of the free anion [found, e.g., by Eq. (1)] furnishes information about the structure of the ion pair. However, application of this approach to solvents exhibiting a high affinity for positively charged species requires certain care. Actually, under the conditions of strong specific solvation of the cation in an ion pair, the specific solvatochromic effect caused by solvation may appear to be similar in value but opposite in sign to the ion-pair effect. Then the spectrum of the ion pair will become close to the spectrum of the free anion. Therefore, to elucidate the structure of a contact ion pair, it is necessary to use such a set of protophilic solvents with which it would be possible to obtain a solvatochromism equation with a high correlation coefficient. This will allow comparison of the free term with that in Eq. (1). The free terms in solvatochromism equations can be directly compared to each other, because, within the Kamlet–Taft parameter scale, they are independent of

Table 3. Characteristics of electronic transitions in the UV spectra of free 4-nitropyrazolide anion, its contact ion pairs with Li^+, and their solvation complexes with two formaldehyde molecules [HF/6-31G*(CI) calculations]

Species	Transition type	ν, cm^{-1}[a]	f
Anion	$n \rightarrow \pi^*$	34 200	0.00
	$n \rightarrow \pi^*$	37 000	0.00
	$\pi \rightarrow \pi^*$	34 800	0.48
	$\pi \rightarrow \pi^*$	38 700	0.04
Ion pair $[N_2^-Li^+]'$	$n \rightarrow \pi^*$	33 600	0.00
	$n \rightarrow \pi^*$	35 600	0.00
	$\pi \rightarrow \pi^*$	39 500	0.40
	$\pi \rightarrow \pi^*$	43 200	0.00
Ion pair $[O_2^-Li^+]$[b]	$n \rightarrow \pi^*$	32 800	0.00
	$n \rightarrow \pi^*$	37 400	0.01
	$\pi \rightarrow \pi^*$	32 600	0.04
	$\pi \rightarrow \pi^*$	33 700	0.81
Solvation complex $[N_2^-Li^+] \cdot (H_2CO)_2$	$n \rightarrow \pi^*$	31 600	0.00
	$n \rightarrow \pi^*$	31 600	0.00
	$n \rightarrow \pi^*$	33 700	0.00
	$n \rightarrow \pi^*$	35 800	0.00
	$\pi \rightarrow \pi^*$	39 000	0.39
	$\pi \rightarrow \pi^*$	43 700	0.00
Solvation complex $[O_2^-Li^+] \cdot (H_2CO)_2$	$n \rightarrow \pi^*$	31 500	0.00
	$n \rightarrow \pi^*$	31 500	0.00
	$n \rightarrow \pi^*$	33 800	0.00
	$n \rightarrow \pi^*$	38 500	0.01
	$\pi \rightarrow \pi^*$	33 000	0.80
	$\pi \rightarrow \pi^*$	33 400	0.04

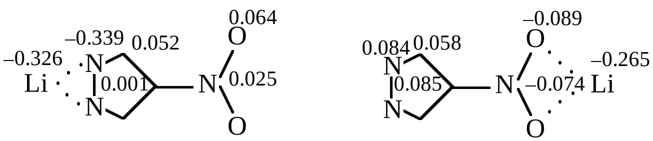
[a] The values of ν in the table correspond to 0.75ν[HF/6-31G*(CI)]. [b] In the range 36 000–46 000 cm^{-1}, there are weak ($f < 0.03$) Rydberg-type electronic transitions ($N \rightarrow R$) to the atomic orbital of the cation.

specific solvation. We emphasize once more that, when directly comparing the wave numbers of absorption maxima of an ion pair and the corresponding free anion in a specific solvent, it is difficult to avoid wrong conclusions originating from differences in the mechanism of solvation of the contact ion pair and free anion.

The third criterion can be used only as a supplement to the second criterion. It is associated with the sensitivity of the spectrum of solvation complexes of contact ion pairs to nonspecific solvation, described by the coefficient s at the empirical parameter π^* in solvatochromism equations. The quantity s, as shown in [12], is determined by the whole set of electrostatic and electrodynamic interactions of solvent molecules with solute molecules in the ground and Franck–Condon excited state. The most general version of the theory of solvatochromism [14] predicts that such interactions are determined, in particular, by the difference between the dipole moment vectors in the ground (μ_g) and electronically excited (μ_e) states. Nonsolvated contact ion pairs of the 4-nitropyrazolide anion and, apparently, the majority of their solvated species have either a symmetry plane or a C_2 axis. Therefore, the angle between the dipole moment vectors μ_g and μ_e will be close to zero, and the difference between these vectors will be determined by the difference between their absolute values. This difference, in turn, will depend on the degree of electron density transfer from the heteroring to the nitro group upon absorption of a quantum by the ion pair. Further prediction is possible if three conditions are met: (1) peripheral specific solvation of the cation, (2) representation of the 4-nitropyrazolide anion as a dipolar molecule [this condition is substantiated by the structure of Eq. (1)], and (3) localization of the electronic excitation in the anionic moiety of the contact ion pair. The latter conditions is fairly rough. It is equivalent to the following requirement: The change in the dipole moment of the contact ion pair upon $\pi \rightarrow \pi^*$ transition is exclusively due to redistribution of the electron density in the anionic moiety. Therefore, the third criterion plays a subordinate role.

Let us consider how the total charge on heavy atoms is redistributed upon formation of contact ion pairs. Scheme 4 shows that the electron density on the atoms of the nitro group in the ground state of the $[N_2^-M^+]$ pair decreases by ~0.15 e relative to the free ion. In the ground state of the $[O_2^-M^+]$ pair, the electron density, on the contrary, is transferred to the nitro group (by ~0.25 e). Upon an intramolecular charge-transfer transition, the extent of the electron density redistribution should change. If at nonspecific solvation the solvatochromism of absorption bands in the spectra of contact ion pairs is mainly determined by orientation and induction interactions, as suggested by high μ_g (Schemes 2, 3), the nonspecific solvatochromic effect ($\Delta\nu = s\pi^*$) in the $[N_2^-M^+]$ pair will be larger, and that in the $[O_2^-M^+]$ pair, smaller than in the free anion.

Scheme 4.



$[N_2^-M^+]$ $[O_2^-M^+]$

Solvatochromism of ion pairs in aprotic protophilic solvents. The effect of aprotic protophilic solvents on the position of the long-wave absorption band of the contact ion pairs of the 4-nitropyrazolide anion is illustrated in Table 4. The correlation between the position of the band maximum ($\nu^{\pm}_{\max}$) and reciprocal radius of the alkali metal cation [$1/R(M^+)$] is linear: $\nu^{\pm}_{\max} = \nu^{\pm}_0 + m/R(M^+)$; its parameters are listed in Table 5.

Let us duscuss this correlation in more detail. The linear correlations $\nu^{\pm}_{\max} \sim 1/R(M^+)$ were found for pure tetrahydrofuran, pyridine, tetramethylurea, and 1,2-dimethoxyethane. The slopes m of the correlations depend on particular solvent (Table 5) and are relatively low in the absolute value. At the best (THF), the difference between the wave numbers of the absorption maxima of the ion pairs with the Li^+ and Cs^+ ions, $\Delta\nu^{\pm}$, does not exceed 700 cm^{-1}, and in the worst case (1,2-dimethoxyethane) it less than 400 cm^{-1}. At the same time, for the ion pairs of phenolate anions with the same cations in 1,2-dimethoxyethane, $\Delta\nu^{\pm}$ varies from 2400 to 3600 cm^{-1} [5]. For the corresponding alkali metal phenylthiolates (in this anion, according to [6], the charge is localized on the sulfur atom), $\Delta\nu^{\pm}$ = 1650 cm^{-1} in THF. In the series of aromatic carbanions, the above-discussed ion-pair effect varies from 1200 to 2800 cm^{-1} depending on the structure of the anion and on the solvent [4, 16]. On the contrary, contact ion pairs of the indolide anion are characterized by extremely weak dependences of the spectral characteristics on the solvent, temperature, and counterion. Vos *et al.* [7] believe that this is due to localization of the cation in the molecular plane of the anion in the vicinity of the nitrogen atom. The bond between the counterions in the contact ion pair of such a structure is so strong that it prevents formation of a loose ion pair even in hexamethylphosphoramide.

Thus, relatively weak ion-pair effect, wide range of dielectric properties of solvents in which it is ob-

Table 4. Solvatochromism of the long-wave absorption band (ν_{max}, cm^{-1}) in the UV spectra of contact ion pairs of the 4-nitropyrazolide anion in aprotic protophilic solvents

Solvent	Solvent parameters[a]				ν_{max} with indicated counterion					ν_{max} for free ion
	ε	α	β	π^*	Li^+	Na^+	K^+	Rb^+	Cs^+	
1,2-Dimethoxyethane	7.2	0.00	0.41	0.53	32 150	31 950	31 850	31 900	31 800	30 450
THF	7.6	0.00	0.55	0.58	32 000	31 600	31 400	31 400	31 300	30 400
Pyridine	12.9	0.00	0.64	0.87	31 150	30 850	30 650	30 600	30 500	30 000
Cyclohexanone	16.1	0.00	0.53	0.76		31 350				
Acetone	20.6	0.08	0.48	0.71	31 800	31 450	31 300[b]	31 200[b]	31 150[b]	30 300
Butanone	18.5	0.06	0.48	0.67	31 900	31 550	[c]		[c]	30 350
Tetramethylurea	23.6	0.00	0.80	0.83	30 750	30 500	30 350	30 350	30 300	30 050

[a] The dielectric permittivities of solvents were taken from [2], and the Kamlet–Taft empirical solvatochromic parameters, from [10, 11]. [b] Values measured in the binary mixture acetone–anisole containing 40 vol % anisole. In pure acetone, ν_{max} 31 000, 31 000 and 30 900 cm^{-1} for K^+, Rb^+, and Cs^+, respectively. [c] In pure butanone, the observed band (ν_{max} 31 250 and 31 100 cm^{-1} for K^+ and Cs^+, respectively) is due to superposition of bands of different ion pairs.

Table 5. Quantitative characteristics of the ion-pair effect, determined from the equation $\nu^{\pm} = \nu_0^{\pm} + m/R(M^+)$,[a] and position of the absorption maximum of the free anion, estimated by Eq. (1)

Solvent	β	Free anion, ν^-_{max}, cm^{-1} (±90)	Contact ion pair $[N_2^-M^+]$				
			$\nu_0^{\pm}$, cm^{-1}	m, Å cm^{-1}	r	sd	n
1,2-Dimethoxyethane	0.41	30 450	31 660 ± 30	290 ± 30	0.980	30	5
Acetone[b]	0.48	30 300	30 850 ± 30	570 ± 30	0.996	30	5
THF	0.55	30 400	30 970 ± 30	610 ± 30	0.997	30	5
Pyridine	0.64	30 000	30230 ± 20	560 ± 20	0.998	20	5
Tetramethylurea	0.80	30 050	30 080 ± 20	400 ± 20	0.995	20	5

[a] The reciprocal radii of Li^+, Na^+, K^+, Rb^+, and Cs^+ are 1.66, 1.05, 0.75, 0.68, and 0.50 Å^{-1}, respectively [15]. [b] For K^+, Rb^+, and Cs^+ in acetone, we used the $\nu^{\pm}_{max}$ values measured in the binary mixture acetone–anisole containing 40 vol % anisole.

served, and previous theoretical studies suggest that, in the contact ion pairs under consideration, the cation is located in the σ plane of the anion in the vicinity of the nitrogen or oxygen atoms. By analogy with [7], it can be assumed that the counterions form a fairly strong three-centered bond preventing dissociation. This bond is manifested spectroscopically as the difference between the $\nu_0^{\pm}$ values obtained by the extrapolation $R(M^+) \to \infty$ and ν^-_{max} values in Table 5, i.e., as the fact that the dependence $\nu^{\pm} \sim 1/R(M^+)$ does not tend to ν^-_{max} of the free anion. Except the case of tetramethylurea as solvent, these discrepancies appreciably exceed the error of the experiment or regression analysis (Table 5). Furthermore, the difference between ν^-_{max} and $\nu_0^{\pm}$ is variable and clearly tends to grow with decreasing parameter β of the solvent (Table 5). The quantity β characterizes the capability of solvent molecules to act as proton acceptors in H complexes with solute molecules [10, 11]. In the broad sense, β can be considered as a measure of the affinity of the solvent molecules for the positive charge. Hence, an increase in β makes the spectrum of the contact ion pair closer to the spectrum of the free ion. With increasing radius of the cation, $\nu^{\pm}_{max}$ varies in the same direction (Table 4). Recall that, according to calculations, the specific solvation of a cation exerts on the spectroscopic characteristics the same effect as an increase in the cationic radius, and the experimental data fully confirm this conclusion.

Although acetone and butanone occupy an intermediate position in the examined series of aprotic protophilic solvents with respect to the dielectric characteristics, the linear correlation between $\nu^{\pm}_{max}$ and $1/R(M^+)$ is not obeyed in these solvents. A specific feature of these ketones is that they exhibit weak proton-donor properties ($\alpha \neq 0$, Table 4). To find why these solvents lie out of the correlation, we used an approach

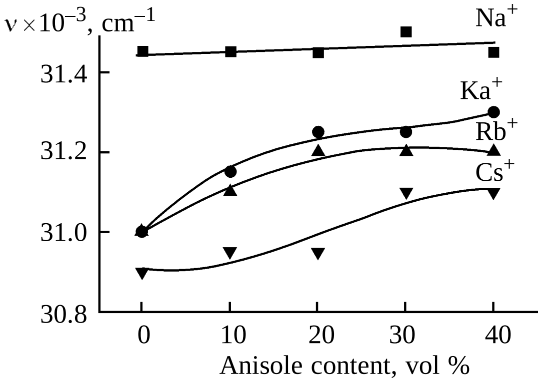


Fig. 1. Effect of selective specific solvation with acetone on the position of the long-wave absorption band in the UV spectra of ion pairs of the 4-nitropyrazolide anion with alkali metal cations in the binary mixture acetone–anisole.

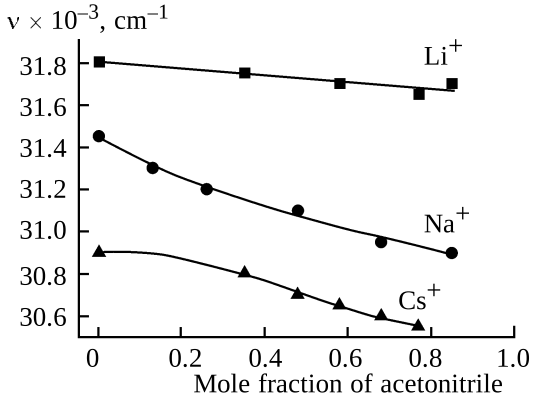


Fig. 2. Effect of selective specific solvation with acetone on the position of the long-wave absorption band in the UV spectra of ionic species of 4-nitropyrazole in the binary mixture acetone–acetonitrile.

based on selective specific solvation of ion pairs in binary mixtures of acetone with another protophilic solvent. As the second component we chose anisole. It does not compete with acetone in specific solvation of a cation [β(PhOMe) 0.22, β(Me_2CO) 0.48] [10, 11]. The capabilities of anisole and acetone for nonspecific solvation of ionic species are similar: π* 0.73 and 0.71, respectively [10, 11], but anisole will favor stabilization of contact ion pairs owing to its low dielectric permittivity (ε 4.3) [2]. Therefore, presumably, acetone–anisole binary mixtures at a moderate content of anisole[2] will differ from pure acetone only in the dielectric permittivity. Figure 1 shows how the experimentally determined absorption maximum of ion pairs is affected by additions of anisole. These dependences are interpreted as follows: (1) sodium 4-nitropyrazolide in pure acetone exists as a contact ion pair; (2) potassium, rubidium, and cesium 4-nitropyrazolides in the same solvent exist as ensembles of at least two types of species: $[A_2^-M^+] \rightleftarrows [A_2^-//M^+]$; (3) in binary mixtures containing 40 vol % anisole, with the same counterions, the equilibrium is fully shifted toward the contact ion pair: The $\nu^{\pm}_{max}$ values obtained in these mixtures (Table 4) fit in the linear correlation of $\nu^{\pm}_{max}$ with $1/R(M^+)$ (Tables 4, 5).

The increased stability of the contact ion pairs with the Li^+ and Na^+ ions is inconsistent with the order of stability of the contact ion pairs with carbanions but is qualitatively consistent with the order found for β-naphtholate contact ion pairs by time-resolved fluorescence [17].

To make sure that the stability orders for the contact ion pairs with the 4-nitropyrazolide anion and carbanions do not coincide, we performed measurements in the binary mixture of acetone (β 0.48, π* 0.71) with acetonitrile (β 0.31, π* 0.75) [10, 11]. With respect to the conditions of selective specific solvation, this mixture is approximately equivalent to the acetone–anisole mixture, but the dielectric permittivity of acetonitrile is high, which should favor transformation of tight ion pairs into loose ion pairs. The results are shown in Fig. 2. As the mole fraction of the polar component in the binary mixture is increased to 0.85, the absorption maximum of the ion pair with Li^+ shifts only slightly. With the Na^+ counterion, the absorption maximum shifts toward lower frequencies, with the shape and half-width of the band remaining virtually unchanged. At the acetonitrile mole fraction of 0.85, the position of the band maximum coincides with that for the ion pair with Cs^+ in pure acetone. The spectrum of the ionic species with Cs^+ in the binary mixture with increasing ε tends to the spectrum of the free ion recorded in dilute ($<10^{-4}$ M) acetonitrile solutions [9]. These results leave no doubt that the contact ion pairs with Li^+ and Na^+ exhibit enhanced stability against dissociation. In view of this fact, we examined the concentration dependence of the spectrum of the Na^+ ion pairs in pure acetonitrile. The results obtained at various concentrations of ions [C] confirm the possibility of formation of ion pairs (or more complex conglomerates) in acetonitrile, which weakly solvates cations but is strongly polar:

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[2] At a large excess of anisole, owing to the statistical factor, the microscopic distribution of solvent molecules in the first solvation shell of a contact ion pair will tend to the macroscopic distribution.

Table 6. Quantitative characteristics of the solvatochromism of the contact ion pairs of the 4-nitropyrazolide anion in aprotic protophilic solvents

Counterion	ν'_0, cm^{-1}	$-b$, cm^{-1}	$-s$, cm^{-1}	*R*	*sd*	*n*
Li^{+a}	34590 ± 210	2440 ± 340	2220 ± 380	0.985	70	5
Na^+	33860 ± 110	2370 ± 230	1730 ± 240	0.990	50	7
K^+	33810 ± 50	2300 ± 120	1950 ± 120	0.999	20	5
Rb^+	33920 ± 180	1970 ± 390	2410 ± 400	0.986	70	5
Cs^+	33790 ± 150	1940 ± 330	2360 ± 330	0.990	60	5

[a] Without including 1,2-dimethoxyethane which, apparently, forms a cyclic solvate with the ion pair. Inclusion of 1,2-dimethoxyethane makes the multiple correlation coefficient considerably lower: $\nu^{\pm}_{max}$ = (34 210 ± 280) – (2360 ± 600)β – (1810 ± 630)π*; *R* 0.952, *sd* 120, *n* 6.

–log [C]	ν_{max}, cm^{-1}
4.24	30 300
4.23	30 250
4.05	30 300
3.64	30 300
1.74	30 800
1.48	30 900
1.32	30 950

The weak concentration dependence was also observed in methanol and dimethylformamide.

Since the data obtained for the binary mixture acetone–anisole extend the sample, it becomes possible to perform multiple linear regression analysis of the whole series of cations and obtain a solvatochromism equation for each contact ion pair. We found that, in aprotic protophilic solvents, two Kamlet–Taft parameters are sufficient to describe the solvatochromism:

$$\nu^{\pm}_{max} = \nu'_0 + b\beta + s\pi^*, \qquad (2)$$

where ν'_0 is $\nu^{\pm}_{max}$ in a medium with $\beta = \pi^* = 0$, and β characterizes the capability of solvent molecules to act as hydrogen bond acceptors in H complexes with solute molecules. The coefficients and free term in this equation are given in Table 5. Comparison of the free terms of Eqs. (1) and (2) shows that, in an inert medium, the spectrum of the ion pair is blue shifted relative to the spectrum of the anion by ~2500–3000 cm^{-1}. Calculations performed for the nonsolvated ion pair $[N_2^-M^+]$ predict a 4700 cm^{-1} increase in the energy of the corresponding $\pi \rightarrow \pi^*$ transition relative to the free ion. In the ion pair $[O_2^-M^+]$, as already noted, the intramolecular charge-transfer transition is red shifted. Thus, in aprotic protophilic solvents, the stable species is the contact ion pair $[N_2^- \cdot M^+S_2]$. The same is indicated by higher values of *s* in Eq. (2) (Table 6) as compared to Eq. (1).

The opposite shifts of the long-wave absorption band in the spectra of the two types of isolated contact ion pairs can be readily explained as follows. When the contact ion pair $[N_2^-M^+]$ absorbs a quantum, the charge is transferred from the nitrogen atoms to the peripheral nitro group. As a result, the ion–ion interactions in the Franck–Condon excited state become weaker, the excited state is additionally destabilized relative to the ground state, and the electronic transition shifts to higher wave numbers. When the ion pair $[O_2^-M^+]$ is excited in the charge-transfer band, the negative charge is also transferred to the nitro group, but the result is opposite, as the excited state becomes stabilized by ion–ion interactions to a greater extent than the ground state.

The negative coefficient *s* in Eq. (2) means that the dipole moment of the contact ion pair $[N_2^-M^+]$ grows upon electronic excitation. The following fact is notable. The absolute value of *s* for the ion pairs is comparable with that in solvatochromism equation (3) for neutral 4-nitropyrazole in aprotic protophilic solvents [9]:

$$\nu_{max} = (38\,950 \pm 70) - (1830 \pm 90)\beta - (1850 \pm 80)\pi^*; \qquad (3)$$

R 0.986, *sd* 70, *n* 13.

The similarity of the solvatochromism equations for neutral 4-nitropyrazole containing the NH bond and for contact pairs of its anion with alkali metal cations is not limited to this fact. The positions of the long-wave maxima in the UV spectra of both species depend on the same solvent parameters, and even the coefficients *b* are close [Eq. (3), Table 6]. This fact requires some comments.

The neutral 4-nitropyrazole molecule forms an H complex [MHS] with a protophilic solvent via the NH bond. Excitation of the complex [MHS] in the charge-transfer band leads to the transfer of the electron density from the pyrrole nitrogen atom to the nitro group. The NH bond becomes additionally polarized, which results in enhancement of the electrostatic interactions between the components of the H complex in its Franck–Condon excited state. As a result, the excited state is stabilized by a protophilic solvent to a greater extent than the ground state. This determines the sign of b in Eq. (3). The value of b, accurate to the relaxation factor, corresponds to the change in the energy of the H bond upon electronic excitation [9].

The specific solvatochromic effect in the spectrum of the contact ion pair is interpreted similarly. The presence of the term $b\beta$ in Eq. (2) suggests that the protophilic solvent molecule acts as electron donor relative to the contact ion pair. Upon electronic excitation, the bond between the counterions becomes weaker owing to charge transfer to the peripheral fragment. On the contrary, the bonds between the cation and solvent molecules in the first solvation shell become stronger. This follows from the experimental data [Eq. (2), Table 6] indicating that the Franck–Condon excited state of the contact ion pair is stabilized by the solvent to a greater extent than the ground state. According to the Franck–Condon principle, the nuclear configuration does not change upon electronic transition. Hence, strengthening of the solvation complex in the nonequilibrium excited state is due to transfer of the electron density not only from the nitrogen atoms of the anion, but also from the cation. This conclusion does not contradict the results of *ab initio* calculations: in the ground electronic state of the contact ion pair, the negative charge is partially delocalized to the counterion (Scheme 4).

EXPERIMENTAL

The UV spectra of ion pairs of the 4-nitropyrazolide anion with alkali metal cations were recorded on a Specord UV-Vis spectrophotometer at 22–25°C in moderately polar solvents saturated with LiOH, NaOMe, $KOH \cdot 0.5H_2O$, $RbOH \cdot H_2O$, and $CsOH \cdot H_2O$. The *ab initio* (HF/6-31G*) calculations of the geometries, energy characteristics, total charge distributions, dipole moments, and UV spectra of the 4-nitropyrazolide anion, its contact ion pairs with Li^+, and their complexes with solvents were performed using the GAUSSIAN 98 software [18]. 4-Nitropyrazole was prepared by nitration of pyrazole followed by isomerization of the resulting 1-nitropyrazole [19].

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