ISSN 1070-3632, Russian Journal of General Chemistry, 2006, Vol. 76, No. 4, pp. 596–614. © Pleiades Publishing, Inc., 2006.
Original Russian Text © A.I. Vokin, A.M. Shulunova, T.N. Aksamentova, G.V. Bozhenkov, V.K. Turchaninov, 2006, published in Zhurnal Obshchei Khimii, 2006, Vol. 76, No. 4, pp. 628–647.

Solvatochromism of Heteroaromatic Compounds: XXVIII.[1] Factors Affecting the Nonspecific Solvatochromic Effect in the UV Spectra of Aromatic Nitro Compounds in Aprotic Protophilic Solvents

A. I. Vokin, A. M. Shulunova, T. N. Aksamentova,
G. V. Bozhenkov, and V. K. Turchaninov

Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian
Academy of Sciences, ul. Favorskogo 1, Irkutsk, 664033 Russia

Received April 19, 2005

Abstract—Examination of the UV spectra of a large series of solvatochromic indicators of the general formula 1-X-4-NO_2-C_6H_4 in aprotic solvents confirmed the proportionality between the dipole moments of these compounds in the ground (μ_g) and first electronically excited ($^1A_1$, μ_e) states: $\mu_e = r_\mu \mu_g$. The coefficient r_μ was determined by applying the equation of the Bakhshiev–Bilot–Kawski solvatochromism theory both to nonspecifically solvated molecules and to their H complexes with aprotic protophilic solvents. An anisotropy of the electron redistribution was revealed for low-symmetry 1-substituted 2,4-dinitrobenzenes. The r_μ value obtained allowed the calculation of the Kamlet–Taft empirical solvatochromic parameter π^* on the basis of generalized characteristics of the solvent.

DOI: 10.1134/S1070363206040189

The main relationships in the effect of an aprotic inert solvent on the position of bands in the electronic absorption spectra of solvatochromic indicators of the general formula 4-$NO_2C_6H_4X$ were discussed in [2]. The solvent effects were considered in that paper with the aid of the Kamlet–Taft empirical relationship (1) and Eq. (2) of the Bakhshiev–Bilot–Kawski solvatochromism theory [3–5]:

$$\nu_{max} = \nu_0 - s\pi^*, \quad (1)$$

$$\nu_{max} = \nu_g - c_1 f_1 - p_2 f_2, \quad (2)$$

where ν_0, c_1, p_2, and s are constants of a given indicator; π^* is the quantitative measure of the capability of the solvent to stabilize dipolar molecules or ions of a solute by the mechanism of nonspecific solvation; ν_g is the wavenumber of the absorption maximum of the indicator vapor; and f_1 and f_2 are functions of "universal" interactions [3–5]. For particular sets of indicators, a linear relationship was found between ν_0 and the first vertical ionization potential of the compound modeling the C_6H_4X subunit. The other constants of indicators (s, c_1, p_2), characterizing their solvatochromic behavior, appeared to be proportional to the dipole moment in the ground electronic state μ_g:

$$s = s_0 + m_0\mu_g, \quad (3)$$

$$c_1 = c_0 + m_1\mu_g, \quad (4)$$

$$p_2 = p_0 + m_2\mu_g, \quad (5)$$

$$m_1 = 2(\mu_e - \mu_g)/a^3, \quad (6)$$

$$m_2 = 3\overline{\Omega}(\mu_e^2 - \mu_g^2)/(a^3\mu_g), \quad (7)$$

where a is the Onsager molecular radius, and $\overline{\Omega}$, mean value of the refractive index function $(n^2 + 1)/(n^2 + 2)$ of the solvent. These relationships allow calculation of the dipole moment of the molecule in the corresponding Franck–Condon $\pi\pi^*$ excited state (μ_e) using only the data furnished by absorption spectroscopy and dielectrometry:

$$\mu_e = r_\mu \mu_g, \quad (8)$$

$$r_\mu = 2m_2/3\overline{\Omega}m_1 - 1.$$

Compounds for which the excitation in the absorption band results in the electron transfer along the vector $\vec{\mu}_g$ are empirically subdivided into two groups. For the first group, $r_\mu = 2.14 \pm 0.21$, and for the second group, $r_\mu = 2.38 + 0.37$. Available data obtained

---

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

Table 1. Results of B3LYP/6-31G*(CI) calculations of low-energy π → π* transitions in the UV spectra of compounds 1-X-2,4-$(NO_2)_2C_6H_3$ and experimental wavenumbers of long-wave absorption maxima in cyclohexane

X	B3LYP/6-31G*(Cl)				Experiment	
	transition[a]	ν, cm^{-1}	*f*	predominant configuration[b]	ππ* state	ν, cm^{-1}
$NHCH_3$	$\pi_8 \rightarrow \pi_9^*$	27230	0.009	$0.62\Psi_m^{m+1}$	S_1	25900
	$\pi_8 \rightarrow \pi_{10}^*$	32550	0.038	$0.59\Psi_m^{m+2}$	S_2	30500
NH_2	$\pi_8 \rightarrow \pi_9^*$	28560	0.009	$0.62\Psi_m^{m+1}$	S_1	27600
	$\pi_8 \rightarrow \pi_{10}^*$	33790	0.033	$0.58\Psi_m^{m+2}$	S_2	32150
OH	$\pi_8 \rightarrow \pi_9^*$	29920	0.006	$0.63\Psi_m^{m+1}$	S_1	29900
	$\pi_8 \rightarrow \pi_{10}^*$	35940	0.019	$0.57\Psi_m^{m+2}$	S_2	38000 sh
	$\pi_7 \rightarrow \pi_9^*$	38740	0.042	$0.55\Psi_{m-1}^{m+1}$	S_3	39200
Cl	$(\pi \rightarrow \pi^*)^c$	30240	0.001	$0.40\Psi_{m-1}^{m+1}$, $0.34\Psi_{m-1}^{m+2}$	S_1	33000 sh
	$(\pi \rightarrow \pi^*)^c$	34610	0.003	$0.43\Psi_m^{m+1}$, $0.39\Psi_{m-1}^{m+2}$	S_2	38500
	$\pi_8 \rightarrow \pi_{10}^*$	36840	0.022	$0.52\Psi_m^{m+2}$	S_3	43150

[a] The electronic nature of the transitions is shown in Fig. 1. [b] To a Ψ_i^j electronic configuration corresponds a $\varphi_i^2 \rightarrow \varphi_j^0$ transition. [c] Multielectron excitation.

by electrooptical methods [6–10] show that such r_μ values agree with the experimental data. For example, the μ_e/μ_g ratio found from the experimental data is 2.26 for nitrobenzene, 2.2–2.5 for 4-nitroaniline, and 2.1–2.2 for *N*,*N*-dimethyl-4-nitroaniline. However, when examining the effects of an inert medium, the μ_g values were measured in CCl_4 in which many aromatic nitro compounds are only sparingly soluble; therefore, the specific features of their solvatochromic behavior were not revealed in full measure. Two important questions remained to be answered: How does r_μ vary in the series of nitroarenes 4-$NO_2C_6H_4X$ and does it vary at all? Does r_μ depend on the chemical nature of the medium?

In this study we examined the solvatochromic behavior of indicators of the above series in an aliphatic aprotic protophilic medium. As solvent for measuring μ_g we chose 1,4-dioxane whose molecules, like those of CCl_4, have no permanent dipole moment. Thanks to the pronounced protophilic properties of dioxane, it appeared possible to vary in a wide range the nature of the auxochrome and appreciably extend the set of compounds with "solvation-active" CH, NH, and OH bonds, and, in particular, to reveal the effect of formation of H-bonded solvation complexes. Also, in the aprotic protophilic medium we analyzed the solvatochromic behavior of those heteroaromatic compounds whose spectral and electrical characteristics in inert solvents obeyed Eqs. (3)–(5) [2]. As low-symmetry aromatic nitro compounds to be studied we chose m-dinitrobenzene derivatives. According to [11], the UV spectra of such compounds may contain a band corresponding to the transition to the ππ* state in which one of the partially occupied π orbitals is localized on the 4-$NO_2C_6H_3X$ fragment, and the other, on the C_6H_3X fragment. To extend the data set, we also obtained new data on the solvatochromic behavior of aromatic nitro compounds 4-$NO_2C_6H_4X$ in an inert medium.

Electronic nature of long-wave absorption bands of 1-substituted 2,4-dinitrobenzenes. The correlation and structure of π-type molecular orbitals of 1-substituted 2,4-dinitrobenzenes are shown in Fig. 1. These data in combination with the theoretical data (Table 1) show that, when an auxochrome is a pronounced electron donor, low-energy π → π* transitions cause one-electron excitation and electron density redistribution either to the chromophore in the p-position only ($\pi_8 \rightarrow \pi_{10}^*$) or to the chromophore in the o-position only ($\pi_8 \rightarrow \pi_9^*$). With a halogen atom as auxochrome, the π → π* transition causing the transfer of the orbital electron density in the 4-nitrobenzene fragment remains one-electron (Table 1). Taking into account the scope of this paper, we considered data for the absorption band corresponding to the $\pi_8 \rightarrow \pi_{10}^*$ transition ($\varphi_m^2 \rightarrow \varphi_{m+2}^0$, electronic configuration Ψ_m^{m+2}, Fig. 1). The B3LYP/6-31G*(CI) calculations showed that this transition is fully similar in the electronic nature and main characteristics to the most intense low-energy transition in the UV spectra of aromatic nitro compounds of the general formula 4-$NO_2C_6H_4X$ (the theoretical and experimental data are given in Table 2; the correlation of the π-type molecular orbitals is shown in Fig. 2). Note that both low-energy

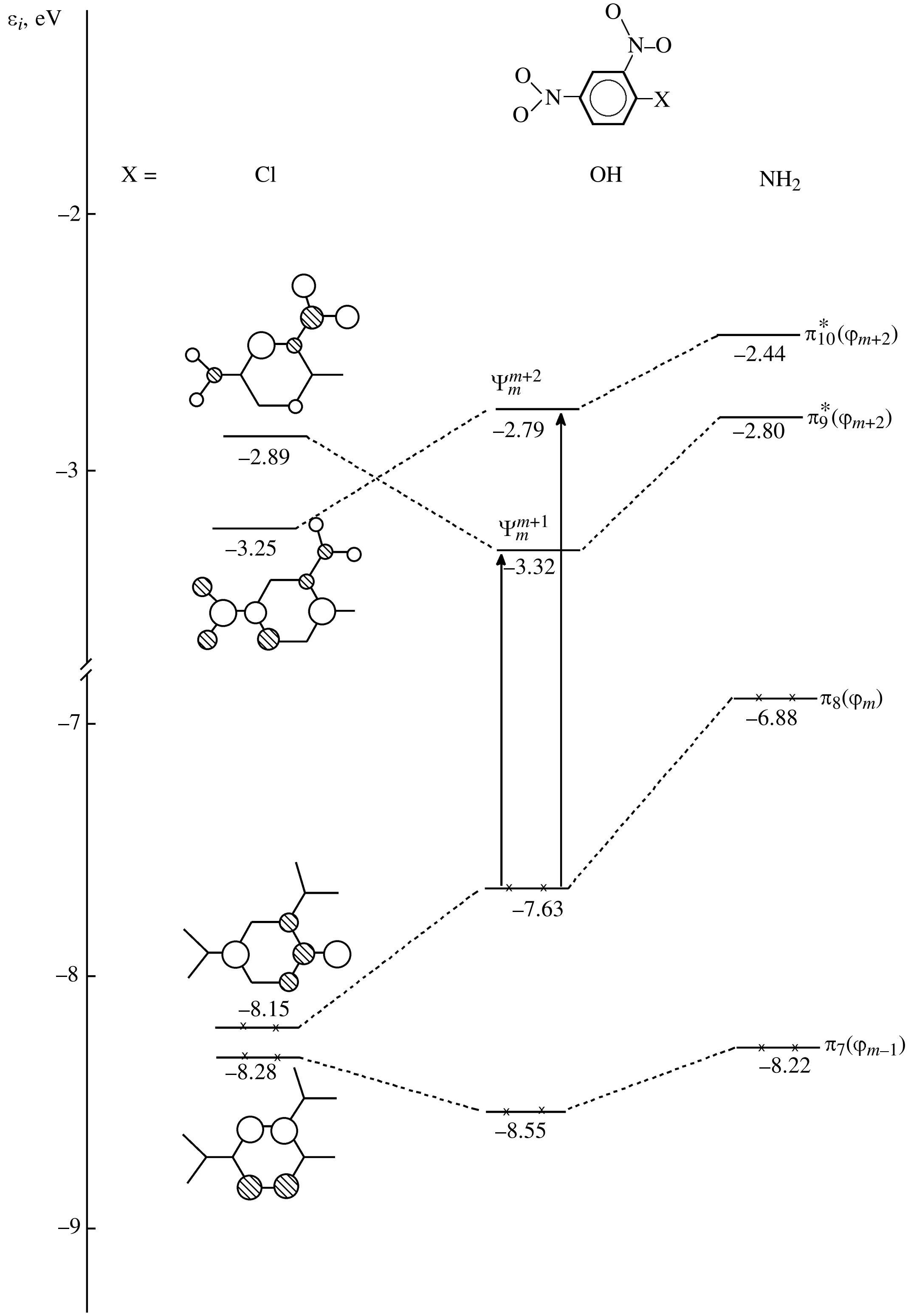

Fig. 1. Correlation of the π molecular orbitals in the series of 1-substituted 2,4-dinitrobenzenes. Data on the orbital energies and electron density distribution were obtained by B3LYP/6-31G* calculations.

π → π* transitions in the UV spectra of compounds belonging to the latter group are one-electron and cause transfer of the orbital electron density to the nitro group: the $\varphi^2_{m-1} \to \varphi^0_{m+1}$ transition, from the benzene ring (forbidden), and the $\varphi^2_m \to \varphi^0_{m+2}$ transition, from the auxochrome. The assignment of the

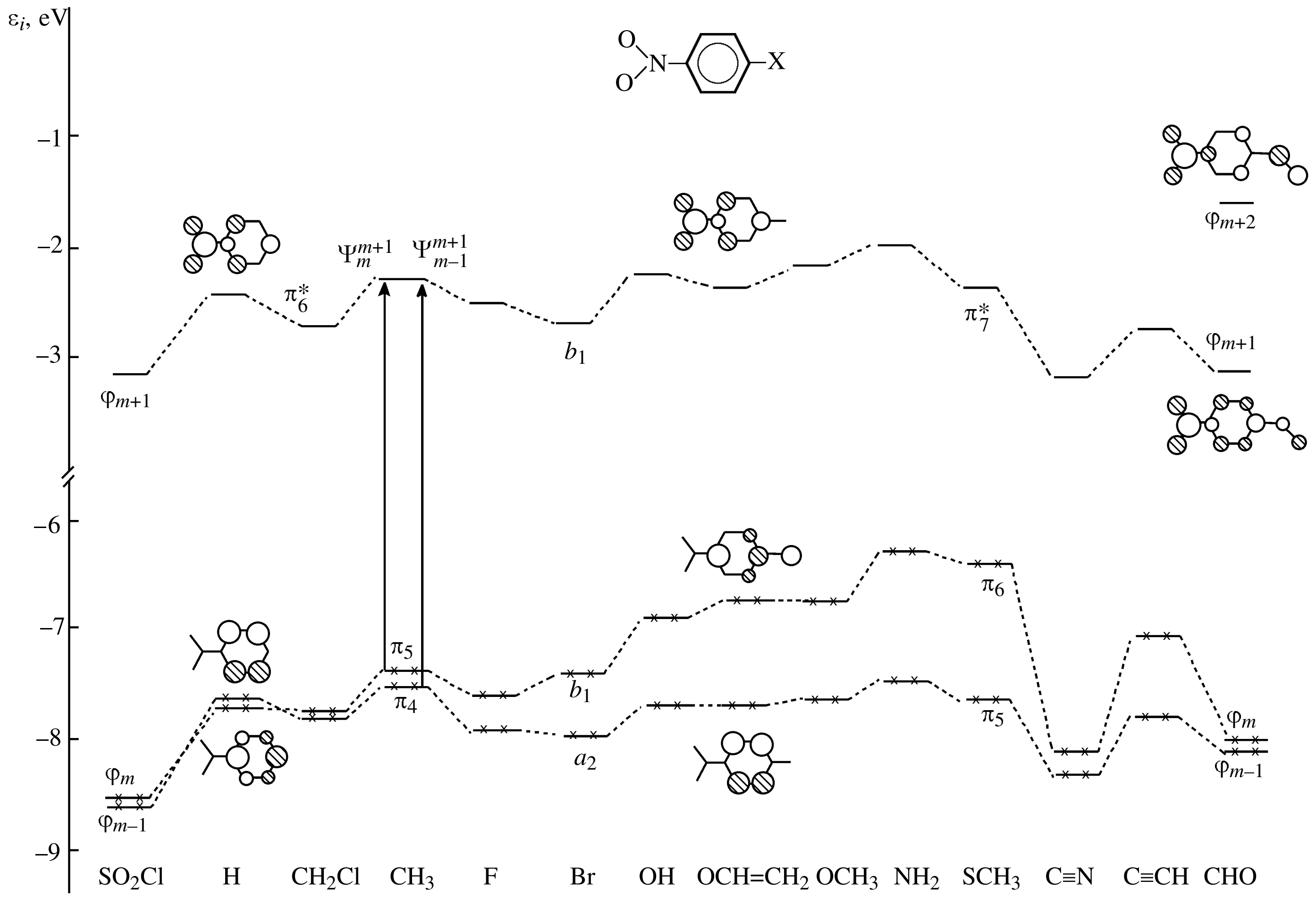

Fig. 2. Correlation of the π molecular orbitals of aromatic nitro compounds 1-X-4-$NO_2C_6H_4$. Data on the orbital energies and electron density distribution were obtained by B3LYP/6-31G* calculations.

electronic absorption bands to π → π* transitions for some of compounds that previously were not studied theoretically is shown in Fig. 3.

A necessary condition for quantitative description of the relationship between the solvatochromism parameters and dipole moment μ_g is that the absorption band of the indicator should have the same electronic nature. Therefore, for all the compounds and solvents examined, we used the band of the transition with the transfer of the orbital electron density from the auxochrome to the *p*-NO_2 group. The weak band in the UV spectra of the indicators 4-$NO_2C_6H_4X$, though being a charge-transfer band, is of little use. Its solvatochromic behavior could be examined only in a few cases. Even if this band is observed at all, with increasing solvent polarity it becomes either severely broadened with the loss of the vibronic structure and observed maximum, or fully obscured by the stronger adjacent band.

An interesting result was obtained in calculation of the UV spectrum of 4-nitrobenzaldehyde. The calculations show that its isomers and/or analogs may exhibit an absorption band corresponding to the π → π* transition with transfer of the orbital electron density to both chromophores simultaneously (Table 2, Fig. 2).

Dipole moment in the ground electronic state μ_g. To determine whether r_μ is a constant for a given set of indicators or it depends on particular auxochrome, it was necessary to examine a wider set of compounds than that in [2] and to consider not only inert solvents but also aliphatic aprotic photophilic solvents. As already noted, the major problem is the low solubility of the indicators (especially anilines and their analogs) in CCl_4. To estimate μ_g in CCl_4 for compounds for which these quantities could not be determined experimentally, we used the relationships between $\mu(CCl_4)$ and the dipole moments measured in dioxane and/or benzene or calculated theoretically (Tables 3, 4).

Table 2. Results of B3LYP/6-31G*(CI) calculations of low-energy π → π* transitions in the UV spectra of compounds 1-X-4-$NO_2C_6H_4$ and experimental wavenumbers of long-wave absorption maxima in cyclohexane

X	B3LYP/6-31G*(Cl)				Experiment	
	transition[a]	ν, cm^{-1}	*f*	predominant configuration[b]	ππ* state	ν, cm^{-1}
SO_2Cl	$\pi_4 \to \pi_6^*$	36810	0.003	$0.57\Psi_m^{m+1}$	S_1	33350, 34500, 35650
	$\pi_5 \to \pi_6^*$	39330	0.050	$0.55\Psi_{m-1}^{m+1}$	S_2	40100
H	$\pi_4 \to \pi_6^*$	35900	0.002	$0.65\Psi_{m-1}^{m+1}$	$S_1(^1B_2)$	~35000
	$\pi_5 \to \pi_6^*$	39350	0.032	$0.61\Psi_m^{m+1}$	$S_2(^1A_1)$	39550
CH_2Cl	$\pi_4 \to \pi_6^*$	35660	0.002	$0.65\Psi_{m-1}^{m+1}$	S_1	~35000
	$\pi_5 \to \pi_6^*$	37820	0.045	$0.61\Psi_m^{m+1}$	S_2	38550
CH_3	$\pi_4 \to \pi_6^*$	35940	0.002	$0.65\Psi_{m-1}^{m+1}$	S_1	–
	$\pi_5 \to \pi_6^*$	37670	0.040	$0.60\Psi_m^{m+1}$	S_2	37650
F	$\pi_5 \to \pi_7^*$	37530	0.001	$0.65\Psi_{m-1}^{m+1}$	$S_1(^1B_2)$	–
	$\pi_6 \to \pi_7^*$	38070	0.033	$0.60\Psi_m^{m+1}$	$S_2(^1A_1)$	38850
Br	$\pi_5 \to \pi_7^*$	36690	0.002	$0.64\Psi_{m-1}^{m+1}$	$S_1(^1B_2)$	~34000, ~35000
	$\pi_6 \to \pi_7^*$	35250	0.040	$0.62\Psi_m^{m+1}$	$S_2(^1A_1)$	36850
OH	$\pi_6 \to \pi_7^*$	35510	0.037	$0.60\Psi_m^{m+1}$	S_1	34900
	$\pi_5 \to \pi_7^*$	37540	0.001	$0.63\Psi_{m-1}^{m+1}$	S_2	–
$OCH=CH_2$[c]	$\pi_6 \to \pi_7^*$	32350	0.038	$0.63\Psi_m^{m+1}$	S_1	34100
	$\pi_5 \to \pi_7^*$	37040	0.001	$0.62\Psi_{m-1}^{m+1}$	S_2	–
OCH_3	$\pi_6 \to \pi_7^*$	34640	0.040	$0.60\Psi_m^{m+1}$	S_1	34000
	$\pi_5 \to \pi_7^*$	37260	0.002	$0.63\Psi_{m-1}^{m+1}$	S_2	–
NH_2	$\pi_6 \to \pi_7^*$	33040	0.041	$0.58\Psi_m^{m+1}$	S_1	32000
	$\pi_5 \to \pi_7^*$	37230	0.000	$0.59\Psi_{m-1}^{m+1}$	S_2	–
$N(CH_2)_2$	$\pi_6 \to \pi_7^*$	32130	0.046	$0.60\Psi_m^{m+1}$	S_1	32000[d]
	$\pi_5 \to \pi_7^*$	36560	0.000	$0.61\Psi_{m-1}^{m+1}$	S_2	–
$N(CH_3)_2$	$\pi_6 \to \pi_7^*$	30670	0.046	$0.59\Psi_m^{m+1}$	S_1	28100[d]
	$\pi_5 \to \pi_7^*$	36590	0.000	$0.51\Psi_{m-1}^{m+1}$	S_2	–
$N(CH_2)_4$	$\pi_6 \to \pi_7^*$	30360	0.050	$0.58\Psi_m^{m+1}$	S_1	27500[d]
	$(\pi \to \pi^*)$[e]	36460	0.000	$0.50\Psi_m^{m+2}$, $0.48\Psi_{m-1}^{m+1}$	S_2	–
SCH_3	$\pi_6 \to \pi_7^*$	30640	0.038	$0.61\Psi_m^{m+1}$	S_1	~29000, 30450
	$\pi_5 \to \pi_7^*$	36250	0.000	$0.59\Psi_{m-1}^{m+1}$	S_2	–
CHO	$\pi_6 \to \pi_7^*$	34240	0.003	$0.60\Psi_m^{m+1}$	S_1	~33000, ~34000, ~35000
	$\pi_5 \to \pi_7^*$	37860	0.053	$0.55\Psi_{m-1}^{m+1}$	S_2	38450
	$\pi_6 \to \pi_8^*$	45500	0.000	$0.60\Psi_m^{m+2}$	S_3	–
C≡N	$\pi_5 \to \pi_7^*$	35890	0.003	$0.64\Psi_{m-1}^{m+1}$	$S_1(^1B_2)$	~33500, ~34500
	$\pi_6 \to \pi_7^*$	37400	0.050	$0.60\Psi_m^{m+1}$	$S_2(^1A_1)$	39450
C≡CH	$\pi_6 \to \pi_7^*$	33570	0.050	$0.60\Psi_m^{m+1}$	$S_1(^1A_1)$	~33000, ~34000, 35400
	$\pi_5 \to \pi_7^*$	35400	0.002	$0.64\Psi_{m-1}^{m+1}$	$S_2(^1B_2)$	–

[a] The electronic nature of the transitions is shown in Fig. 2. [b] To a Ψ_i^j electronic configuration corresponds a $\varphi_i^2 \to \varphi_j^0$ transition. [c] The π molecular orbitals are classed without taking into account fragment orbitals of the vinyl group. [d] Data of [12]. [e] Multielectron excitation.

For indicators that are nonspecifically solvated with 1,4-dioxane, the dipole moments $\mu(C_4H_8O_2)$ can be estimated as follows [2]:

$$\mu(C_4H_8O_2) = (0.02 \pm 0.07) + (1.05 \pm 0.02)\mu(CCl_4), \quad (9)$$
$$r\ 0.996,\ sd\ 0.13,\ n\ 28.$$

For hydrogen bond-donors, which are specifically solvated with 1,4-dioxane, the formula for calculating the dipole moments is somewhat different [2]:

$$\mu(C_4H_8O_2) = (0.22 \pm 0.07) + (1.07 \pm 0.02)\mu(CCl_4), \quad (10)$$
$$r\ 0.998,\ sd\ 0.10,\ n\ 14.$$

The relationship between the μ_g values measured in benzene and in CCl_4 is as follows:

$$\mu(C_6H_6) = (-0.07 \pm 0.05) + (1.04 \pm 0.01)\mu(CCl_4), \quad (11)$$
$$r\ 0.996,\ sd\ 0.13,\ n\ 65.$$

This equation is based on available [13] and newly obtained data which will be published later. It is valid for all isomers of aromatic and heteroaromatic nitro compounds except phenol derivatives and indicators with the COR, C≡N, and N=O chromophores.

The results of comparison of the theoretically calculated (HF/6-31G*) dipole moments μ_g and those measured in CCl_4 require certain comments. Since the calculation procedure used reproduces the bond configuration at the aniline N atom insufficiently ade-

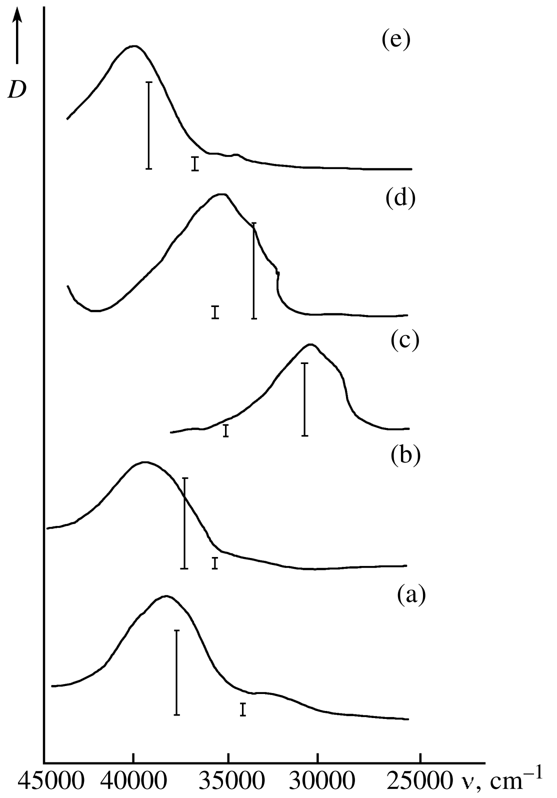

Fig. 3. Assignment of bands in the electronic absorption spectra of aromatic nitro compounds 1-X-4-NO_2-C_6H_4 in cyclohexane [X: (a) CHO, (b) C≡N, (c) SCH_3, (d) C≡CH, (e) SO_2Cl] to low-energy π → π* transitions calculated by the B3LYP/6-31G*(CI) method.

Table 3. Dipole moments of compounds 1-X-4-NO_2PhR

X	R	Method	μ, D
$N(CH_2)_4$	H	HF/6-31G*	8.39
		Dielectrometry, benzene	7.26^{a,b}
		Dielectrometry, dioxane	7.45
$N(CH_2)_2$	H	HF/6-31G*	6.44
$N(C_2H_5)_2$	H	HF/6-31G*	7.99
		Dielectrometry, benzene	7.14^{a,b}
		Dielectrometry, dioxane	7.30
$N(CH_2)_5$	H	Dielectrometry, benzene	6.74^{a,b}
$NHN=C(CH_3)_2$	H	"	7.27
		Dielectrometry, dioxane	7.62
$NHN=C(CH_2)_5$	H	Dielectrometry, benzene	7.10
		Dielectrometry, dioxane	7.37
NH_2	2,6-Br_2	HF/6-31G*	5.57
		Dielectrometry, benzene	4.70
		Dielectrometry, dioxane	5.43
$NHN(CH_3)_2$	H	"	7.57
NH_2	2-NO_2	Dielectrometry, benzene	5.87^{a}
		Dielectrometry, dioxane	6.50^{a,b}

Table 3 (Contd.)

X	R	Method	μ, D
$NHCH_3$	2-NO_2	Dielectrometry, benzene	6.36[a]
		Dielectrometry, dioxane	6.58[a]
NH–C_6H_4-4'-NO_2	H	HF/6-31G*	4.70
		Dielectrometry, dioxane	4.81
$NHCOCH_3$	H	"	6.62
NHN=C(*n*-Pr)–CH=CCl_2	H	"	7.24
NHN=C(*n*-Pr)–CCl=CHCl	H	"	7.00

[a] Data of [13]. [b] Mean value.

Table 4. Theoretical (HF/6-31G*) and experimental (CCl_4) dipole moments (D) of substituted anilines, pyridines, and nitrobenzenes in the ground state

Compound	HF/6-31G*	CCl_4	Compound	HF/6-31G*	CCl_4
Anilines			Pyridines		
N,N-Me$_2$-2-OMe	0.88	1.18	2-*N,N*-Me$_2$	1.73	1.99
N,N-Me$_2$-4-*N,N*-Me$_2$	1.22	1.33	4-*N,N*-Me$_2$	4.26	4.17
N,N-Me$_2$	1.46	1.55	2-*N,N*-Me$_2$-4-Me-5-NO_2	6.92	6.04
N,N-Me$_2$-2-Cl	2.46	2.21	Nitrobenzenes		
N,N-Me$_2$-4-Cl	3.84	3.35	4-SO_2Cl	1.59	1.25
N,N-Me$_2$-4-Br	3.89	3.37	4-CHO	3.12	2.23
N,N-Me$_2$-3-NO_2	6.11	5.15	4-Cl	3.14	2.69
N,N-Me$_2$-4-NO_2	7.88	6.87	4-Br	3.27	2.63
3-NO_2-4-Me	5.35	4.41	3-NO_2-4-OH	3.77	2.92
3-NO_2	5.74	4.84	3,5-Br-4-OH	3.83	3.27
3-NO_2-6-Me	5.97	4.92	2-OH	3.98	3.20
2,4,6-Me$_3$	1.39	1.31	3-NO_2	4.78	3.69
NCOMe-2-NO_2	1.48	1.61	H	5.07	3.88
NCOMe-2-NO_2-4-Me	1.79	1.79	4-N$(CH_2)_4$	8.39	7.05
NMe-2-NO_2	5.00	4.27	4-OCH=CH_2	5.25	4.02
NMe	1.48	1.71	3-Me	5.33	4.23
H	1.54	1.46	2-Cl	5.58	4.41
N,N-Et$_2$-4-NO_2	7.99	6.90	4-Me	5.61	4.45
2-NO_2-4-OMe	4.04	3.60	2-OMe	6.11	4.77
2-NO_2	5.04	4.25	4-OMe	6.14	4.90
2-NO_2-4-Me	5.19	4.08	4-OEt	6.36	5.07
2-OMe-5-NO_2	6.64	5.46			
NPh-2-NO_2	5.18	3.99			

quately, the correlation between μ(CCl_4) and μ(HF/6-31G*) is described by the system of three equations (for specific data, see Table 4):

N-Substituted anilines

$$\mu(\mathrm{CCl_4}) = (0.39\pm0.10) + (0.81\pm0.02)\mu(\mathrm{HF/_{6}\text{-}_{31}G^*}), \quad (12)$$

$$r\ 0.996,\ sd\ 0.18,\ n\ 11.$$

N-Unsubstituted anilines

$$\mu(\mathrm{CCl_4}) = (0.26\pm0.11) + (0.78\pm0.02)\mu(\mathrm{HF/6\text{-}31G^*}), \quad (13)$$

$$r\ 0.997,\ sd\ 0.12,\ n\ 9.$$

Other aromatic nitro compounds

$$\mu(\mathrm{CCl_4}) = (0.04\pm0.11) + (0.78\pm0.02)\mu(\mathrm{HF/_{6}\text{-}_{31}G^*}), \quad (14)$$

$$r\ 0.994,\ sd\ 0.12,\ n\ 17.$$

Apparently, nitro derivatives of diphenylamines are exceptions: Their representative 4,4'-dinitrodiphenylamine (Table 4) falls into the third, rather than first, group.

Description of solvatochromism. Data on the effect of aliphatic aprotic protophilic solvents on the indicator absorption band of aromatic *p*-nitro compounds with auxochrome X = NR_2, OR, COR, C≡CH, and also of 1-methyl-4-nitroimidazole and 1-methyl-3-nitropyrazole were taken from the literature [12, 14–34]. Data for the other compounds of this series will be published in further papers. As aprotic protophilic solvents we used ethers, esters, trimethoxymethane, tertiary amines, amides, nitriles, ketones, carbonates, HMPA, nitromethane, tetramethylurea, sulfolane, and DMSO. New data obtained in inert solvents are given in Table 5.

Table 5. Solvatochromism of the strongest long-wave absorption band in the UV spectra of indicators 1-X-4-$NO_2C_6H_4$ in inert aprotic solvents

Solvent	π*[a]	X					
		F	Cl	COOMe	$COCH_2Br$	$COOCH_2SiF_3$	$OSiMe_3$
Hexane	–0.08	39100	37700	38650	38050	39550	34800
Heptane	–0.02	38950	37700	–	38000	39550	34650
Cyclohexane	0.00	38850	37750[b]	38650	38000	38850[c]	34550
Octane	0.01	39050[d]	37650	38700[b]	38000	39400	34600
Decane	0.03	38900	37600	–	38000	–	34550
Dodecane	0.08	38800	37550	–	37900	39300	34500
Carbon tetrachloride	0.28	38500	37100	38250	37750	–	34100
1-Chlorobutane	0.39	38300	36950	38150	37650	–	33700
1-Bromobutane	0.48	37900	–	–	37500	–	33550
1,2-Dichloroethane	0.81	37600	–	37650	37300	38500	32950
Dichloromethane	0.82	37600	36300	37700	37350	–	33000
1,1,2,2-Tetrachloroethane	0.95	37300	36100	–	37150	38400	32600

Table 5. (Contd.)

Solvent	π*[a]	X				
		$OCH_2SiMe(OMe)_2$	$OCH_2Si(OMe)_3$	$NHN=CMe_2$	NH–4'-NO_2–C6H4	1-NH_2–2,6-Br_2
Hexane	–0.08	33850	33800	28600	–	30900
Heptane	–0.02	33750	33750	28500	–	30850
Cyclohexane	0.00	33550	33600	28300	–	30700
Octane	0.01	33850[b]	33850[b]	28400	–	30750
Decane	0.03	33650	33650	28300	–	30600
Didecane	0.08	–	–	28250	–	–
Carbon tetrachloride	0.28	33000	33050	27550	26950	30200
1-Chlorobutane	0.39	32650	32800	28650[b]	27100[e]	29700
1-Bromobutane	0.48	–	–	26900	26200[c]	–
1,2-Dichloroethane	0.81	32000	32150	26050	25450	–
Dichloromethane	0.82	32000	32100	26100	25550	29000
1,1,2,2-Tetrachloroethane	0.95	31550	31700	25650	25400	28600

Solvent	π*[a]	X			
		$NHN=C(CH_2)_5$	$NHN=C(Pr)–CH=CCl_2$	NHN=C(Pr)–CCl=CHCl	NHCOMe
Hexane	–0.08	28300	27650	28350	33500
Heptane	–0.02	28100	27500	28150	33250

Table 5. (Contd.)

Solvent	π^* [a]	X			
		$NHN{=}C(CH_2)_5$	$NHN{=}C(Pr){-}CH{=}CCl_2$	$NHN{=}C(Pr){-}CCl{=}CHCl$	NHCOMe
Cyclohexane	0.00	28000	27400	28000	33250
Octane	0.01	28000	27500	28100	33300
Decane	0.03	27800	–	–	–
Didecane	0.08	27800	–	–	–
Carbon tetrachloride	0.28	27350	26950	27450	32700
1-Chlorobutane	0.39	26650	26450	26850	31800 [f]
1-Bromobutane	0.48	28350 [b]	25950 [g]	26650 [g]	–
1,2-Dichloroethane	0.81	25650	25700	26300	31500
Dichloromethane	0.82	25750	25700	26300	31550
1,1,2,2-Tetrachloroethane	0.95	25350	25300	25850	31350

[a] The polarity parameter was taken from [35, 36]. [b] Measured in pentane (π^* –0.08). [c] In trichloroethylene (π^* 0.53). [d] In isooctane (π^* 0.00). [e] In decalin (π^* 0.09). [f] In chloroform (π^* 0.58). [g] In pentachloroethane (π^* 0.62).

To describe the solvatochromism of indicators in inert solvents, we used Eq. (1). For aprotic protophilic solvents, the nonspecific ($s\pi^*$) and specific ($b\beta$) solvatochromic effects were calculated by Kamlet–Taft empirical equation (15):

$$\nu = \nu_0 - s\pi^* - b\beta - e\xi, \qquad (15)$$

where β is the quantitative measure of the capability of a solvent molecule to act as H-bond acceptor in an H complex with the solute; ξ is the group measure of the covalence of the coordination bond [37]. The form of Eq. (15) suggests that the contributions to the spectral shift from the specific ($\Delta\nu_{\text{spec}} = b\beta$) and nonspecific ($\Delta\nu_{\text{nonspec}} = s\pi^*$) solvation mechanisms are additive. This is due to the fact that H complexes with the solvent are individual species with a common center of gravity and the inherent set of geometric and other (in particular, μ_g) parameters. Such species are not proton donors and are solvated by the nonspecific mechanism only, similarly to molecules without "solvation-active" bonds.

The spectral information suitable for quantitative study of universal interactions of solvation H complexes with the solvent can be readily obtained by transforming Eq. (15) into (16):

$$\nu = \nu_0 - \Delta\nu_{\text{nonspec}}. \qquad (16)$$

This transformation lifts obstacles to application of the solvatochromism theory to specifically solvating media. The use of Eq. (16) also eliminates doubts expressed by some authors [38–41] in the correctness of directly using the functions of universal interactions in cases when indicators are potentially capable to form hydrogen bonds with solvent molecules.

The $\nu_{\max}$ values in the gas-phase spectra of indicators (ν_g), required for applying Eq. (2) to aprotic protophilic solvents, were calculated by empirical equation (15) (at $\pi^* = \pi^*_g = -1.10$, $\beta = \xi = 0$). This is caused by several factors. First, ν_g cannot be measured at temperatures close to 20°C for the majority of compounds because of their low volatility. Second, solvation H complexes in the vapor have low stability and occur in equilibrium with the free subunits. Third, extrapolation of data obtained at high temperatures to 20°C often involves large errors.

To check the validity of the ν_g values thus calculated, they were compared with the available experimental data (Table 6). It is seen that the estimated and directly measured values of ν_g are well consistent, except the data for X = Br and $N(C_2H_5)_2$. However, in this case the deviation is about 800 cm^{-1} (to different sides), which coincides with the interval between the vibronic components of the indicator band (see [2] and Figs. 3c, 3d). This fact suggests that a change in the aggregation state leads in some cases to a change in the relative intensities of the vibronic components, causing a jumpwise shift of the global maximum of the absorption band. Hence, the use of calculated values of ν_g is preferable when considering the spectra of condensed phases.

Relationship between s and μ_g. Linear equation (3) can become common for all aprotic solvents if two conditions are met: If variation of the chemical nature of the solvent affects μ_g and μ_e of an indicator similarly and if formation of a solvation complex similarly affects the characteristics of the ground electronic and Franck–Condon excited states of the indicator. To elucidate the general relationship between s and μ_g, we primarily used the most representative group of indicators ($4\text{-}NO_2C_6H_4X$, where X = H, C≡N, CHO, $OCH{=}CH_2$, CH_3, OH, NH_2, $NHCH_3$, and also 2,6-dibromo-4-nitrophenol and 1-methyl-4-nitroimidazole) among those described in [2]. In accordance with the data newly obtained for an inert medium, this group was supplemented by the compounds $4\text{-}NO_2C_6H_4X$ with X = Cl, $NHC_6H_4\text{-}p\text{-}NO_2$, and $N(CH_2)_5$. The dipolarity of the indicators in an inert medium was characterized by $\mu_g(CCl_4)$, and in aprotic protophilic solvents, by $\mu_g(C_4H_8O_2)$. The solvatochromic behavi- of the compounds in aprotic inert and protophilic solvents was characterized separately. The necessity of separate description of the solvatochromism in the electronic absorption spectra of nitroazoles was demonstrated in [31] by the example of isomeric nitropyrazoles. For aromatic nitro compounds, different types of aprotic solvents should also be considered separately, as indicated by data for *N,N*-dimethyl-4-nitroaniline (see below) whose UV spectra were examined in detail in three sets of solvents: [12, 14, 16, 18, 21, 22, 25, 26, 29].

Aprotic media	μ_g (solvent), D	ν_0, cm^{-1}	$-s$, cm^{-1}	r	sd	n
Inert	6.87 (CCl_4)	28150±40	3270±80	0.995	140	20
Protophilic aromatic	6.85, 6.96, 6.93 (C_6H_6)	28150±110	3330±140	0.976	130	29
Protophilic aliphatic	7.27 ($C_4H_8O_2$)	28120±50	3490±70	0.992	90	43

The relationship between s and μ_g for the group of indicators under consideration is shown in Fig. 4. The relationship is common for all nonspecifically solvated aromatic nitro compounds. Variation of the chemical nature of the solvent affects only the characteristics of 1-methyl-4-nitroimidazole (Fig. 4, point *22*). The second condition is met for weak hydrogen-bond donors with X = $NHC_6H_4\text{-}p\text{-}NO_2$, NH_2, and $NHCH_3$. Formation of a strong intermolecular hydrogen bond between the solvent and 4-nitrophenol (two-centered) or 2,6-dibromo-4-nitrophenol (three-centered) disturbs the relationship between s and μ_g valid for the other representatives of this group (Fig. 4, points *12*, *19*). The general correlation equation (17) obtained after exclusion of the three above-mentioned compounds does not differ from Eq. (18) obtained previously [2] for an inert medium:

Aprotic protophilic solvents

$$s = (290 \pm 30) + (450 \pm 10)\mu_g, \quad r\ 0.997,\ sd\ 70,\ n\ 33. \tag{17}$$

Inert medium [2]

$$s = (230 \pm 60) + (460 \pm 10)\mu_g, \quad r\ 0.997,\ sd\ 70,\ n\ 11. \tag{18}$$

The next of the groups distinguished in [2] ($4\text{-}NO_2C_6H_4X$, where X = SO_2Cl, Br, C≡CH, CH_2Cl, SCH_3, OCH_3, or OC_2H_5, and 1-methyl-3-nitropyrazole) was supplemented by the indicators $4\text{-}NO_2C_6H_4X$ with X = $N(C_2H_5)_2$ and $N(CH_2)_4$, and also by 2,6-dibromo-4-nitroaniline. In this group, in going from inert to aprotic protophilic solvents, the first of the conditions formulated above is not met for nitroarenes with auxochromes X = SO_2Cl, Br, CH_2Cl, SCH_3. The second condition is not met for the solvation complex with a bifurcate hydrogen bond between the solvent and 2,6-dibromo-4-nitroaniline. Relationship (19) between s and μ_g, obtained in an aprotic protophilic medium

Table 6. Measured (gas phase) and calculated [Eq. (15)] wavenumbers of absorption maxima of compounds $1\text{-}X\text{-}4\text{-}NO_2C_6H_4$

X	ν_g, cm^{-1}	
	calculated	measured^a
H	41830	41650, 41820, 41940
CH_2Cl	40880	40800^b (50–90°C)
CH_3	40490	39850, 39970, 40330
F	40820	40140, 40800
Cl	39420	39250, 39650^b (50–90°C), 39790
Br	38600	39250^b (50–90°C), 39520
OH	37250	37310, 37910, 37940
OCH_3	37000	36870, 36900, 37100, 37110
OC_2H_5	36470	36700^b (50–90°C)
NH_2	34520	34210, 34370, 34480, 34680
$NHCH_3$	32750	32620
$N(CH_3)_2$	31960	31370, 31460
$N(C_2H_5)_2$	31160	30390

[a] Data from [25, 42–46]; the temperature ranges are indicated in these papers. [b] This work.

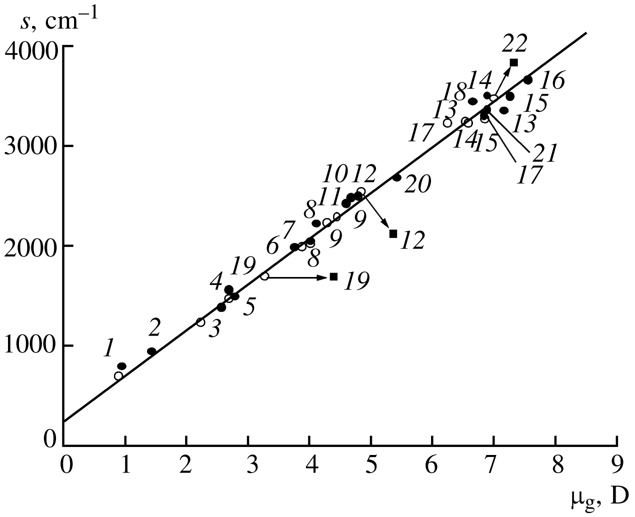

Fig. 4. Correlation between the regression coefficient s and ground-state dipole moment of aromatic compounds X-4-NO_2PhR. Aprotic inert medium is denoted by light circles, and prortophilic medium, by dark circles. R = H; X: (*1*) C≡N, (*2*) SO_2Cl, (*3*) CHO, (*4*) Cl, (*5*) Br, (*6*) CH_2Cl, (*7*) H, (*8*) $OCH{=}CH_2$, (*9*) NH-4'-$NO_2C_6H_4$, (*10*) CH_2-4'-$NO_2C_6H_4$, (*11*) CH_3, (*12*) OH, (*13*) $NHCH_3$, (*14*) $N(CH_2)_5$, (*15*) $N(CH_3)_2$, (*16*) $NHN(CH_3)_2$, (*17*) NH_2, (*18*) $NHNH_2$; (*19*) R = 2,6-Br_2, X = OH; (*20*) R = 2,6-Br_2, X = NH_2; (*21*) R = 2-NO_2, X = $NHNH_2$; (*22*) 1-CH_3-4-NO_2-imidazole.

for this narrow range of indicators (excluding 4-NO_2-$C_6H_4SCH_3$), coincides with general relationship (17) characterizing the previous group:

$$s = (300 \pm 40) + (440 \pm 10)\mu_g, \quad r\ 0.999,\ sd\ 30,\ n\ 4. \qquad (19)$$

Thus, in some cases transfer of an indicator from an inert solvent to an aprotic protophilic solvent moves is from one group to another.

Taking into account such movements, all the solvatochromic indicators examined in aprotic medium can be subdivided into five groups (Table 7). The relationship between s and μ_g is described by a set of linear correlations with somewhat differing slopes (m_0) and absolute terms (s_0) (see the next section).

It is well known that, in complexes with a weak hydrogen bond, the electronic excitation is not delocalized to the second subunit of the complex. Therefore, when discussing the effect of formation of the solvation complex, we could attribute changes in s to a sharp increase in the Onsager radius, with the arm of the molecular dipole changing insignificantly (especially if μ_g of the electron-donor subunit is close to zero). The available quantitative data on the effect exerted on s by the structural chemical size of auxochrome X in compounds 4-$NO_3C_6H_4$X, obtained at μ_g = const (Table 8), seem to be consistent with this assumption.

Table 7. Ground-state dipole moments and quantitative characterisitcs of solvatochromism of aromatic (1-X-4-NO_2PhR) and heterocyclic nitro compounds in aprotic inert (IN) and protophilic (PR) media

X	R	Medium	μ,	$\nu_{max} = \nu_0 - s\pi^*$					$\nu_{max} = \nu_g - c_1f_1 - c_2f_2$					
			D	ν_0, cm^{-1}	s, cm^{-1}	r	sd	n	ν_g, cm^{-1}	c_1, cm^{-1}	p_2, cm^{-1}	R	sd	n
First group														
F	H	IN	2.60	38950 ± 20	1690 ± 40	0.997	50	12	40850 ± 100	2020 ± 130	7920 ± 430	0.988	110	12
		PR	2.68	38850 ± 50	1770 ± 60	0.991	60	16	40750 ± 90	1450 ± 130	8670 ± 510	0.989	90	16
Cl	2-NO_2	IN	3.40	43300 ± 60	2140 ± 150	0.986	150	8	45670 ± 150	2480 ± 200	9690 ± 640	0.985	150	9
SCH_3	H	PR	4.56	30980 ± 80	2500 ± 120	0.989	100	11	33710 ± 90	2080 ± 140	12410 ± 530	0.996	90	11
1-CH_3-4-NO_2-Imidazol		PR	7.33	35340 ± 70	3830 ± 100	0.995	110	19	39370 ± 250	3300 ± 270	17950 ± 1280	0.980	260	19
Second group														
C≡N	H	IN	0.90	39430 ± 10	690 ± 10	0.998	60	12	39800 ± 50	710 ± 100	3510 ± 270	0.990	50	6
		PR	0.96	39150 ± 40	790 ± 60	0.971	50	14	40000 ± 60	620 ± 90	3910 ± 350	0.978	60	14
SO_2Cl	H	PR	1.43	40340 ± 30	940 ± 40	0.990	60	12	41340 ± 70	810 ± 100	4450 ± 390	0.981	70	12
CHO	H	IN	2.23	38470 ± 20	1230 ± 40	0.995	40	13	39820 ± 70	1420 ± 80	5550 ± 280	0.988	70	12
		PR	2.58	38680 ± 40	1380 ± 60	0.991	50	13	40190 ± 80	1200 ± 110	6630 ± 460	0.990	80	12
Cl	H	IN	2.69	37640 ± 10	1470 ± 20	0.999	60	10	39270 ± 60	1830 ± 80	6850 ± 240	0.995	60	10
		PR	2.70	37700 ± 40	1560 ± 60	0.990	50	16	39370 ± 70	1220 ± 100	7790 ± 430	0.991	80	16
Br	H	PR	2.80	36980 ± 40	1490 ± 50	0.993	60	14	38580 ± 80	1270 ± 100	7090 ± 440	0.989	90	14
OH	2,6-Br_2	IN	3.27	34680 ± 30	1690 ± 60	0.994	70	11	36590 ± 110	2000 ± 150	7950 ± 480	0.987	120	11

Table 7. (Contd.)

X	R	Medium	μ,	$\nu_{max} = \nu_0 - s\pi^*$					$\nu_{max} = \nu_g - c_1f_1 - c_2f_2$					
			D	ν_0, cm^{-1}	s, cm^{-1}	r	sd	n	ν_g, cm^{-1}	c_1, cm^{-1}	p_2, cm^{-1}	R	sd	n
Second group														
CH_2Cl	H	PR	3.77	38700 ± 60	1980 ± 90	0.991	70	11	40870 ± 80	1660 ± 130	9750 ± 480	0.995	80	11
H	H	IN	3.88	39600 ± 20	1990 ± 40	0.998	80	12	41850 ± 130	2300 ± 170	9290 ± 540	0.985	130	11
		PR	4.03	39590 ± 60	2040 ± 80	0.991	70	13	41670 ± 90	1720 ± 150	9400 ± 580	0.992	100	13
$OCH{=}CH_2$	H	IN	4.02	34130 ± 30	2010 ± 70	0.996	70	9	36430 ± 130	2640 ± 210	9280 ± 570	0.989	140	8
		PR	4.12	34210 ± 60	2220 ± 90	0.990	90	13	36640 ± 110	1910 ± 140	10810 ± 590	0.991	120	13
NH-4'-NO_2-C_6H_4	H	IN	4.3	27400 ± 120	2230 ± 180	0.987	140	6	29850 ± 130	2730 ± 190	10270 ± 540	0.993	130	7
		PR	4.81	27130 ± 70	2490 ± 100	0.985	90	21	29750 ± 120	2220 ± 150	11370 ± 650	0.987	130	21
CH_2-4'-NO_2-C_6H_4	H	PR	4.68	37600 ± 50	2480 ± 80	0.993	80	17	40300 ± 120	2070 ± 140	12140 ± 620	0.990	130	17
CH_3	H	IN	4.45	37650 ± 40	2280 ± 80	0.995	100	12	40180 ± 170	2760 ± 220	10450 ± 750	0.983	180	11
		PR	4.61	37830 ± 50	2420 ± 70	0.994	70	18	40470 ± 100	2010 ± 120	11820 ± 530	0.992	110	18
OH	H	IN	4.85	35100 ± 50	2540 ± 100	0.990	150	14	38060 ± 160	2810 ± 220	12400 ± 680	0.983	180	14
NH_2	2,6-Br_2	PR	5.43	31110 ± 80	2680 ± 100	0.986	100	18	33940 ± 130	2300 ± 150	12660 ± 690	0.988	140	18
$NHCH_3$	H	IN	6.55	29380 ± 40	3240 ± 90	0.997	110	11	32960 ± 150	3930 ± 220	14820 ± 660	0.990	170	12
		PR	7.17	29060 ± 70	3350 ± 90	0.993	70	18	32680 ± 130	2970 ± 150	15860 ± 660	0.993	140	18
$N(CH_2)_5$	H	IN	6.6	27860 ± 110	3220 ± 190	0.993	140	6	31630 ± 240	3780 ± 370	15690 ± 1050	0.989	240	7
		PR	6.9	27970 ± 110	3500 ± 160	0.992	100	9	31760 ± 120	3140 ± 280	16670 ± 890	0.997	120	8
$N(CH_3)_2$	H	IN	6.87	28150 ± 40	3270 ± 80	0.995	140	20	31890 ± 160	4100 ± 230	15380 ± 650	0.989	200	16
		PR	7.27	28120 ± 50	3490 ± 70	0.992	90	43	31570 ± 220	6090 ± 180	15270 ± 1010	0.962	240	39
1-CH_3-4-NO_2-Imidazol		IN	7.0	35450 ± 60	3470 ± 120	0.993	160	14	39320 ± 180	4230 ± 230	15890 ± 790	0.990	190	13
NHN · $(CH_3)_2$	H	PR	7.57	29570 ± 100	3650 ± 130	0.986	120	18	33520 ± 170	6090 ± 230	17620 ± 1000	0.990	180	18
NH_2	H	IN	6.25	31170 ± 30	3220 ± 80	0.996	130	17	34780 ± 130	4020 ± 180	14890 ± 560	0.991	150	17
		PR	6.85	60890 ± 80	3300 ± 90	0.988	110	27	34300 ± 170	2890 ± 160	15120 ± 830	0.981	190	27
$NHNH_2$	H	PR	6.67	29590 ± 140	3440 ± 200	0.978	150	15	33230 ± 190	2920 ± 270	16350 ± 1100	0.988	200	15
$NHNH_2$	2-NO_2	PR	6.90	60710 ± 70	3360 ± 130	0.991	60	15	34250 ± 190	2640 ± 340	16490 ± 1220	0.987	200	15
Third group														
SO_2Cl	H	IN	1.25	40150 ± 20	720 ± 40	0.985	50	12	40980 ± 60	830 ± 80	3490 ± 270	0.975	70	12
Br	H	IN	2.63	36910 ± 20	1320 ± 30	0.997	40	12	38410 ± 120	1690 ± 160	6370 ± 490	0.975	120	11
C≡CH	H	IN	3.49	25490 ± 30	1600 ± 50	0.994	70	12	37320 ± 120	1830 ± 160	7700 ± 520	0.981	130	12
		PR	3.65	36100 ± 40	1580 ± 50	0.992	40	17	37800 ± 80	1340 ± 90	7590 ± 420	0.989	80	17
CH_2Cl	H	IN	3.68	38610 ± 20	1700 ± 30	0.998	40	11	40520 ± 80	2040 ± 100	7930 ± 340	0.993	80	11
SCH_3	H	IN	4.39	60540 ± 30	2010 ± 60	0.996	70	11	32790 ± 130	2410 ± 160	9310 ± 560	0.988	130	10
NH_2	2,6-Br_2	IN	4.7	60730 ± 40	2210 ± 80	0.995	90	9	33180 ± 120	2860 ± 180	10040 ± 510	0.991	120	9
OCH_3	H	IN	4.90	34190 ± 40	2310 ± 80	0.990	130	20	36880 ± 140	2700 ± 190	11300 ± 600	0.983	160	16
		PR	5.20	34260 ± 50	2460 ± 70	0.983	100	41	36780 ± 150	2080 ± 130	11400 ± 680	0.963	170	39
OC_2H_5	H	IN	5.07	33760 ± 40	2360 ± 70	0.996	80	10	36390 ± 160	2940 ± 210	10630 ± 670	0.988	160	9
		PR	5.27	33810 ± 60	2420 ± 80	0.994	80	13	36430 ± 110	2090 ± 130	11670 ± 540	0.993	110	13
1-CH_3-3-NO_2-Pirazol		IN	5.75	39510 ± 30	2640 ± 60	0.998	70	11	42460 ± 170	3170 ± 220	12200 ± 700	0.988	170	11
		PR	6.20	39300 ± 70	2850 ± 100	0.994	80	12	42300 ± 180	2610 ± 280	12920 ± 1070	0.987	180	12
$N(C_2H_5)_2$	H	IN	6.90	27650 ± 40	3190 ± 100	0.996	120	11	31200 ± 190	3760 ± 280	14750 ± 830	0.984	210	12
		PR	7.30	27550 ± 50	3280 ± 70	0.996	80	19	31040 ± 150	2960 ± 140	15180 ± 710	0.991	150	19

Table 7. (Contd.)

X	R	Medium	μ,	$\nu_{max} = \nu_0 - s\pi^*$					$\nu_{max} = \nu_g - c_1f_1 - c_2f_2$					
			D	ν_0, cm^{-1}	s, cm^{-1}	r	sd	n	ν_g, cm^{-1}	c_1, cm^{-1}	p_2, cm^{-1}	R	sd	n
Third group														
$N(CH_2)_4$	H	IN	7.10	27550 ± 110	3190 ± 200	0.993	140	6	31070 ± 280	3650 ± 450	14730 ± 1210	0.985	280	6
		PR	7.45	27520 ± 120	3270 ± 180	0.990	110	9	31060 ± 120	2970 ± 290	15490 ± 930	0.997	120	8
NH_2	2-NO_2	IN	5.7	32160 ± 50	2610 ± 120	0.988	140	14	35130 ± 170	2890 ± 220	12320 ± 690	0.982	180	13
1,2-$(CH_3)_2$-4-NO_2-Imidazol		PR	7.64	34950 ± 80	3450 ± 110	0.994	100	15	38590 ± 230	2920 ± 330	16410 ± 1360	0.982	240	15
Fourth group														
$COOCH_2 \cdot SiF_3$	H	IN	2.87	39450 ± 20	1140 ± 50	0.996	50	7	40720 ± 90	1340 ± 140	5380 ± 400	0.985	90	8
		PR	3.40	39600 ± 80	1350 ± 50	0.985	60	13	41070 ± 100	1200 ± 140	6530 ± 540	0.979	100	13
$COCH_3$	H	PR	3.43	38720 ± 40	1330 ± 60	0.989	60	15	40160 ± 100	1080 ± 110	6580 ± 510	0.979	100	15
$CONH \cdot NH_2$	H	PR	3.95	39070 ± 40	1640 ± 60	0.991	40	11	40810 ± 110	1400 ± 160	7880 ± 620	0.986	110	11
OH	2,6-Br_2	PR	4.41	34870 ± 90	1680 ± 120	0.987	70	17	36600 ± 110	1480 ± 150	7680 ± 600	0.978	120	17
$OCH_2Si \cdot CH_3F_2$	H	PR	4.70	33820 ± 70	1800 ± 120	0.982	60	10	35790 ± 170	1760 ± 310	8800 ± 1000	0.972	170	9
OH	H	PR	5.38	34920 ± 70	2120 ± 100	0.988	80	24	37100 ± 140	1840 ± 130	9710 ± 660	0.974	150	24
$OCH_2Si \cdot CH_3 \cdot (OCH_3)_2$	H	IN	5.40	33650 ± 40	2130 ± 80	0.995	90	10	36060 ± 170	2510 ± 220	9960 ± 740	0.982	170	10
	H	PR	5.73	33680 ± 50	2240 ± 70	0.993	70	17	36070 ± 130	1850 ± 150	11090 ± 670	0.986	130	16
$N(CH_2)_2$	H	IN	5.6	32010 ± 100	2250 ± 170	0.985	120	7	34520 ± 160	2590 ± 260	10480 ± 710	0.988	160	7
NH_2	2-NO_2	PR	6.50	32080 ± 80	2710 ± 120	0.988	80	20	34940 ± 130	2450 ± 140	12360 ± 650	0.988	140	20
$NHCH_3$	2-NO_2	PR	6.58	60510 ± 60	2590 ± 60	0.989	80	22	33240 ± 120	2310 ± 110	11960 ± 570	0.989	130	22
$NHN{=}C \cdot (CH_2)_5$	H	IN	6.8	28020 ± 40	2870 ± 90	0.995	110	12	31240 ± 120	3430 ± 170	13290 ± 590	0.992	140	12
		PR	7.37	27960 ± 120	2960 ± 160	0.973	130	17	31130 ± 150	2350 ± 200	14580 ± 850	0.989	150	17
$NHN{=}C \cdot (CH_3)_2$	H	IN	7.1	28390 ± 20	2890 ± 50	0.999	60	12	31610 ± 150	3430 ± 190	13340 ± 660	0.990	160	12
		PR	7.62	28240 ± 70	2990 ± 100	0.985	90	22	31400 ± 150	2600 ± 180	14010 ± 810	0.985	160	22
Fifth group														
$COCH_2Br$	H	IN	2.67	37990 ± 20	880 ± 30	0.993	40	12	38970 ± 80	1030 ± 90	4060 ± 320	0.976	80	11
		PR	2.85	38190 ± 60	870 ± 80	0.955	60	15	39130 ± 70	590 ± 130	4650 ± 480	0.972	80	15
$COCH_3$	H	IN	3.25	38600 ± 20	1140 ± 40	0.997	40	7	39860 ± 100	1310 ± 140	5200 ± 430	0.983	100	7
$OCH_2Si \cdot (OCH_3)_3$	H	IN	5.52	33660 ± 30	1980 ± 60	0.997	70	10	35900 ± 160	2330 ± 210	9280 ± 710	0.981	170	10
		PR	5.61	33730 ± 40	2080 ± 70	0.993	50	16	35930 ± 100	1680 ± 150	10270 ± 610	0.989	110	15
$OSi(CH_3)_3$	H	IN	5.62	34610 ± 30	2070 ± 50	0.997	60	12	36940 ± 120	2470 ± 150	9600 ± 510	0.989	120	11
$NHCO \cdot CH_3$	H	IN	6.0	33260 ± 50	2140 ± 90	0.994	110	9	35630 ± 140	2620 ± 180	9780 ± 610	0.988	140	10
$NHCH_3$	2-NO_2	IN	6.2	60500 ± 60	2280 ± 130	0.986	160	11	33000 ± 150	2780 ± 190	10310 ± 660	0.987	150	11
$NHN{=}C \cdot (Pr)CCl{=}CHCl$	H	IN	6.3	28070 ± 60	2290 ± 110	0.990	140	10	60680 ± 170	2710 ± 230	10750 ± 730	0.984	180	10
$NHN{=}C \cdot (Pr)CH{=}CCl_2$	H	IN	6.6	27460 ± 40	2240 ± 80	0.996	90	10	29970 ± 160	2690 ± 220	10410 ± 690	0.985	170	10

Within the framework of this hypothesis, it is easy to explain the movement of 4-nitrophenol and 2,6-dibromo-4-nitrophenol from the second to the fourth group (characterized by lower s at the same μ_g) upon formation of the solvation complex (Table 7). However, it remains unclear why in the series of weak H-bond donors (4-nitroaniline, *N*-methyl-4-nitroaniline, etc., Table 7) the molecules and their solvation complexes belong to the same group and why 2,6-dibromo-4-nitroaniline moves from the third to the second group whose representative, at the same dipolarity, have relatively higher values of *s*. Passing from molecules to solvation complexes can be simulated by passing from 4-nitrotoluene to 4,4'-dinitrodiphenylmethane, or from 4-nitroaniline to 4,4'-dinitrodiphenylmethane. In these pairs of compounds, the electronic excitation is localized within similar fragment, and the second molecule in each pair is considerably larger than the first molecule. Nevertheless, the molecules and solvation complexes of all the four indicators belong to the second group (Table 7).

The pattern becomes more understandable if we assume that the Onsager radius in the spectroscopic sense is determined by the molecular system fragment on which the electronic excitation is localized (orientation–induction interactions in the excited state do not involve the periphery of the solvation shell). As a result, the same group may include both molecules with different structural chemical radii and solvation complexes of weak H-bond donors. Then the movement of an indicator from one group to another upon formation of a relatively strong two-centered hydrogen bond with solvent molecules can be readily explained. In such complexes, not only the XH bond but also the aromatic fragment as a whole is polarized, which affects the μ_g/a^3 ratio. This assumption opens the way to understanding the specific features of the spectroscopic behavior of three-centered solvation complexes. They differ from the initial molecules by the lower strength of the intramolecular hydrogen bond and from two-centered H complexes by the mutual orientation of the subunits [34, 47–49].

Relationship between p_2 and μ_g. The relationship between these quantities is similar to that between *s* and μ_g (see below). Furthermore, there is a linear correlation (20) between s_0 and p_0:

$$s_0 = (-59 \pm 7) + (0.226 \pm 0.005)p_0, \quad (20)$$
$$r\ 0.999,\ sd\ 13,\ n\ 5.$$

Table 8. Effect of substituent in compounds $4\text{-}NO_2C_6H_4X$ on the solvatochromic coefficient *s*

X	Inert medium		Aprotic protophilic medium	
	μ_g, D	*s*, cm^{-1}	μ_g, D	*s*, cm^{-1}
F	2.60	1690	2.68	1770
Cl	2.69	1470	2.70	1560
Br	2.63	1320	2.80	1490
NH_2	6.25	3220	–	–
NHN=C(Pr)CCl=CHCl	6.3	2290	–	–
$NHCH_3$	6.55	3240	–	–
$NHN{=}C(Pr)CH{=}CCl_2$	6.6	2240	–	–
$N(CH_3)_2$	6.87	3270	7.27	3490
$N(C_2H_5)_2$	6.90	3190	7.30	3280
$NHN{=}C(CH_2)_5$	6.8	2870	–	–

This means that the contribution from dispersion–polarization interactions to *s* for a given group of indicators is approximately constant; in going from one group to another, this contribution regularly changes; subdivision of indicators into groups is partially governed by changes in the extent of compensation of the spectroscopic effect of these interactions. If the subdivision of indicators into groups is fully governed by a change in the contribution of dispersion–polarization interactions to *s*, the groups will be characterized by equal values of m_0 and m_2, which is the case for the first and second groups (Table 9).

Thus, there are two factors causing the movement of an indicator from one group to another: changes in the μ_g/a^3 ratio and in the contribution of the dispersion–polarization interactions to *s*. The first factor leads to variations of the slope of the linear dependences $s = s_0 + m_0\mu_g$, and the second factor determines a jumpwise change in the absolute term.

Relationship between c_1 and μ_g. Contrary to the expectations, when considering the relationship $c_1 \sim f(\mu_g)$, we obtained an essentially different result.

Table 9. Parameters of Eqs. (3) and (4) for separate groups of indicators

Group	$s = s_0 + m_0\mu_g$				$p_2 = p_0 + m_2\mu_g$				*n*
	s_0, cm^{-1}	m_0, $cm^{-1}\,D^{-1}$	*r*	*sd*	p_0, cm^{-1}	m_2, $cm^{-1}\,D^{-1}$	*r*	*sd*	
First	570 ± 80	440 ± 20	0.998	70	2800 ± 310	2070 ± 70	0.998	270	5
Second	290 ± 30	450 ± 10	0.997	70	1540 ± 260	2080 ± 50	0.991	570	33
Third	150 ± 40	430 ± 10	0.997	60	860 ± 230	1990 ± 40	0.996	310	19
Fourth	–70 ± 60	410 ± 10	0.995	70	–80 ± 360	1900 ± 60	0.992	370	16
Fifth	–150 ± 80	380 ± 20	0.993	70	–340 ± 500	1730 ± 90	0.988	430	10

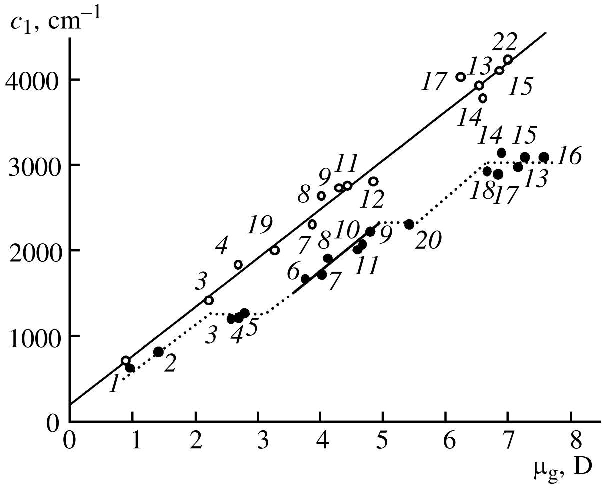

Fig. 5. Correlation between the regression coefficient c_1 and ground-state dipole moment of aromatic compounds 1-X-4-NO_2PhR. Aprotic inert solvents are denoted by light circles, and protophilic solvents, by dark circles. For numbering of the indicators, see caption to Fig. 4.

The parameter c_1 of the solvatochromism theory determines the orientation–induction term of the spectral shift and is related to the molecular parameters as follows [9]:

$$c_1 = 2\mu_g(\mu_e\cos\varphi - \mu_g)/a^3, \qquad (21)$$

where φ is the angle between the vectors of the moments $\vec{\mu}_g$ and $\vec{\mu}_e$. In the chosen aromatic nitro compounds, $\varphi = 0$, i.e., $c_1 = 2\mu_g(\mu_e - \mu_g)/a^3$. We found that the following relationship is valid for a separate group of indicators in an inert medium: $c_1 \cong 2(r_\mu - 1)\mu_g^2/a^3$, where r_μ = const and μ_g/a^3 = const. Hence, if r_μ is independent of the group properties of solvents, transfer of an indicator from an inert solvent into an aprotic protophilic solvent should cause c_1 and s to increase. However, actually c_1 regularly decreases at such transfer. Irrespective of the solvation mechanism, this trend is the more pronounced, the higher the dipolarity of the indicator molecule (Fig. 5).

Such an unexpected relationship between c_1 and μ_g, manifested in aprotic protophilic solvents, is most likely associated with the fact that aprotic solvents are more diverse in the chemical nature than inert solvents. We failed to reveal any specific factor responsible for distortion of the linear relationship between c_1 and μ_g in aprotic protophilic solvents. Analysis of the whole data set on c_1 and μ_g showed that the correlation consists of several linear sections with the slopes close to those found for inert solvents, separated by steps (as shown in Fig. 5). Therefore, the distortion of the linear correlation should be attributed to two approximations of the theory: neglect of the relief of the electron density distribution in indicator molecules and assumption of their constant polarizability (this assumption actually leads to the final equation suitable for practical purposes). Both approximations (neglect of higher multipoles and of variation of the polarizability) can lead to underestimation of an additional contribution to c_1, which depends in a certain fashion on the auxochrome and on solvent properties. If such contributions actually exist, it can be assumed that the true value of c_1, c_1^t, is close to that found on the basis of the solvatochromism theory in an inert medium, as in the case of s and p_2. In turn, this assumption means that the p_2/c_1^t ratio only weakly depends on the solvent, and this conclusion can be indirectly verified. Indeed, assuming p_2/c_1^t to be a constant of the given indicator series, independent of the chemical structure of the solvent, we can readily estimate the solvent parameters π^* on the basis of universal interaction functions and compare them with the empirically obtained values of c_1^t.

According to definitions of [29], $\pi^* = (\nu_{ch} - \nu_s) \times (\nu_{ch} - \nu_{DMSO})^{-1}$, where ν_{ch}, ν_s, and ν_{DMSO} are the wavenumbers of the absorption maxima in the UV or visible range in cyclohexane, given solvent, and DMSO, respectively. With expression (2), it can be readily shown that the correlation of π^* with f_1 and f_2 of a varied solvent is as follows:

$$\pi^* = \pi_g^* + \gamma f_1 + \gamma(p_2/c_1)f_2, \qquad (22)$$

where $\gamma = 1/(0.84 + 0.026p_2/c_1)$, π_g^* (value of π^* for gas phase) $= -0.257\gamma p_2/c_1$, $f_1 = (2n^2 + 1)/(n^2 + 2) \times [(\varepsilon - 1)/(\varepsilon + 2) - (n^2 - 1)/(n^2 + 2)]^{-1}$, $f_2 = (n^2 - 1) \times (n^2 + 2)^{-1}$, ε is the static dielectric permittivity of a medium, and n is its refractive index.

To check this assumption, we used a set of aprotic solvents with the group parameter δ 0. In this set, the parameters π^*, f_1, and f_2 are varied in a wide range. The parameter δ additionally takes into account differences in the polarizability of aliphatic (δ 0.0), halogen-containing (δ 0.5), and aromatic (δ 1.0) solvents [50]. The p_2/c_1^t ratio was taken equal to that estimated for all types of solvents on the basis of data for inert medium ($\overline{p_2/c_1^t} = 3.87$). We excluded from the sample the indicators with a low dipole moment, since the p_2/c_1 ratio for them may have a large error because of weakly pronounced solvatochromism. The final sample consisted of 32 indicators. The estimated values of π^* of the gas and of the most frequently used solvents with δ 0 (π^*_{calc}) are given in Table 10, together with the empirical values of this solvatochromic parameter

Table 10. Parameters characterizing the capability of a medium for nonspecific solvation

No.	Solvent	f_1	f_2	π^*_{KT}	π^*_{calc}	No.	Solvent	f_1	f_2	π^*_{KT}	π^*_{calc}
1	Gas phase	0	0	–1.1	–1.06	18	Acetone	0.79	0.22	0.71	0.69
2	Pentane	0	0.22	–0.08	–0.15	19	Acetonitrile	0.86	0.21	0.75	0.72
3	Hexane	0	0.23	–0.08	–0.11	20	Ethyl formate	0.55	0.22	0.61	0.43
4	Heptane	0	0.24	–0.02	–0.07	21	Ethyl chloroacetate	0.65	0.25	0.70	0.66
5	Cyclohexane	0	0.26	0	0.01	22	Propylene carbonate	0.88	0.25	0.83	0.90
6	Octane	0.01	0.24	0.01	–0.06	23	Tetramethylurea	0.79	0.27	0.83	0.89
7	Decane	0	0.25	0.03	–0.03	24	Nitromethane	0.85	0.24	0.85	0.83
8	Dodecane	0	0.25	0.08	–0.03	25	HMPA	0.81	0.27	0.87	0.91
9	Triethylamine	0.07	0.24	0.14	0	26	Butyrolactone	0.84	0.26	0.87	0.90
10	Dibutyl ether	0.21	0.24	0.24	0.15	27	DMF	0.84	0.26	0.88	0.90
11	Diethyl ether	0.38	0.22	0.27	0.25	28	1-Methyl-2-pyrrolidone	0.81	0.28	0.92	0.95
12	Diisopropyl ether	0.33	0.23	0.27	0.24	29	DMSO	0.84	0.28	1.00	0.98
13	Butyl acetate	0.41	0.24	0.50	0.36	30	Ethyl trichloroacetate	0.54	0.27	0.61	0.62
14	Ethyl acetate	0.49	0.23	0.55	0.41	31	Cyclohexanone	0.71	0.27	0.76	0.81
15	1,2-Dimethoxyethane	0.49	0.23	0.53	0.41	32	Sulfolane	0.83	0.28	0.98	0.97
16	THF	0.55	0.25	0.58	0.55	33	Tributylamine	0.05	0.26	0.16	0.06
17	Butanone	0.77	0.23	0.68	0.71						

(π^*_{KT}) taken from [35, 36] and given for comparison. Taking into account the fact that π^*_{calc} and π^*_{KT} were determined using different sets of indicators, the correlation between the two scales can be considered as very good [Eq. (23)]:

$$\pi^*_{calc} = (-0.05 \pm 0.02) + (1.03 \pm 0.03)\pi^*_{KT}, \qquad (23)$$

$$r\ 0.991,\ sd\ 0.06,\ n\ 33.$$

Estimation of μ_e. As noted above, the absorption band chosen for the analysis belongs to the most intense π → π* transition in the UV spectra of the indicators. Note that this transition does not always lead to the first excited state. In aromatic nitro compounds, an inversion of the ππ* states S_1 and S_2 on the energy scale is observed as the electron-withdrawing power of the auxochrome is enhanced (Table 2). The relative position of the indicator band in heteroaromatic nitro compounds also varies [32, 51].

To estimate μ_e, we used Eq. (8). The factors m_2 required to calculate the proportionality coefficient r_μ have already been presented. The factors m_1 determined, for the above reason, in an inert medium are given below together with r_μ ($\overline{\Omega}$ = 0.755).

Group	c_0, cm^{-1}	m_1, cm^{-1} D^{-1}	r	sd	n	r_μ
2	200±90	570±20	0.994	120	14	2.23±0.19
3	260±120	500±20	0.989	140	11	2.48±0.23
4	–180±180	510±30	0.994	110	5	2.33±0.32
5	–150±110	450±20	0.995	80	7	2.44±0.35

It is seen that r_μ randomly varies from one group to another, with the difference between its maximal and minimal values being within the determination error. Thus, within the errors arising in quantitative description of the solvatochromism, the coefficient r_μ can be considered as constant for the given series of aromatic and heteroaromatic nitro compounds. At its mean value (r_μ ~2.35), the calculated and directly measured [8–10] values of μ_e of compounds 1-X-4-$NO_2C_6H_4$ are in reasonable agreement (Table 11).

Anisotropy of electron redistribution. Changes in the direction of $\vec{\mu}_e$ relative to $\vec{\mu}_g$ should be expected in the case of 1-substituted 2,4-dinitrobenzenes, because of low symmetry of the nitrobenzene fragment in these compounds. Quantitative data on the solvatochromism of these indicators are given in Table 12. The mutual orientation of $\vec{\mu}_e$ and $\vec{\mu}_g$ of these compounds can be readily revealed using Bakhshiev–Bilot–Kawski equation (2). In this equation, c_1 is a function of angle φ between the vectors of the dipole

Table 11. Calculated [Eq. (8)] and directly measured [8–10] excited-state dipole moments of compounds 1-X-4-$NO_2C_6H_4$ (S_2 for introbenzene, S_1 for *p*-nitroanilines)

X	Solvent	μ_e, D	
		calculated (r_μ 2.35)	found
H	Dioxane	9.4	9.5 ± 1.0
	CCl_4	9.1	–
NH_2	Dioxane	16.0	15.5 ± 2.8
	Benznene	–	14.0
	CCl_4	14.7	–
$N(CH_3)_2$	Dioxane	17.1	–
	Benzene	–	15.0
	CCl_4	16.1	–

moments of the ground and excited states and p_2 is independent of this angle. Therefore, using p_2, it is easy to determine the group to which the given indicator belongs. Then the angle φ of this indicator can be determined from the actual values of c_1 and μ_g using the group linear relationship $c_1(\varphi = 0) = f(\mu_g)$.

The simplest procedure for estimating φ is that based on data for an inert medium [Eq. (24)]:

$$\cos\varphi = [1 + (r_\mu - 1)/\chi]r_\mu, \qquad (24)$$

where $\chi = [c_1(\varphi = 0) - c_0]/[c_1(\varphi) - c_0]$.

Calculation of φ from data for aprotic protophilic solvents is more difficult. In this case, at least one more indicator with the same μ_g but with highly symmetrical nitrobenzene fragment is required.

In the series of the chosen 1-substituted 2,4-dinitrobenzenes, only in three cases (Table 13) we were able to estimate φ. These results suggest that the auxochrome structure noticeably affects this angle.

EXPERIMENTAL

The UV spectra of solutions of compounds in inert and protophilic solvents were recorded on a Specord UV–Vis spectrophotometer at 22–25°C. The dielectric permittivities of solutions of nitro compounds in CCl_4, benzene, and 1,4-dioxane were measured on an Sh2-5 device (Angarsk OKBA Joint-Stock Company) at 1 MHz and 25°C. The dipole moments were calculated by Higasi's formula [52].

Acetone and hexanone 4-nitrophenylhydrazones were prepared by the standard procedure [53]. Organosilicon derivatives of nitrobenzene were prepared by procedures described in [54, 55], and heterocyclic nitro compounds, by procedures described in [56, 57]. The other aromatic nitro compounds with substituents *para* relative to the nitro group are commercial products (chemically pure grade); they were puri-

Table 12. Quantitative characteristics of the solvatochromism of compounds 1-X-2,4-$NO_2C_6H_3$

X	Medium[a]	ν_0, cm^{-1}	*s*, cm^{-1}	*b*, cm^{-1}	*r*(*R*)	*sd*	*n*
Cl	IN	43300 ± 60	2140 ± 150	–	0.986	150	8
$NHNH_2$	PR	30710 ± 70	3360 ± 130	410 ± 90	(0.991)	60	15
NH_2	IN	32160 ± 50	2610 ± 120	–	0.988	140	14
	PR	32080 ± 80	2710 ± 120	1220 ± 110	(0.988)	80	20
$NHCH_3$	IN	30500 ± 60	2280 ± 130	–	0.986	160	11
	PR	30510 ± 60	2590 ± 60	540 ± 90	(0.989)	80	22

[a] Here and hereinafter: IN, inert medium; PR, protophilic medium.

Table 13. Parameters of Eq. (2) for compounds 1-X-2,4-$NO_2C_6H_3$ and angles φ between the vectors of the dipole moments in the ground and excited states

X	Medium	μ_g, D	c_1, cm^{-1}	p_2, cm^{-1}	*R*	*sd*	*n*	Group	φ, deg
Cl	IN	3.40	2480 ± 200	9690 ± 640	0.985	150	9	First	–
$NHNH_2$	PR	6.90	2640 ± 340	16490 ± 1220	0.987	200	15	Second	~20
NH_2	IN	5.7	2890 ± 220	12320 ± 690	0.982	180	13	Third	~17
	PR	6.50	2450 ± 140	12360 ± 650	0.988	140	20	Fourth	–
$NHCH_3$	IN	6.2	2780 ± 190	10310 ± 660	0.987	150	11	Fifth	0
	PR	6.58	2310 ± 110	11960 ± 570	0.989	130	22	Fourth	–

fied by recrystallization from organic solvents or vacuum sublimation. The purity of compounds and solvents was checked by physicochemical methods.

Ab initio calculations of the ground-state dipole moments and characteristics of UV spectra of nitro compounds were performed with the GAUSSIAN-98 program package [58].

Propyl 2,2-dichlorovinyl ketone 4-nitrophenylhydrazone. Propyl 2,2-dichlorovinyl ketone (1.67 g) was slowly added to a solution of 1.53 g of 4-nitrophenylhydrazine in 40 ml of ethanol containing 0.5 ml of sulfuric acid. The reaction mixture was stirred for 30 min and left overnight. The precipitate was filtered off, washed with water to neutral reaction, and dried. Yield 2.87 g (95%), mp 115–117°C. IR spectrum, ν, cm^{-1}: 3300 (NH); 3030 (=CH); 2950, 2920, 2870 (C_3H_7); 1600 (C=N); 1585 (C=C); 1550, 1310 (NO_2). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.91 t (3H, CH_3, *J* 7.2 Hz), 1.46 m (2H, CH_2, *J* 7.2 Hz), 2.46 t (2H, CH_2, *J* 7.2 Hz), 6.71 s (1H, H^4), 7.28 d (2H, $H^{2',6'}$, *J* 7.3 Hz), 8.09 d (2H, $H^{3',5'}$, *J* 7.3 Hz), 10.32 s (1H, NH). Found, %: C 43.83; H 4.35; Cl 23.23; N 13.95. $C_{12}H_{13}Cl_2N_3O_2$. Calculated, %: C 47.80; H 4.32; Cl 23.22; N 13.94.

Propyl 1,2-dichlorovinyl ketone 4-nitrophenylhydrazone was prepared similarly from 1.53 g of 4-nitrophenylhydrazine and 1.67 g of propyl 1,2-dichlorovinyl ketone. Yield 2.82 g (98%), mp 114–116°C. IR spectrum, ν, cm^{-1}: 3295 (NH); 3180, 3075 (=CH); 2950, 2910 (C_3H_7); 1600 (C=N); 1590 (C=C); 1520, 1310 (NO_2). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.01 t (3H, CH_3, J 7.7 Hz), 1.59 m (2H, CH_2, *J* 7.7 Hz), 2.60 t (2H, CH_2, *J* 7.7 Hz), 7.34 d (2H, $H^{2',6'}$, *J* 7.4 Hz), 7.37 s (1H, H^5), 8.12 d (2H, $H^{3',5'}$, *J* 7.4 Hz), 10.34 (1H, NH). Found, %: C 47.70; H 4.34; Cl 23.47; N 13.91. $C_{12}H_{13}Cl_2N_3O_2$. Calculated, %: C 47.68; H 4.35; Cl 23.45; N 13.90.

REFERENCES

1. Vokin, A.I., Oznobikhina, L.P., Shulunova, A.M., Fedorov, S.V., and Turchaninov, V.K., *Russ. J. Gen. Chem.,* 2005, vol. 75, no. 10, p. 1566.
2. Turchaninov, V.K., Vokin, A.I., Aksamentova, T.N., Krivoruchka, I.G., Shulunova, A.M., and Andriyankova, L.V., *Russ. J. Gen. Chem.,* 2003, vol. 73, no. 5, p. 743.
3. Kamlet, M.J., Abboud, J.-L., and Taft, R.W., J. *Am. Chem. Soc.,* 1977, vol. 99, no. 18, p. 6027.
4. Bakhshiev, N.G., *Opt. Spektrosk.,* 1961, vol. 10, no. 6, p. 717.
5. Bilot, L. and Kawski, A., *Z. Naturforsch. A,* 1962, vol. 17, no. 7, p. 621.
6. Czekalla, J. and Wick, G., *Z. Elektrochem.,* 1961, vol. 65, no. 9, p. 727.
7. Labhart, H. and Wagniere, G., *Helv. Chim. Acta,* 1963, vol. 46, nos. 1–4, p. 1314.
8. Liptay, W., Eberlein, W., Weidenberg, H., and Elflein, O., *Ber. Bunsenges. Phys. Chem.,* 1967, vol. 71, no. 6, p. 548.
9. Bakhshiev, N.G., Knyazhanskii, M.I., Minkin, V.I., Osipov, O.A., and Saidov, G.V., *Usp. Khim.,* 1969, vol. 38, no. 9, p. 1644.
10. Sinha, H.K. and Yates, K., *J. Chem. Phys.,* 1990, vol. 93, no. 10, p. 7085.
11. Milliaresi, E.E. and Ruchkin, V.E., *Dokl. Akad. Nauk SSSR,* 1971, vol. 198, no. 1, p. 108.
12. Kamlet, M.J., Minesinger, R.R., Kayser, E.G., Aldridge, M.H., and Eastes, J.W., *J. Org. Chem.,* 1971, vol. 36, no. 25, p. 3852.
13. Osipov, O.A., Minkin, V.I., and Garnovskii, A.D., *Spravochnik po dipol'nym momentam* (Handbook of Dipole Moments), Moscow: Vysshaya Shkola, 1971.
14. Semba, K., *Bull. Chem. Soc. Jpn.,* 1961, vol. 34, no. 5, p. 722.
15. Suppan, P., *J. Chem. Soc. A,* 1968, no. 12, p. 3125.
16. Lutskii, A.E., Bocharova, V.V., and Kreslavskii, M.R., *Zh. Obshch. Khim.,* 1975, vol. 45, no. 10, p. 2276.
17. Kamlet, M.J. and Taft, R.W., *J. Am. Chem. Soc.,* 1976, vol. 98, no. 2, p. 377.
18. Yokoyama, T., *Aust. J. Chem.,* 1976, vol. 29, no. 7, p. 1469.
19. Taft, R.W. and Kamlet, M.J., *J. Am. Chem. Soc.,* 1976, vol. 98, no. 10, p. 2886.
20. Minesinger, R.R., Jones, M.E., Taft, R.W., and Kamlet, M.J., *J. Org. Chem.,* 1977, vol. 42, no. 11, p. 1929.
21. Kamlet, M.J., Hall, T.N., Boykin, J., and Taft, R.W., *J. Org. Chem.,* 1979, vol. 4, no. 15, p. 2599.
22. Launay, G., Wojtkowiak, B., and Krygowski, T.M., *Can. J. Chem.,* 1979, vol. 57, no. 23, p. 3065.
23. Bekarek, V. and Jurina, J., *Collect. Czech. Chem. Commun.,* 1982, vol. 47, no. 4, p. 1060.
24. Yokoyama, T., Taft, R.W., and Kamlet, M.J., *Aust. J. Chem.,* 1983, vol. 36, no. 4, p. 701.
25. Nicolet, P. and Laurence, C., *J. Chem. Soc., Perkin Trans. 2,* 1986, no. 7, p. 1071.
26. Laurence, C., Nicolet, P., and Helbert, M., *J. Chem. Soc., Perkin Trans. 2,* 1986, no. 7, p. 1081.
27. Bekarek, V., *Chem. Listy,* 1988, vol. 82, no. 2, p. 212.
28. Abraham, M.H., Buist, G.J., Grellier, P.L., McGill, R.A., Prior, D.V., Oliver, S., Turner, E., Morris, J.J., Taylor, P.J., Nicolet, P., Maria, P.-C., Gal, J.-F., Abboud, J.-L.M., Doherty, R.M., Kam-

let, M.J., Shuely, W.J., and Taft, R.W., *J. Phys. Org. Chem.,* 1989, vol. 2, no. 7, p. 540.

29. Laurence, C., Nicolet, P., Dalati, M.T., Abboud, J.-L.M., and Notario, R., *J. Phys. Chem.,* 1994, vol. 98, no. 23, p. 5807.
30. Kolling, O.W., *J. Phys. Chem.,* 1996, vol. 100, no. 2, p. 519.
31. Vokin, A.I., Shulunova, A.M., Aksamentova, T.N., Es'kova, L.A., Elokhina, V.N., Lopyrev, V.A., and Turchaninov, V.K., *Russ. J. Gen. Chem.,* 2001, vol. 71, no. 1, p. 137.
32. Vokin, A.I., Sherstyannikova, L.V., Krivoruchka, I.G., Aksamentova, T.N., Krylova, O.V., and Turchaninov, V.K., *Russ. J. Gen. Chem.,* 2003, vol. 73, no. 6, p. 973.
33. Turchaninov, V.K., Vokin, A.I., Gavrilova, G.A., Aksamentova, T.N., Chipanina, N.N., Kanitskaya, L.V., Fedorov, S.V., Shulunova, A.M., Trofimova, O.M., and Voronkov, M.G., *Russ. J. Gen. Chem.,* 2004, vol. 74, no. 4, p. 559.
34. Fedorov, S.V., Krivoruchka, I.G., Shulunova, A.M., Sherstyannikova, L.V., Trofimova, O.M., Vokin, A.I., and Turchaninov, V.K., *Russ. J. Gen. Chem.,* 2005, vol. 75, no. 1, p. 100.
35. Kamlet, M.J., Abboud, J.-L., Abraham, M.H., and Taft, R.W., *J. Org. Chem.,* 1983, vol. 48, no. 17, p. 2877.
36. Abraham, M.H., Grellier, P.L., Abboud, J.-L.M., Doherty, R.M., and Taft, R.W., *Can. J. Chem.,* 1988, vol. 66, no. 11, p. 2673.
37. Kamlet, M.J., Gal, J.-F., Maria, P-C., and Taft, R.W., *J. Chem. Soc., Perkin Trans. 2,* 1985, no. 10, p. 1583.
38. Zhmyreva, I.A., Zelinskii, V.V., Kolobkov, V.P., Kochemirovskii, A.S., and Reznikova, I.I., *Opt. Spektrosk.,* 1960, vol. 8, no. 3, p. 412.
39. Mostoslavskii, M.A., Izmail'skii, V.A., and Shapkina, M.M., *Zh. Obshch. Khim.,* 1962, vol. 32, no. 6, p. 1746.
40. Zelinskii, V.V. and Kolobkov, V.P., *Opt. Spektrosk.,* 1964, vol. 16, no. 2, p. 345.
41. Bakhshiev, N.G. and Neporent, B.S., *Opt. Spektrosk.,* 1964, vol. 16, no. 2, p. 351.
42. Schubert, W.M., Steadly, H., and Craven, J.M., *J. Am. Chem. Soc.,* 1960, vol. 82, no. 5, p. 1353.
43. Saidov, G.V., Sverdlova, O.V., and Bakhshiev, N.G., *Dokl. Akad. Nauk SSSR,* 1968, vol. 182, no. 3, p. 638.
44. Millefiori, S., Favini, G., Millefiori, A., and Grasso, D., *Spectrochim. Acta, A,* 1977, vol. 33, no. 1, p. 21.
45. Millefiori, S., Zuccarello, F., and Buemi, G., *J. Chem. Soc., Perkin Trans. 2,* 1978, no. 9, p. 849.
46. Zuccarello, F., Millefiori, S., and Buemi, G., *Spectrochim. Acta, A,* 1979, vol. 35, no. 3, p. 223.
47. Krivoruchka, I.G., Vokin, A.I., Turchaninov, V.K., *Zh. Org. Khim.,* 2002, vol. 38, no. 10, p. 1509.
48. Krivoruchka, I.G., Vokin, A.I., Aksamentova, T.N., Shulunova, A.M., Sorokin, M.S., Dubinskaya, E.I., and Turchaninov, V.K., *Russ. J. Gen. Chem.,* 2004, vol. 74, no. 1, p. 120.
49. Vokin, A.I., Gavrilova, G.A., Shulunova, A.M., Krivoruchka, I.G., Aksamentova, T.N., and Turchaninov, V.K., *Russ. J. Gen. Chem.,* 2004, vol. 74, no. 2, p. 239.
50. Taft, R.W., Abboud, J.-L.M., and Kamlet, M.J., *J. Am. Chem. Soc.,* 1981, vol. 103, no. 5, p. 1080.
51. Vokin, A.I., Shulunova, A.M., Lopyrev, V.A., Komarova, T.N., and Turchaninov, V.K., *Zh. Obshch. Khim.,* 1999, vol. 69, no. 9, p. 1550.
52. Minkin, V.I., Osipov, O.A., and Zhdanov, Yu.A., *Dipol'nye momenty v organicheskoi khimii* (Dipole Moments in Organic Chemistry), Leningrad: Khimiya, 1968.
53. *Beilsteins Handbuch der organischen Chemie,* vol. 15, p. 469.
54. Voronkov, M.G., Frolov, Yu.L., D'yakov, V.M., Chipanina, N.N., Gubanova, L.I., Gavrilova, G.A., Klyba, L.V., and Aksamentova, T.N., *J. Organomet. Chem.,* 1980, vol. 201, no. 1, p. 165.
55. Trofimova, O.M., *Cand. Sci. (Chem.) Dissertation,* Irkutsk, 1995.
56. Bhagwat, V. and Pyman, F., *J. Chem. Soc.,* 1925, vol. 125, no. 5, p. 1832.
57. Gallo, G.G., Pasqualucci, C.R., Radaelli, P., and Lancini, G.C., *J. Org. Chem.,* 1964, vol. 29, no. 4, p. 862.
58. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Zakrzewski, V.G., Montgomery, J.A., Stratmann, R.E., Burant, J.C., Dapprich, S., Millam, J.M., Daniels, A.D., Kudin, K.N., Strain, M.C., Farkas, O., Tomasi, J., Barone, V., Cossi, M., Cammi, R., Mennucci, B., Pomelli, C., Adamo, C., Clifford, S., Ochterski, J., Petersson, G.A., Ayala, P.Y., Cui, Q., Morokuma, K., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Cioslowski, J., Ortiz, J.V., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Gomperts, R., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Gonzalez, C., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Andres, J.L., Gonzalez, C., Head-Gordon, M., Replogle, E.S., and Pople, J.A., *GAUSSIAN-98,* Rev. A.6, Pittsburgh: Gaussian, 1998.