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Solvatochromism of Heteroaromatic Compounds: XIX.[1] Factors Affecting Quantitative Characteristics of Solvatochromism in Aprotic Inert Media

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Abstract—The effects of aprotic inert media on the electronic absorption spectra of aromatic nitro compounds p-$NO_2C_6H_4R$ were used as evidence for the linear correlation between the slope s_a of the solvatochromism equations $\nu_{max} = \nu_0 + s_a\pi^*$ and the dipole moments of the molecules in their ground electronic state μ_g. A linear correlation was established between ν_0 and the first ionization potential of subunits C_6H_5R. A new approach to estimating the dipole moment of electronically excited molecules (μ_e) for molecules like p-$NO_2C_6H_4R$ on the basis of the correlation $\mu_e = r\mu_g$ was proposed.

In terms of the approach developed by Kamlet, Taft, and co-workers [2–4], the position of the maximum of the solvatochromic band in the electronic absorption spectrum of a substance (indicator) is determined, in the case of nonspecific interactions of its molecules with the medium, by the polarity/polarizability solvent parameter π^* [Eq. (1)].

$$\nu_{max} = \nu_0 + s_a\pi^*. \qquad (1)$$

Here ν_0 and s_a are constants. Factors affecting the ν_0 values of solvatochromic indicators were considered in detail in [2]. It was found that ν_0 depends on electron-acceptor properties of the chromophore, electron-donor properties of substituents (auxochromes) and their relative position, i.e. on the length of the chromophoric chain, and on some other molecular characteristics of the indicator. Apparently, s_a, too, is determined by molecular parameters of the latter, but the physical meaning of this constant is yet unclear. In [5, 6], s_a values were empirically correlated with ground-state molecular dipole moments (μ_g). As indicators, nitropyrazoles [6] and derivatives of 4-nitroaniline (**I**), 4-nitrophenol (**II**), and 2-nitroaniline (**III**), as well as some other compounds were used [5]. Two types of s_a–μ_g correlations were found: linear for aromatic and nonlinear for heteroaromatic nitro compounds. This result might be considered to indicate a complicated nature of the coefficient s_a and determine the line of further research. However, Novaki and El Seoud [5] made use of the μ_g values obtained by semiempirical PM3 calculations for s_a–μ_g correlations, and, therefore, their results are to be refined. The aim of the present work was to correlate s_a and μ_g in aprotic inert media for aromatic nitro compounds containing an O_2N–C=C–C=C–X chromophoric chain. In addition, we continued our investigations into relationships between ν_0 and the electron-donor properties of the p-nitroarene subunits of indicator molecules.

Heteroaromatic nitro compounds, too, call for further reseach, since they were represented by isomeric nitropyrazoles only. In the present work we dwelt on two representatives of this class of compounds [1-methyl-3-nitropyrazole (**IV**) and 1-methyl-4-nitroimidazole (**V**)], that fit earlier established trends for aromatic molecules. More information on nitroazoles and *ortho*- and *meta*-nitroarenes we will present in following communications of this series.

Description of solvatochromism. The effects of the medium on the electronic absorption spectra of aromatic nitro compounds p-$NO_2C_6H_4R$ containing an electron-donor group NR_2 or OR [4-nitroaniline (**I**), 4-nitrophenol (**II**), 4-nitroanisole (**VI**), *N*-methyl-4-nitroaniline (**VII**), *N,N*-dimethyl-4-nitroaniline (**VIII**), *N*-ethyl-4-nitroaniline (**IX**), *N,N*-diethyl-4-nitroaniline (**X**), *N*-(4-nitrophenyl)aziridine (**XI**), *N*-(4-nitrophenyl)pyrrolidone (**XII**)], and their unsymmetrical analogs [3-methyl-4-nitroaniline (**XIII**), 5-nitroindoline (**XIV**)] have been well-documented [7–25]. This literature was used as a source of required experimental information. Data on the effect of the solvent

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

Table 1. Solvatochromism of nitrobenzene (**XV**), 4-nitrotoluene (**XVI**), 4-ethoxynitrobenzene (**XVII**), 4-(methylthio)nitrobenzene (**XVIII**), 4-bromonitrobenzene (**XIX**), 4-nitrobenzaldehyde (**XX**), 4-nitrobenzonitrile (**XXI**), 4-ethylnitrobenzene (**XXII**), 4-nitro(vinyloxy)benzene (**XXIII**), 4-(chloromethyl)nitrobenzene (**XXIV**), 4-(chlorosulfonyl)nitrobenzene (**XXV**), and 2,6-dibrom-4-nitrophenol (**XXVI**) in aprotic inert media

Solvent	π^* [a]	$\nu_{max} \times 10^{-3}$, cm^{-1}											
		XV	**XVI**	**XVII**	**XVIII**	**XIX**	**XX**	**XXI**	**XXII**	**XXIII**	**XXIV**	**XXV**	**XXVI**
Pentane	–0.08	39.75	37.90	–	–	37.00	38.60	–	35.70 (0–2)	–	38.80	40.30	–
Hexane	–0.08	39.80	37.80	33.95	30.65	37.05	38.55	39.45	35.65 (0–2)	34.30	38.75	40.25	34.80
Heptan1	–0.02	39.70[b]	37.70	33.90	30.65	37.00	38.55	39.45	35.55 (0–2)	34.20	38.65	40.10[c]	34.75
Cyclohexane	0.00	39.55[b]	37.65	33.80	30.45	36.85	38.45	39.45	35.40 (0–2)	34.10	38.55	40.10	34.65
Octan1	0.01	39.60	–	–	30.50	36.90	38.50	39.40[c]	–	–	38.55	40.10	–
Dodecane	0.08	39.70[b,d]	37.60[c]	33.40[e]	30.45	36.85[c]	38.35[c]	39.40	35.35 (0–2)	33.90[e]	38.50	40.10	34.60
Carbon tetrachloride	0.28	39.10[b]	37.10	33.20	30.05	36.40	38.15	38.80	35.05 (0–2)	33.65	38.20	39.90	34.25
Butyl chloride	0.39	38.70	36.70	32.80	29.70	36.30	38.00	38.80	34.75	33.30	37.95	38.85	–
Butyl bromide	0.48	–	36.55	32.55	29.55	36.15[f]	37.90[g]	38.65	–	33.10	–	–	33.75
Chloroform	0.58	–	36.10	–	–	–	37.70	38.65	34.50	32.70	–	39.65	33.60
Pentachloroethane	0.62	38.25	–	–	–	35.90	38.50[d]	–	34.40	–	–	–	33.65
1,2-Dichloroethane	0.81	38.05	35.95	31.85	28.90	35.70	37.50	38.45	34.30	–	37.20	39.60	33.35
Dichloromethane	0.82	38.00	35.80	31.90	29.00	35.75	37.50	38.45	34.25	32.60	37.25	39.55	33.40
1,1,2,2-Tetrachloroethane	0.95	–	35.50	31.50	28.55	–	–	38.35	33.95	32.15	37.00	39.50	33.05

[a] The polarity parameter from [2–4]. [b] Mean of the author's values and those in [26–28]. [c] In decane (π^* 0.03). [d] In isooctane (π^* 0.00). [e] In decaline (π^* 0.09). [f] In heptyl bromide (π^* 0.48). [g] In *cis*-1,2-dichloroethene (π^* 0.44).

on the position of the long-wave intramolecular charge-transfer band of other aromatic compounds with a nitrobenzene fragment possessing a high local symmetry [nitrobenzene (**XV**), 4-nitrotoluene (**XVI**), 4-ethoxynitrobenzene (**XVII**), 4-(methylthio)nitrobenzene (**XVIII**), 4-bromonitrobenzene (**XIX**), 4-nitrobenzaldehyde (**XX**), 4-nitrobenzonitrile (**XXI**), 4-ethylnitrobenzene (**XXII**), 4-nitro(vinyloxy)benzene (**XXIII**), 4-(chloromethyl)nitrobenzene (**XXIV**), 4-(chlorosulfonyl)nitrobenzene (**XXV**), 2,6-dibromo-4-nitrophenol (**XXVI**)] are presented in Table 1. The qualitative description of the solvatochromism was performed in terms of Eq. (1). As inert media we used saturated hydrocarbons and their halo derivatives. The results of linear regression analysis are given in Table 2. Let us dwell on compounds with a low ground-state dipole moment and, consequently, with a relatively weak solvatochromism. The position of their asorption maximum depends not only on a general parameter π^*, but also on a group parameter δ (approximate measure of solvent polarizability) [2–4]. Thus, for 4-bromonitrobenzene we found Eq. (2).

$$\nu_{max} = (36910 \pm 20) - (1320 \pm 30)(\pi^* + 0.2\delta); \quad (2)$$

$$r\ 0.997,\ s\ 40,\ n\ 12.$$

A similar equation was obtained for 4-nitrobenzonitrile.

$$\nu_{max} = (39430 \pm 10) - (690 \pm 10)(\pi^* + 1.2\delta); \quad (3)$$

$$r\ 0.998,\ s\ 30,\ n\ 12.$$

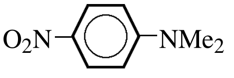
Correlation of ν_0 with electron-donor properties of molecular subunits. The low-energy transition in the compounds in hand can be considered to involve elec-

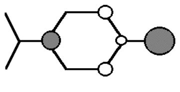
Table 2. Molecular parameters and quantitative characteristics of the solvatochromism of aromatic nitro compounds in aprotic inert media

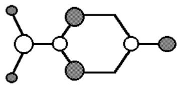
Compound	IP_1,[a] eV	μ_g,[b] D	ν_0, cm^{-1}	$-s_a$, cm^{-1}	r	s	n[c]
Nitrobenzene	9.24	3.88[d]	39600±20	1990±40	0.998	80	12[e]
4-Nitrotoluene	8.85	4.45	37650±40	2280±80	0.995	100	12
4-Nitrophenol	8.67	4.85[f]	35100±50	2540±100	0.990	150	14
4-Nitroanisole	8.46	4.90[d]	34190±40	2310±80	0.990	130	20
4-Ethoxynitrobenzene	8.41	5.07	33760±40	2360±70	0.996	80	10
4-(Methylthio)nitrobenzene	8.07	4.39	30540±30	2010±60	0.996	70	11
4-Nitroaniline	8.05	6.25[f]	31170±30	3220±80	0.996	130	17
N-Methyl-4-nitroaniline	7.65	6.55[f]	29380±40	3240±90	0.997	110	11
N,N-Dimethyl-4-nitroaniline	7.37	6.87[d]	28150±40	3270±80	0.995	140	20
N-Ethyl-4-nitroaniline	7.67		29150±50	3250±90	0.998	80	6
N,N-Diethyl-4-nitroaniline	7.20		27650±40	3190±100	0.996	120	11
4-Bromonitrobenzene	9.04	2.63	36910±20	1320±30[g]	0.997	40	12
4-Nitrobenzaldehyde	9.59	2.23	38470±20	1230±40	0.995	40	13
4-Nitrobenzonitrile	9.71	0.9[f]	39430±10	690±10[h]	0.998	30	12
4-Ethynylnitrobenzene	8.78	3.49	35490±30	1600±50	0.994	70	12
4-Nitro(vinyloxy)benzene		4.02	34130±30	2010±70	0.996	70	9
4-(Chloromethyl)nitrobenzene	9.27	3.68	38610±20	1700±30	0.998	40	11
N-(4-Nitrophenyl)aziridine		1.25	40150±20	720±40	0.985	50	12
4-(Chlorosulfonyl)nitrobenzene	8.19		32010±100	2250±170	0.985	120	7
N-(4-Nitrophenyl)pyrrolidone	7.29		27550±110	3190±200	0.993	140	6
3-Methyl-4-nitroaniline	7.66		31450±60	3430±120	0.997	100	7
5-Nitroindoline	7.67		28590±50	3560±120	0.993	180	15
2,6-Dibromo-4-nitrophenol		3.27	34680±30	1690±60	0.994	70	11

[a] Data from [29–31]. [b] Measured at 25°C in CCl_4. [c] Experimental data: ν_{max} from Table 1 and [7–25]. [d] From [32]. [e] With account for ν_{max} (41750 cm^{-1}) of vapors (π –1.10). [f] Estimated by Eq. (2) or Eq. (3). [g] Coefficient of the parameter $\pi^* + 0.2\delta$. [h] Coefficient of the parameter $\pi^* + 1.2\delta$.

tron density redistribution between two electronic subsystems localized on the NO_2 and C_6H_4R atomic groups. Based on this concept and gas-phase experimental, Saidov *et al.* [33] deduced: $\nu_{max} \sim IP_D - EA$ (IP_D and EA relate to the donor and acceptor subsystems in the same molecule). Analyzing this problem in terms of the molecular orbital approximation (single-configuration theory), it is easy to show that the proportionality coefficient between ν_{max} and IP_D will tend to unit when the fragment π orbitals mix with each other neither in the ground nor in the excited electronic states. As follows from the orbital analysis, aromatic nitro compounds with a high local symmetry have the highest occupied molecular orbital (HOMO) localized on the electron-donor part of the molecule (C_6H_4R) and the lowest unoccupied molecular orbital (LUMO) appreciably delocalized over the whole molecular π system.




HOMO


LUMO

The proportionality coefficient between vapor ν_{max} and IP_D (C_6H_4R subunit) in the series of nitro compounds in study should much differ from unit. As the optical characteristic of these compounds in solution one better use ν_0 rather than ν_{max}, since in terms of the accepted approach the former is independent of solvation and is detemined exclusively by the phase state and structure of the indicator (Table 2). In what follows we will measure the electron-donor properties of the subunit by the first ionization potential of a compound modeling the C_6H_4R fragment (IP_1, Table 2). In searching for the desired correlation we had to take into account that the observed absorption band in most cases has no vibrational structure. As the nature of auxochrome changes, the global maximum of this band may migrate from one vibronic component to another. In its turn, this would violate the linear correlation between ν_0 and IP_1. Actually,

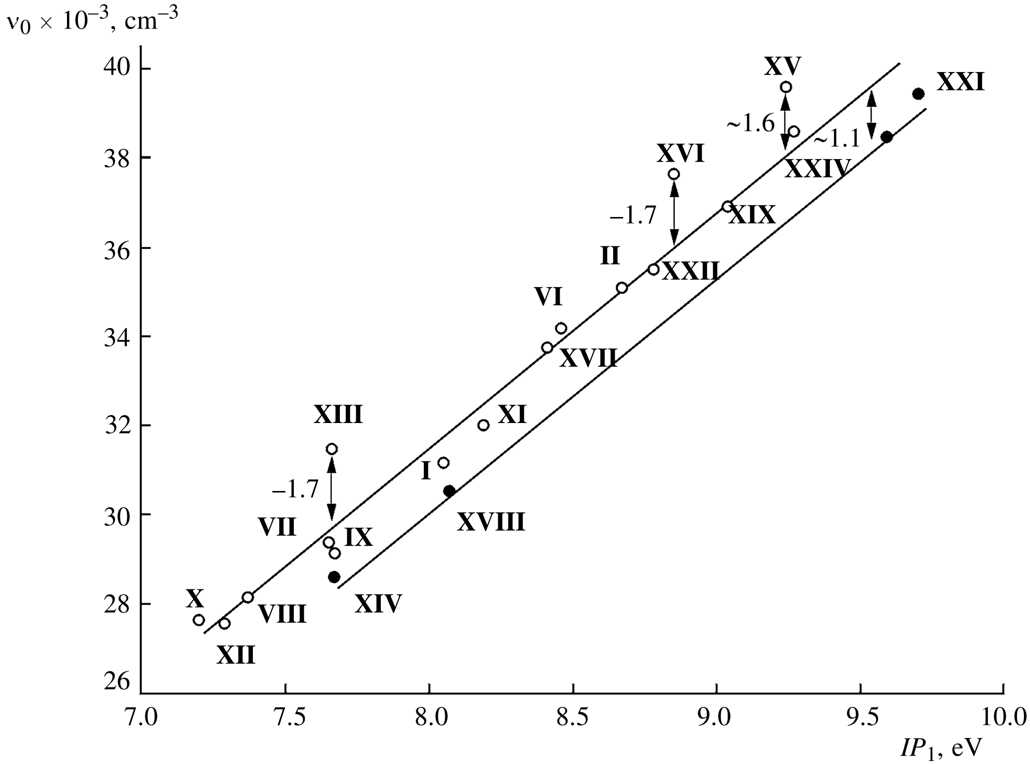


Fig. 1. Correlation of the free term in the solvatochromic equations (ν_0) for aromatic nitro compounds p-$NO_2C_6H_4R$ with the first ionization potential of subunit C_6H_5R (IP_1) (data from Table 2). For compound numbers, see text.

with the whole data set, regression equation (4) has a low correlation coefficient.

$$\nu_0 = (0.65 \pm 0.03)IP_1\ (\text{cm}^{-1}) - (10720 \pm 2330); \quad (4)$$

$$r\ 0.976,\ s\ 940,\ n\ 20.$$

However, two groups of indicators can be recognized, with linear $\nu_0 \sim IP_1$ (cm^{-1}) correlations. These correlations are depicted in Fig. 1. The first group comprises 5-nitroindoline (**XIV**), 4-(methylthio)-nitrobenzene (**XVIII**), 4-nitrobenzaldehyde (**XX**), and 4-nitrobenzonitrile (**XXI**), and the corresponding correlation has Eq. (5).

$$\nu_0 = (0.65 \pm 0.01)IP_1\ (\text{cm}^{-1}) - (11910 \pm 880); \quad (5)$$

$$r\ 0.999,\ s\ 180,\ n\ 4.$$

The second group comprises 4-nitroaniline (**I**), 4-nitrophenol (**II**), 4-nitroanisole (**VI**), *N*-methyl-4-nitroaniline (**VII**), *N,N*-dimethyl-4-nitroaniline (**VIII**), *N*-ethyl-4-nitroaniline (**IX**), *N,N*-diethyl-4-nitroaniline (**X**), *N*-(4-nitrophenyl)aziridine (**XI**), *N*-(4-nitrophenyl)pyrrolidone (**XII**), 4-ethoxynitrobenzene (**XVII**), 4-bromonitrobenzene (**XIX**), 4-ethylnitrobenzene (**XXII**), 4-(chloromethyl)nitrobenzene (**XXIV**), and the corresponding correlation has Eq. (6).

$$\nu_0 = (0.67 \pm 0.02)IP_1\ (\text{cm}^{-1}) - (11930 \pm 1170); \quad (6)$$

$$r\ 0.996,\ s\ 340,\ n\ 13.$$

The distance between these two plots in the range $7.0 < IP_1 < 10.0$ eV is ~1100 cm^{-1}. The points corresponding to 3-methyl-4-nitroaniline (**XIII**), nitrobenzene (**XV**), and 4-nitrotoluene (**XVI**) deviate from the linear regressions by a multiple of ~900 cm^{-1}, which much exceeds the approximation uncertainty. Thus, the above equations suggest that in going from one aromatic nitro compound p-$NO_2C_6H_4R$ to another the global maximum of its structureless band “jumps” from one vibronic component to another. The slopes of particular linear dependences $\nu_0 \sim IP_1$ are much lower than unit, which provides evidence for the theoretical predictions that fragment π-MOs strongly mix with each other in the first electronically excited state.

Dipole moment in the ground electronic state (μ_g). For correlations with quantitative solvatochromic characteristics in aprotic inert media we made use of the μ_g values measured at 25°C in CCl_4. Such correlations assumed varying μ_g over a wide range, but this was prevented by the limited solubility of certain compounds (for example, 4-nitrophenol, 4-nitroaniline, *N*-methyl-4-nitroaniline, 4-nitrobenzonitrile) in this solvent. The μ_g values in these cases were estimated

Table 3. Dipole moments in carbon tetrachloride and 1,4-dioxane at 25°C

Compound	μ_g, D		Compound	μ_g, D	
	CCl_4	$C_4H_8O_2$		CCl_4	$C_4H_8O_2$
			Nonspecific solvation with dioxane		
Nitrobenzene	3.88[a]	4.03[a]	2-Bromonitrobenzene	3.91[a]	4.46
4-Nitrotoluene	4.45[a]	4.61	2-Ethylnitrobenzene	3.93	4.01
4-Ethoxynitrobenzene	5.07	5.27	2,5-Di-*tert*-butylnitrobenzene	3.63	3.74
4-(Methylthio)nitrobenzene	4.39	4.56	2,6-Dinitrotoluene	2.74[a]	2.85[a]
N,N-Dimethyl-4-nitroaniline	6.87[a]	7.27[a]	2,4-Dinitrochlorobenzene	3.40	3.47
4-Bromonitrobenzene	2.63[a]	2.80	2,4-Dinitrobenzaldehyde	4.40	4.53
4-Nitrobenzaldehyde	2.23	2.58	2,4,6-Tri-*tert*-butylnitrobenzene	3.32	3.61
4-Nitrobenzonitrile	–	0.96	2,4,6-Trinitrotoluene	0.98	1.00[a]
4-Ethylnitrobenzene	3.49	3.65	2-(*N,N*-Dimethylamino)-4-methyl-5-nitropyridine	6.04[b,c]	6.24[c]
4-Nitro(vinyloxy)benzene	4.02	4.12	1-Nitropyrazole	3.64[d]	3.60[d]
4-(Chloromethyl)nitrobenzene	3.68	3.77	1-Methyl-3-nitropyrazole	5.75[d]	6.20[d]
4-(Chlorosulfonyl)nitrobenzene	1.25	1.43	1-Methyl-4-nitropyrazole	4.35[d]	4.83[d]
Anisole	1.26[a,e]	1.30[a,e]	1,3,5-Trimethyl-4-nitropyrazole	4.53[d]	4.89[d]
N,N-Dimethylaniline	1.55[a,e]	1.63[a,e]	3,5-Dimethyl-4-nitro-1-vinylpyrazole	4.07[d]	4.19[d]
2-Ethylnitrobenzene	4.19	4.27			
			Specific solvation with dioxane		
4-Nitroaniline	–	6.92[a]	3-Nitroaniline	4.84	5.24[a]
N-Methyl-4-nitroaniline	–	7.22[a]	4-Methyl-3-nitroaniline	4.41	4.96
Phenol	1.49[a]	1.78[a]	3-Methyl-6-nitroaniline	4.92	5.48
Aniline	1.46[a]	1.77[a]	2,4,6-Trimethylaniline	1.31[a]	1.56[a]
2-Nitroaniline	4.25[a]	4.62, 4.68[a]	2,4,6-Tribromoaniline	1.61[a]	1.97[a]
4-Methoxy-2-nitroaniline	3.60	4.14	2-*N*-(Methylamino)-4-methyl-5-nitropyridine	5.70[b,c]	6.19[c]
4-Methyl-2-nitroaniline	4.08	4.61	2-*N*-(Methylamino)-6-methyl-5-nitropyridine	5.04[b,c]	5.82[c]
3-Nitrophenol	3.80	4.39	Pyrrole	1.76[a]	2.13[a]

[a] Data from [32]. [b] In tetrabromoethene. [c] Data from [34, 35]. [d] Data from [6]. [e] Mean of the values reported in [32].

from the linear equations relating μ_g in CCl_4 and 1,4-dioxane for a wide range of compounds (Table 3). For the case of nonspecific solvation with dioxane we have Eq. (7).

$$\mu = (0.02 \pm 0.07) + (1.05 \pm 0.02)\mu_{CCl_4}; \qquad (7)$$

$$r\ 0.996,\ s\ 0.13,\ n\ 28.$$

Under conditions of specific solvation with dioxane, we have Eq. (8).

$$\mu = (0.22 \pm 0.07) + (1.07 \pm 0.02)\mu_{CCl_4}; \qquad (8)$$

$$r\ 0.998,\ s\ 0.10,\ n\ 14.$$

The resulting equations have almost equal slopes. This implies equal effects of nonspecific solvation with dioxane on the dipole moments of molecules and solvation of H complexes. Specific interactions with dioxane reveal themselves in that the equations have different free terms. Specific solvation additionally increases μ_g by ~0.2 D, and, therewith, the value of the increment depends neither of the number of "solvation-active" bonds in the solute nor on the nature of such bonds (Table 3). Detailed discussion of this effect is beyond the scope of the present communication.

Correlation of s_a and μ_g. For compounds $p\text{-}NO_2 \cdot C_6H_4R$ in aprotic inert media we obtained two linear correlations (Fig. 2, Table 2) with close parameters and high correlation coefficients. The first relates to 4-nitroaniline (**I**), 4-nitrophenol (**II**), *N*-methyl-4-nitroaniline (**VII**), *N,N*-dimethyl-4-nitroaniline (**VIII**), nitrobenzene (**XV**), 4-nitrotoluene (**XVI**), 4-nitrobenzaldehyde (**XX**), 4-nitrobenzonitrile (**XXI**), 4-nitro(viniloxy)benzene (**XXIII**), and 2,6-dibromo-4-nitrophenol (**XXVI**) [Eq. (9)].

$$s_a = (240 \pm 60) + (460 \pm 10)\mu_g;\ r\ 0.997,\ s\ 70,\ n\ 10. \qquad (9)$$

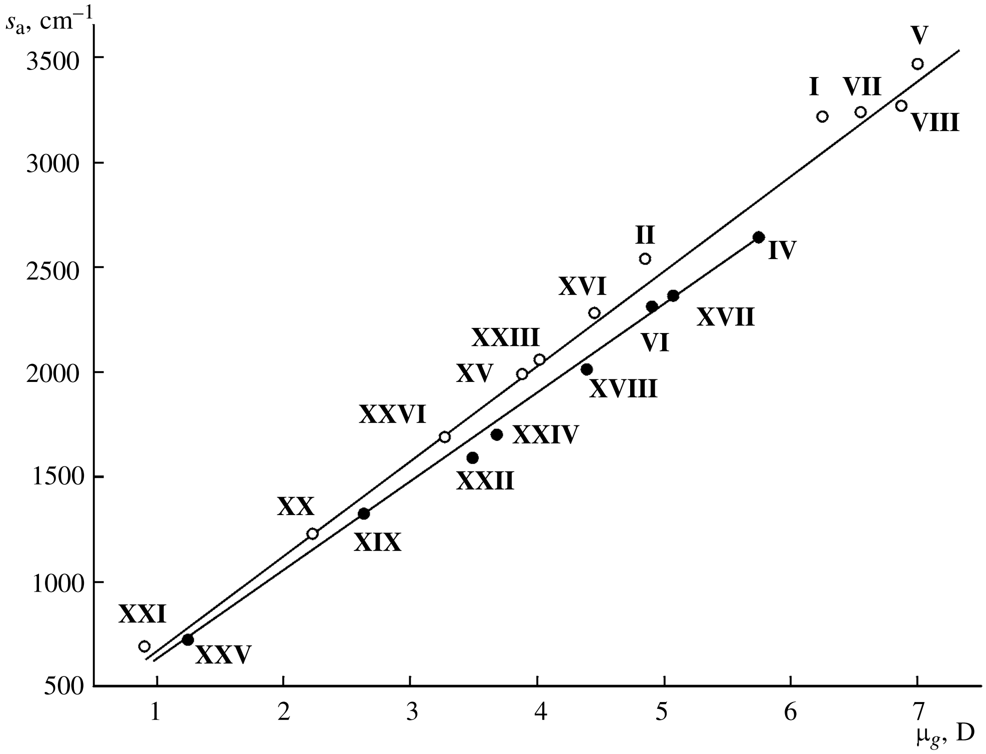


Fig. 2. Correlation between the coefficient of the polarity parameter (s_a) and the ground-state dipole moment (μ_g, D) for aromatic and heteroaromatic nitro compounds (data from Table 2). For compound numbers, see text.

The other correlation equation relates to 4-nitroanisole (**VI**), 4-ethoxynitrobenzene (**XVII**), 4-(methylthio)nitrobenzene (**XVIII**), 4-bromonitrobenzene (**XIX**), 4-ethylnitrobenzene (**XXII**), 4-(chloromethyl)nitrobenzene (**XXIV**), and 4-(chlorosulfonyl)nitrobenzene (**XXV**) [Eq. (10)].

$$s_a = (160 \pm 60) + (430 \pm 10)\mu_g;\ r\ 0.997,\ s\ 50,\ n\ 7. \quad (10)$$

The above results leave no room for doubts that s_a linearly vary with μ_g, at least for compounds with a high local symmetry of the nitro-containing fragment. Note that of the unsymmetrical nitro compounds, 1-methyl-4-nitroimidazole (**V**) fits Eq. (9) (Fig. 2): s_a 3470 ± 120 cm^{-1} (the results of research into the solvatochromism of the long-wave absorption band in the UV spectrum of this compounds will be presented elsewhere) and $\mu(CCl_4)$ 7.0 D [estimated from μ(dioxane) 7.33 D]. With account of these characteristics, we transform Eq. (9) into Eq. (11).

$$s_a = (230 \pm 60) + (460 \pm 10)\mu_g;\ r\ 0.997,\ s\ 70,\ n\ 11. \quad (11)$$

Equation (10) fits the characteristics of the other nitroanisole, 1-methyl-3-nitropyrazole (**IV**): s_a 2640 ± 60 cm^{-1} and $\mu(CCl_4)$ 5.75 D [6] (Fig. 2). Their treatment together with the above data gives Eq. (12).

$$s_a = (160 \pm 50) + (430 \pm 10)\mu_g;\ r\ 0.998,\ s\ 40,\ n\ 8. \quad (12)$$

The form of Eqs. (11) and (12) raises the following questions. Why these equations have statistically significant free terms? What reasons are responsible for the values of these terms? What is the reason for the linear dependence of s_a, a parameter that measures the change in the stabilization energy of states by the medium, induced by light absorption, on the dipolarity parameter of the ground electronic state?

To answer these questions, one cannot do without solvatochromism theories. Two of them have made the best showing in the description of experimentally observed trends and regularities, as well as in the estimation of certain parameters of excited states [17]. These are the theories of Bakhshiev, based on the model concepts of the dielectrics physics [36, 37], and of Bilot–Kawski, a quantum-chemical description of solute–solvent interactions in terms of the second-order perturbation theory [38]. Under certain, sufficiently substantiated approximations, the two theories give similar solvatochromic equations (for details, see [39]). Since, formally, the Bilot–Kawski theory is a particular case of the Bakhshiev theory, giving a more rigorous description of the orientating inductive contribution to the spectral shift, the solvato-

Table 4. Parameters of the Bakhshiev–Bilot–Kawski equation for aromatic nitro compounds[a]

Compound	c_1, cm^{-1}	p_2, cm^{-1}	r	s	n[b]
Nitrobenzene	2300±170	9290±540	0.985	130	11
4-Nitrotoluene	2760±220	10450±750	0.983	180	11
4-Nitrophenol	2810±220	12400±680	0.983	180	14
4-Nitroanisole	2700±190	11300±600	0.983	160	16
4-Ethoxynitrobenzene	2940±210	10630±670	0.988	160	9
4-(Methylthio)nitrobenzene	2410±160	9310±560	0.988	130	10
4-Nitroaniline	4020±180	14890±560	0.991	150	17
N-Methyl-4-nitroaniline	3930±220	14820±660	0.990	170	12
N,N-Dimethyl-4-nitroaniline	4100±230	15380±650	0.989	200	16
N-Ethyl-4-nitroaniline	3820±380	14970±1090	0.986	250	7
N,N-Diethyl-4-nitroaniline	3760±280	14750±830	0.984	210	12
4-Bromonitrobenzene	1690±160	6370±490	0.975	120	11
4-Nitrobenzaldehyde	1420±80	5550±280	0.988	70	12
4-Nitrobenzonitrile	710±100	3510±270	0.990	50	6[c]
4-Ethylnitrobenzene	1830±160	7700±520	0.981	130	12
4-Nitro(vinyloxy)benzene	2640±210	9280±570	0.989	140	8
4-(Chloromethyl)nitrobenzene	2040±100	7930±340	0.993	80	11
4-(Chlorosulfonyl)nitrobenzene	830±80	3490±270	0.975	70	12
N-(4-Nitrophenyl)aziridine	2430±310	10530±880	0.979	200	8
N-(4-Nitrophenyl)pyrrolidone	3650±450	14730±1210	0.985	280	6
3-Methyl-4-nitroaniline	3990±340	15850±970	0.987	240	8
5-Nitroindoline	4530±190	15510±630	0.993	160	13
2,6-Dibromo-4-nitrophenol	2000±150	7950±480	0.987	120	11

[a] The parameters were calculated as described in [6]. [b] Experimental $\nu_{\max}$ from Table 1 and [7–25]. [c] In halohydrocarbons.

chromic equation can generally be called a Bakhshiev–Bilot–Kawski equation and written in form (13).

$$\nu_{\max} = \nu_g - c_1 f_1 - p_2 f_2. \tag{13}$$

Here ν_g is the wave number in the vapor absorption maximum, $f_1 = (2n^2 + 1)/(n^2 + 2)[(\varepsilon - 1)/(\varepsilon + 2) - (n^2 - 1)/(n^2 + 2)]$, $f_2 = (n^2 - 1)/(n^2 + 2)$, $c_1 = (2\mu_g/a^3)\cdot(\mu_e \cos\varphi - \mu_g)$, $p_2 = p_0 + (3\overline{\Omega}/a^3)(\mu_e^2 - \mu_g^2)$, where $\overline{\Omega}$ is the mean value of the function $(n^2 + 1)/(n^2 + 2)$, μ_e is the dipole moment of the excited state, φ is the angle between the μ_e and μ_g vectors, a is the Onsager molecular radius, and r_0 is a parameter that measures the polarization- and dispersion-induced spectral shift.

The parameters of the Bakhshiev–Bilot–Kawski equation (13), obtained by fitting the effects of the medium on the spectra of the compounds studied are given in Table 4 (for calculation details, see [6]). In their quality, the many-parameter Bakhshiev–Bilot–Kawski equation ranks slightly below the Kamlet–Taft equation. Therefore, to reveal specific features of solvatochromism, and, especially, to class indicators into groups, one should make use of the empirical polarity/polarizability parameter (π^*). This would allow adequate application of theoretical relationships. Special tests showed that, as would be expected, the c_1 parameter is independent of the form of the $p_i f_i$ function (after Bakhshiev or after Bilot–Kawski), i.e. is a constant of a given indicator. The c_1 value, like s_a (these two values are close to each other, cf. Tables 2 and 4), is linearly related to μ_g (Tables 2–4) [with inclusion of 1-methyl-3-nitropyrazole (**IV**), c_1 3170±220 cm^{-1}, and of 1-methyl-4-nitroimidazole (**V**), c_1 4230±230 cm^{-1}]. Compounds **I**, **II**, **V**, **VII**, **VIII**, **XV, XVI, XX, XXI, XXIII**, and **XXVI** fit Eq. (14).

$$c_1 = (130 \pm 90) + (590 \pm 20)\mu_g;\ r\ 0.996,\ s\ 120,\ n\ 11. \tag{14}$$

A similar equation was obtained for compounds **IV, VI, XVII–XIX, XXII, XXIV**, and **XXV**.

$$c_1 = (190 \pm 120) + (510 \pm 30)\mu_g;\ r\ 0.991,\ s\ 110,\ n\ 8. \tag{15}$$

In qualitative agreement with the theory, the free terms of Eqs. (14) and (15) are close to zero and statistically insignificant. It is appropriate at this point to note the following. In describing solvatochromism in terms of theoretical equations one faces the necessity, according to the criteria of correlation analysis, to exclude from the data set some halogen-containing solvents, most commonly 1-BuCl and 1-BuBr. Previously [6] we explained this result by uncertainties in the determination one of the generalized parameters (ε, n). The revealed tendency in deviations of certain points over a wide range of compounds argues in favor of another hypothesis. Most likely, the deviations are explained by neglecting the theory of higher multipoles. Probably, this is the reason for the nonzero free terms in Eqs. (14) and (15).

Linear correlation between c_1 and μ_g takes place when the condition $(2/a^3)(\mu_e \cos\varphi - \mu_g) = \text{const} = m$ is fulfilled. Since Eqs. (14) and (15) hold for compounds whose molecular symmetry is C_{2v} (orbital electron density on light absorption is transferred along the second-order rotation axis), then for the whole set of indicators $\cos\varphi = 1$, i.e. $m = (2/a^3)(\mu_e - \mu_g)$. In other words, linear correlation between c_1 and μ_g is realized if the ratio of the moment difference to the cube of the Onsager radius for the given series of compounds is a constant value. Since the s_a and c_1 values also linearly related to each other [$s_a = (100 \pm 60) + (0.80 \pm 0.02)c_1$, r 0.993, s 100, n 25], this conclusion also relates to the s_a parameter of empirical solvatochromic equations.

Let us now correlate p_2 and μ_g. According to the Bakhshiev–Bilot–Kawski equation, the p_2 parameter is contributed by the orientating inductive component of the spectral shift, as well as by dispersion and polarization interactions of molecules with solvation shells. It can be admitted that, provided that $(\mu_e - \mu_g)/a^3 = \text{const}$, the difference in the dispersion and polarization components of the spectral shift are independent of μ_g. Comparison of p_2 and μ_g [with inclusion of 1-methyl-3-nitropyrazole (**IV**), p_2 12220 ± 700 cm^{-1}, and of 1-methyl-4-nitroimidazole (**V**), p_2 15890 ± 790 cm^{-1}] shows that Eqs. (16) and (17) actually have statistically significant free terms. Compounds **I, II, V, VII, VIII, XV, XVI, XX, XXI, XXIII**, and **XXVI** fit Eq. (16).

$$p_2 = (1260 \pm 360) + (2100 \pm 70)\mu_g;\ r\ 0.995,\ s\ 450, n\ 11. \quad (16)$$

A similar equation was obtained for compounds **IV, VI, XVII–XIX, XXII, XXIV**, and **XXV**.

$$p_2 = (1030 \pm 390) + (1950 \pm 100)\mu_g;\ r\ 0.993,\ s\ 370,\ n\ 8. \quad (17)$$

The values of the free terms for both groups of indicators are almost the same. Further we will show that $\mu_e = r\mu_g$. Under this condition, p_2 is a linear function of c_1, and this makes clear why Eqs. (9) and (10) have statistically significant free terms, what is the nature of the latter, and why s_a linearly varies with μ_g.

Estimation of the dipole moment of the first excited state. As already mentioned, for the series of compounds in study solvatochromic parameters are linear functions of ground-state dipole moments [Eqs. (18)].

$$c_1 = m_1\mu_g,\ p_2 = p_0 + m_2\mu_g,\ m_1 = 2(\mu_e - \mu_g)/a^3,$$
$$m_2 = 3\overline{\Omega}(\mu_e^2 - \mu_g^2)/a3\mu_g,\ \overline{\Omega} = 0.755. \quad (18)$$

The m_1 and m_2 constants are mean values for the set of indicators whose excitation at the long-wave absorption band produces electron density transfer along the vector of the ground-state dipole moment. It is easy to show that here one needs not know the Onsager radius for estimating μ_e [Eq. (19)].

$$\mu_e = \mu_g(2m_2/3m_1\overline{\Omega} - 1). \quad (19)$$

It follows from Eqs. (14)–(19) that for sufficiently symmetrical indicators with an $O_2N–C=C–C=C–R$ chromophoric chain and for certain heterocyclic nitro compounds the dipole moment in the first excited state is proportional to their ground-state dipole moment: $\mu_e = r\mu_g$. The first group that comprises nitrobenzene, 4-nitrotoluene, 4-nitrophenol, 4-nitroaniline, *N*-methyl-4-nitroaniline, *N,N*-dimethyl-4-nitroaniline, 4-nitrobenzaldehyde, 4-nitrobenzonitrile, 4-nitro(vinyloxy)benzene, 2,6-dibromo-4-nitrophenol, and 1-methyl-4-nitroimidazole has $r = 2.14 \pm 0.21$, and the second group comprising 4-nitroanisole, 4-ethoxynitrobenzene, 4-(methylthio)nitrobenzene, 4-bromonitrobenzene, 4-ethylnitrobenzene, 4-(chloromethyl)nitrobenzene, 4-(chlorosulfonyl)nitrobenzene, and 1-methyl-3-nitropyrazole, $r = 2.38 \pm 0.37$. The μ_e values estimated by formula (19) are listed in Table 5.

It will be emphasized that the aforesaid relates exclusively to aprotic inert media. In force of the violated mutual compensation of the dispersion and polarization components of the spectral shift, the same relationships not necessarily valid for aprotic protophilic solvents even if they effect nonspecific solvation of solvatochromic indicators. However, the empirical polarity/polarizability solvent parameter π^* is a reliable auxiliary tool for recognizing groups of compounds whose dipole moments μ_e and μ_g are specifically related to each other. Therefore, it is no question that the developed approach works with protophilic solvents. Moreover, our present findings suggest that the physical basis of the very scale of solvatochromic parameter π^* is the constancy of the μ_e/μ_g ratio in the series of indicators used, and the value of this ratio can be calculated from generalized medium parameters (ε, n).

Table 5. Dipole moments of aromatic and heteroaromatic nitro compounds in their first excited π,π^* states, estimated for carbon tetrachloride solutions

Compound	μ_e, D	Compound	μ_e, D
Nitrobenzene	8.3 ± 0.8	4-Nitrobenzaldehyde	4.8 ± 0.5
4-Nitrotoluene	9.5 ± 0.9	4-Nitrobenzonitrile	1.9 ± 0.2
4-Nitrophenol	10.4 ± 1.0	4-Ethylnitrobenzene	8.3 ± 1.3
4-Nitroanisole	11.7 ± 1.8	4-Nitro(vinyloxy)benzene	8.6 ± 0.8
4-Ethoxynitrobenzene	12.1 ± 1.9	4-(Chloromethyl)nitrobenzene	8.8 ± 1.4
4-(Methylthio)nitrobenzene	10.4 ± 1.6	4-(Chlorosulfonyl)nitrobenzene	3.0 ± 0.5
4-Nitroaniline	13.4 ± 1.3	2,6-Dibromo-4-nitrophenol	7.0 ± 0.7
N-Methyl-4-nitroaniline	14.0 ± 1.4	1-Methyl-3-nitropyrazole	13.7 ± 2.1
N,N-Dimethyl-4-nitroaniline	14.7 ± 1.4	1-Methyl-4-nitroimidazole	15.0 ± 1.5
4-Bromonitrobenzene	6.3 ± 1.0		

EXPERIMENTAL

The UV spectra were obtained on a Specord UV-Vis spectrophotometer at 22–25°C. The dielectric constants were measured on an Sh2-5 instrument (Angarsk, Experimental Design Office of Automation Joint-Stock Company) at 1 MHz (25°C). The dipole moments were calculated by the Higasi formula [40].

The compounds studied were commercial products of chemical grade. They were purified by recrystallization from organic solvents and vacuum sublimation. The purity of the compounds and solvents was controlled by physicochemical methods.

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