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Molecular Polarizability of Organic Compounds and Their Complexes: L.[1] Molar Volumes and Steric Structure of Some Schiff Bases and Their Structural Analogs in Infinitely Dilute Solutions

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Abstract — Molar volumes of a wide series of Schiff bases and their structural analogs, such as *N*-benzylideneaniline *N*-oxides and azo compounds, in infinitely dilute solutions were determined. Analysis of the obtained values in terms of the additivity scheme showed that molecular fragments and substituting groups in these compounds are strongly solvated by solvent molecules, which leads to deviation of most molecules from the planar arrangement of the aryl moieties and bridging groups. Most compounds in which *H*-chelate rings are formed due to intramolecular hydrogen bonding are characterized by contraction of molar volumes, indicating their entropy stabilization in solution via release of solvent molecules from the solvate shell upon chelation. Methods for the determination of dipole moments and Kerr constants in solution can be simplified to a considerable extent for those compounds for which the additivity scheme was applied to calculate the molar volumes.

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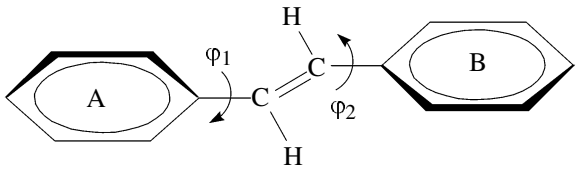
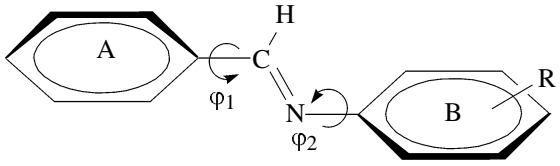
Using the molar volume technique, we previously [1] studied biphenyl, its substituted derivatives, and related aromatic compounds whose molecules allow rotation of the aromatic rings about formally single bonds. The goal of that study was to elucidate whether additivity analysis of their molar volumes makes it possible to estimate their conformations in solution. We have found that the aromatic rings in the molecules of the above compounds in solution are not coplanar to each other. In continuation of studies in this line, in the present work we examined the molar volumes of compounds in which the aromatic rings are linked through such bridging groups as –CH=N–, – N=N–, –CH=CH–, and –CH=N(O)– and are capable of rotating about single bonds in those groups. Thus the subjects for study were *trans*-stilbene (**I**), substituted *N*-benzylideneanilines **II**–**XII**, *N*-(1-phenylethylidene)anilines **XIII**–**XIV**, *N*-salicylideneanilines **XVI**–**XXVIII**, *N*-salicylidene-1,1-dimethylethanamines **XXIX**–**XXXII**, *N*-[1-(2-hydroxyphenyl)ethylidene]anilines **XXXIII**–**XXXIV**, *N*-(diphenylmethylidene)aniline (**XV**), *N*-[phenyl(2-hydroxyphenyl)methylidene]aniline **XXXV**), as well as *N*-benzylideneaniline *N*-oxides **XXXVI**–**XL**, azobenzenes **XLI**–**XLVII**, and 2-hydroxy-5-methylazobenzenes **XLVIII**–**XLIX**; as solvents we used carbon tetrachloride and dioxane.

The aromatic rings and bridging groups in molecules **I**–**XLIX** tend to adopt planar arrangement due to π–π conjugation. However, repulsion between the *ortho*-hydrogen atoms in the aromatic rings, on the one hand, and hydrogen and oxygen atoms, substituents, and unshared electron pairs in the bridging groups, on the other, forces the aromatic rings to turn aside. If a bridging group contains a nitrogen atom, *n*–π conjugation between the lone electron pair on the nitrogen and π system of the aromatic ring also favors deviation of the latter from the bridging group plane. Joint action of the above electronic and steric factors determines the steric structure of such compounds; their configuration can also depend to a considerable extent on the nature of substituents in the aromatic rings [2–10]. Therefore, it was interesting to examine the steric structure of compounds **I**–**XLIX** in solution

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



I



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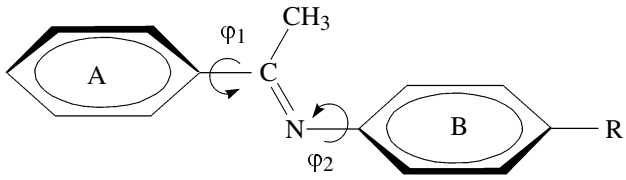

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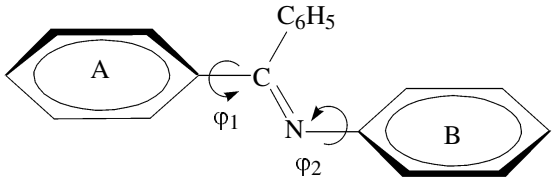
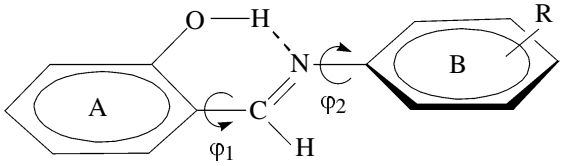
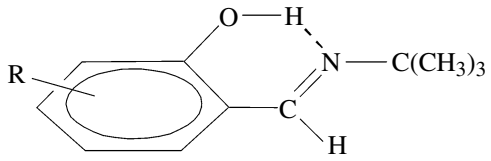


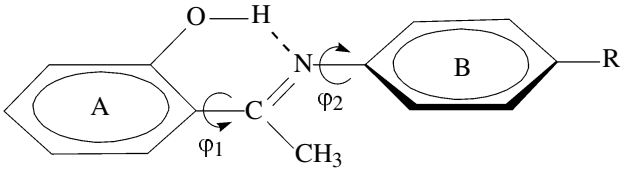
XV



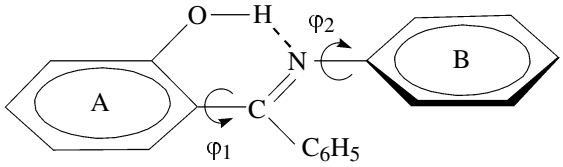
XVI–XXVIII



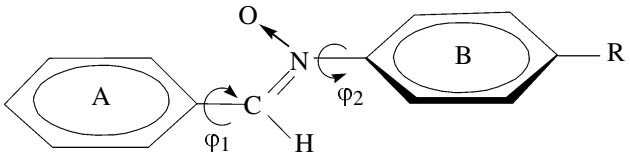
XXIX–XXXII



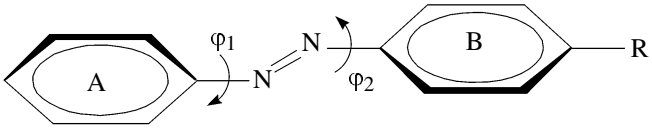
XXXIII, **XXXIV**



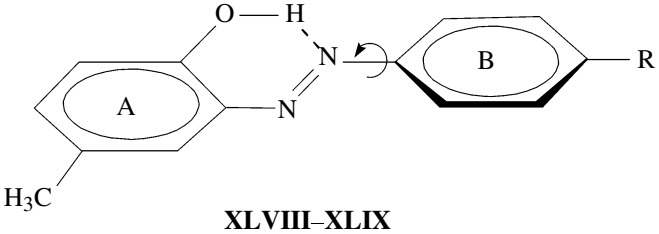
XXXV



XXXVI–XL



XLI–XLVII



XLVIII–XLIX

II, XVI, R = 4-Me_2N; **III, XVII**, R = 4-MeO; **IV, XVIII**, R = 4-Me; **V, XIII, XIX, XXIX, XXXIII, XXXVIII, XLIII, XLVIII**, R = H; **VI, XX**, R = 4-Cl; **VII, XXI**, R = 4-Br; **VIII, XXII**, R = 4-I; **IX, XXIII**, R = 4-O_2N; **X, XXIV**, R = 3-Cl; **XI, XXVI**, R = 3-Br; **XII, XXV**, R = 2-Cl; **XIV, XXXIV, XXXVII, XLII, XLIX**, R = Me; **XXVII**, R = 2-Me; **XXVIII**, R = 2,4,6-Me_3; **XXX**, R = 3-Me; **XXXI**, R = 5-Me; **XXXII**, R = 5-Cl; **XXXVI**, R = Me_2N; **XXXIX, XLIV**, R = Cl; **XL, XLV**, R = Br; **XLI**, R = MeO; **XLVI**, R = I; **XLVII**, R = O_2N.

by the molar volume technique. It should be noted that compounds like **I**–**XLIX** were studied previously by several methods, including X-ray analysis [11–17], gas-phase electron diffraction [18–20], ^{1}H NMR [21–24] and UV spectroscopy [25–28], and Kerr effect in combination with dipole moments [7–10, 29–33]. Studies by the molar volume method in solution were not reported. We set ourselves the task of estimating

the molar volumes of compounds **I**–**XLIX** in solution at infinite dilution and analyzing the obtained data in terms of the additivity scheme with a view to determine their structure.

The results of molar volume determination are summarized in Table 1. Let us consider first those systems which contain no *ortho*-hydroxy group in the aromatic rings, i.e., compounds **I**–**XV** and **XXXVI**–

Table 1. Molar volumes of Schiff bases and their structural analogs in infinitely dilute solutions and calculation of molar volumes according to the additivity scheme. Determination of the dipole moments and Kerr constants in solution using the additive molar volumes (25°C) [a]

Comp. no.	Solvent	β	${}^{\infty}V_2$, $cm^3\,mol^{-1}$	V_{ad}, $cm^3\,mol^{-1}$	ε_V, %	Calculation by the simplified procedure		Experimental data		Reference
						μ, D	${}_{\infty}({}_mK_2)\times 10^{12}$, esu	μ, D	${}_{\infty}({}_mK_2)\times 10^{12}$, esu	
I	CCl_4	–0.5019	170.9	–	–	–	–	–	–	[7]
II	CCl_4	–0.4781	209.3	206.4	1.4	2.04	758	2.03	758	[7]
III	CCl_4	–0.4176	189.0	189.0	0	1.77	–54	1.76	–54	[7]
IV	CCl_4	–0.4945	184.2	185.0	0.4	1.33	14	1.40	14	[7]
V	CCl_4	–0.4742	168.6	–	–	–	–	–	–	[7]
VI	CCl_4	–0.3698	186.4	180.7, [b] 182.3 [c]	3.1, 2.3	2.43, 2.44	1043	2.53	1043	[7]
				182.9	1.9	2.44				
VII	CCl_4	–0.1647	191.2	186.8	2.3	2.47	1066	2.48	1066	[7]
VIII	CCl_4	–0.0364	200.9	192.4	4.2	2.33	1010	2.35	1010	[7]
IX	Dioxane	0.1690	183.1	182.8, [b] 180.2 [c]	0.2, 1.6	5.22, 5.22	6822	5.21	6385	[7]
X	CCl_4	–0.3611	185.3	180.7, [b] 182.2 [c]	2.5, 1.7	2.30, 2.31	402	2.31	402	[8]
				182.9	1.3	2.31				
XI	CCl_4	–0.1205	184.0	186.8	1.5	2.28	505	2.27	505	[8]
XII	CCl_4	–0.3276	180.7	180.7, [b] 182.2 [c]	0, 0.8	2.32, 2.33	–26	2.31	–26	[8]
				182.9	1.2	2.33				
XIII	CCl_4	–0.5258	188.0	185.0	1.6	1.91	40	1.92	40	[29]
XIV	CCl_4	–0.5482	204.5	201.4	1.5	1.86	–64	1.87	–64	[29]
XV	Dioxane	0.0619	235.1	255.9	8.9	1.68	46	1.59	46	[29]
XVI	CCl_4	–0.3725	208.2	212.0	1.8	3.78	2282	3.76	2282	[9]
XVII	CCl_4	–0.3197	189.3	191.7	1.3	2.85	347	2.84	347	[9]
XVIII	CCl_4	–0.3872	185.0	186.9	1.0	2.58	111	2.56	111	[9]
XIX	CCl_4	–0.3684	170.3	171.3	0.6	2.37	–3.5	2.37	–3.5	[32]
XX	CCl_4	–0.2686	185.5	189.2	2.0	2.23	144	2.21	144	[9]
XXI	CCl_4	–0.0850	189.1	193.9	2.5	2.19	138	2.15	138	[9]
XXII	CCl_4	–0.0563	215.4	203.6	5.5	2.21	89	2.17	89	[9]
XXIII	Dioxane	0.2374	179.9	185.8	3.3	4.46	4157	4.44	4156	[9]
XXIV	CCl_4	–0.2366	180.8	189.2	4.6	2.48	–28	2.45	–28	[9]
XXV	CCl_4	–0.2591	184.1	189.2	2.8	3.37	–7	3.35	–8	[9]
XXVI	CCl_4	–0.1262	196.3	193.9	1.2	2.45	–134	2.44	–134	[9]
XXVII	CCl_4	–0.3921	185.6	186.9	0.7	2.16	–68	2.16	–68	[9]
XXVIII	CCl_4	–0.4505	219.1	220.5	0.6	2.59	–126	2.59	–126	[9]
XXIX	CCl_4	–0.6424	183.7	–	–	–	–	–	–	[32]
XXX	CCl_4	–0.6234	196.0	200.1	2.1	2.38	195	2.38	195	[32]
XXXI	CCl_4	–0.6658	201.6	200.1	0.7	2.86	78	2.87	78	[32]
XXXII	CCl_4	–0.4767	197.3	198.0	0.4	2.78	468	2.77	468	[32]
XXXIII	CCl_4	–0.4137	188.5	190.7	1.2	3.01	–192	3.01	–192	[33]
XXXIV	CCl_4	–0.5242	216.7	207.2	4.4	3.04	–199	3.06	–199	[33]
XXXV	Dioxane	0.0603	250.1	237.8	4.9	3.00	122	3.03	122	[33]
XXXVI	Dioxane	0.1775	192.5	204.5	6.2	4.86	1693	4.83	1692	[30]

Table 1. (Contd.)

Comp. no.	Solvent	β	${}_{\infty}V_2$, $cm^3\ mol^{-1}$	V_{ad}, $cm^3\ mol^{-1}$	ε_V, %	Calculation by the simplified procedure		Experimental data		Reference
						μ, D	${}_{\infty}({}_mK_2)\times 10^{12}$, esu	μ, D	${}_{\infty}({}_mK_2)\times 10^{12}$, esu	
XXXVII	Dioxane	0.1042	184.3	183.1	0.7	3.78	–239	3.78	–239	[30]
XXXVIII	Dioxane	0.1322	166.7	–	–	–	–	–	–	[30]
XXXIX	Dioxane	0.1907	182.6	178.8,[b] 180.3[c]	2.1, 1.3	3.35, 3.35	27	3.36	27	[30]
				181.0	0.88	3.35				
XL	Dioxane	0.2689	196.6	184.9	6.0	3.11	–50	3.14	–50	[30]
XLI	CCl_4	–0.4073	188.5	187.8	0.4	1.53	244	1.52	244	[31]
XLII	CCl_4	–0.4849	183.9	183.8	0.05	0.41	137	0.40	137	[31]
XLIII	CCl_4	–0.4553	167.4	–	–	–	–	–	–	[31]
XLIV	CCl_4	–0.2942	177.0	179.5,[b] 181.0[c]	1.4, 2.3	1.50, 1.51,	728	1.49	728	[31]
				181.7	2.6	1.51				
XLV	CCl_4	–0.0816	178.2	185.6	4.2	1.51	724	1.47	724	[31]
XLVI	CCl_4	–0.0525	204.7	191.2	7.1	1.29	734	1.25	734	[31]
XLVII	Dioxane	0.1816	181.1	181.6,[b] 179.0[c]	0.3, 1.2	4.49	4450	4.52	4450	[31]
XLVIII	Dioxane	0.1034	185.3	186.5	0.6	1.29	249	1.29	249	[10]
XLIX	Dioxane	0.0681	206.3	203.0	1.6	1.68	702	1.68	702	[10]

[a] β is the concentration coefficient, ${}_{\infty}V_2$ is the molar volume extrapolated to infinite dilution, ε_V is the relative deviation of the experimental values of ${}_{\infty}V_2$ from those calculated by the additivity scheme (V_{ad}), μ is the dipole moment, and ${}_{\infty}({}_mK_2)$ is the Kerr constant. [b] Substituent increments from the data for solutions in benzene. [c] Substituent increments from the data for solutions in chloroform; the other values were determined from the data for solutions in carbon tetrachloride.

XLVII. Their molar volumes V_{ad} were calculated by the additivity scheme using Eq. (1).

$$V_{ad} = {}_{\infty}V_2(R = H) + V(R). \quad (1)$$

Here, ${}_{\infty}V_2(R = H)$ is the molar volume of unsubstituted compound (*N*-benzylideneaniline, *N*-benzilideneaniline *N*-oxide, or azobenzene), and *V*(R) is the molar volume increment of the R group. The *V*(R) values were determined by us previously from the data for solutions of monosubstituted benzenes (Table 2). The results of the additivity calculations are given in Table 1 together with the relative deviations ε_V (%) of the calculated (V_{ad}) from experimental values (${}_{\infty}V_2$). It is seen that the experimantal molar volumes (${}_{\infty}V_2$) and those calculated by the additivity scheme (V_{ad}) are in a good agreement with each other, the corresponding deviations approaching the experimental errors (5–7%). The largest deviation is observed for *N*-(diphenylmethylidene)aniline (**XV**). Presumably, this is the result of either overload of its molecule with phenyl rings (which is not taken into account by the additivity calculation) or experimental error, for the density of solutions weakly depends on the concentration and the coefficient β is very small [28]. We can conclude that the molar volumes of *N*-benzylideneanilines, azobenzenes, *N*-benzylideneaniline *N*-oxides, and *trans*-stilbene in infinitely dilute solutions are additive with respect to the substituting groups and parent structures **V**, **XXXVII**, and **XLIII** (Table 1).

The additivity of ${}_{\infty}V_2$ is quite notable. It indicates that the corresponding parent compounds (R = H) are good models of the steric structure of substituted derivatives. Otherwise, more significant deviations of the additive molar volumes from the experimental values would be observed. Presumably, the only conclusion that could be drawn is the absence of perfect coplanarity between the aromatic rings and –CH=N–, –N=N–, –CH=CH–, and –CH=N(O)– bridging groups.

Similarity of the molar volumes of isoelectronic *trans*-stilbene (**I**, 170.9 $cm^3\ mol^{-1}$), *N*-benzylideneaniline (**V**, 168.8 $cm^3\ mol^{-1}$), and azobenzene (**XLIII**, 167.4 $cm^3\ mol^{-1}$) within experimental error attracts interest. The molar volume increments of the –CH=CH–, –CH=N–, and –N=N– groups turned out to be also similar. These increments can readily be calculated by the formula $\Delta V(\text{bridge}) = {}_{\infty}V_2 - 2V(C_6H_5)$, where ${}_{\infty}V_2$ is the molar volume of *trans*-stilbene, *N*-benzylideneaniline, or azobenzene, and

Table 2. Molar volume increments of bonds and groups

Bond or group	ΔV, $cm^3\ mol^{-1}$	Reference
$N(CH_3)_2$ [a]	37.8	–
OCH_3	20.4	[34]
CH_3	16.4	[34]
H	12.3	[1]
Cl	12.1 [b]	[34]
	13.6 [c]	
	14.3	
Br	18.2	[34]
I	23.8	[34]
NO_2	14.2 [b]	[34]
	11.6 [c]	
OH	2.7	[34]
C_6H_5 [d]	75.0	–

[a] Determined in the present work as the difference in the molar volumes of dimethylaniline and benzene (neat) [34]. [b] Determined from the data for solutions in benzene. [c] Determined from the data for solutions in chloroform, otherwise, in carbon tetrachloride. [d] Calculated by the formula $V(C_6H_5) = {}_\infty V_2$(benzene) – ΔV(CH), where ΔV(CH) = 12.3 $cm^3\,mol^{-1}$ is the increment of the C–H bond [1].

$V(C_6H_5)$ is the molar volume of the phenyl group (Table 2). We thus obtained the following ΔV(bridge) values: 20.9, 18.6, and 17.4 $cm^3\ mol^{-1}$ for –CH=CH–, –CH=N–, and –N=N–, respectively. Subtraction of the contribution of the C–N bond (Tables 2) gives values of 3.7, 6.3, and 17.4 $cm^3\ mol^{-1}$, respectively. These values attract certain interest. The negative value of the –C=C– increment is quite admissible; its sign indicates only shielding of the bridging bond by the rotating aromatic rings [1]. The small value of the –C=N– increment implies an analogous effect. The latter value suggests that the –N=N– bridging group is well accessible by solvent and that it is less shielded by the *ortho*-hydrogen atoms in the aromatic rings. Therefore, we can conclude that molecules of *trans*-stilbene (**I**) and *N*-benzylideneaniline (**V**) in solution are not planar, while *trans*-azobenzene molecule **XLIII** is almost planar. This conclusion is very consistent with the data obtained by measuring the Kerr effects and dipole moments [7, 31], according to which the aromatic rings in *trans*-stilbene are turned in a conrotatory mode through an angle of 26–30° with respect to the bridging bond [35]; in the *N*-benzylideneaniline molecule, the aldehyde benzene ring is coplanar to the bridging fragment, while the aniline ring is turned through an angle of 59°; and azobenzene molecule is almost planar. It should be noted that, in keeping with the Kerr effect data, substituents in the aniline ring of *N*-benzylideneanilines influence its orientation [7, 8]. Donor substituents like $N(CH_3)_2$ and OCH_3 favor coplanar arrangement of the aromatic ring with respect to the –CH=N– moiety, whereas electron-withdrawing groups (suach as NO_2) increase the dihedral angle φ_2, as compared to the unsubstituted parent molecule. On the other hand, no dependence of ${}_\infty V_2$ upon φ_2 is observed for *N*-benzylideneanilines. Presumably, perfectly coplanar arrangement of the aniline ring and bridging group is not achieved, and the angle φ_2 is no less than that in the *trans*-stilbene molecule. The agreement between the results of additivity calculations and experimental data indicates that the aromatic rings in the examined compounds are well solvated from every side by solvent molecules; however, the same does not apply to all bridging bonds between the aromatic rings.

The molar volumes ${}_\infty V_2$ of compounds **XVI**–**XXXV**, **XLVIII**, and **XLIX** having a hydroxy group in the *ortho* position of the aromatic rings are also given in Table 1. The additive molar volumes V_{ad} of *N*-salicylideneanilines **XVI**–**XXVIII** were calculated in two ways using formula (2):

$$V_{ad} = {}_\infty V_2 + V(R). \quad (2)$$

In the first version, ${}_\infty V_2$ is the molar volume of *N*-benzylideneaniline or its substituted derivatives **II**–**XII**, and V(R) is the increment of the OH group (Table 2). According to the second version, ${}_\infty V_2$ is the molar volume of *N*-salicylideneaniline (**XIX**), and V(R) is the increment of the substituent R (Table 2) in molecule **XVI**–**XVIII** or **XX**–**XXVIII**. The results of additivity calculation of the molar volumes V_{ad} of *N*-salicylideneanilines according to the first version are given in Table 1 together with the experimental data, and Table 3 compares the results of calculations by the two versions and the experimental molar volumes.

Likewise, we calculated the additive molar volumes V_{ad} of *N*-salicylidene-1,1-dimethylethanamines **XXIX**–**XXXII**, *N*-[1-(2-hydroxyphenyl)ethylidene]anilines **XXXIII**, and **XXXIV**, *N*-[2-hydroxyphenyl(phenyl)-methylidene)aniline (**XXXV**), and 2-hydroxy-5-methylazobenzenes **XLVIII** and **XLIX**. In the first version (except for compounds **XXIX**–**XXXII**, **XLVIII**, and **XLIX**), ${}_\infty V_2$ was the molar volume of the corresponding structure having no *ortho*-hydroxy group (compounds **XIII**–**XV**), and V(R) was the OH increment (Table 2). In the second version, ${}_\infty V_2$ was the molar volume of molecule **XXIX** or **XXXIII** having a hydroxy group in the **ortho** position but no other substituent, and V(R) was the increment of the corresponding substituent R. In the calculations of 2-hydroxy-5-

Table 3. Contraction of the molar volumes of compounds having a hydroxy group in the *ortho* position of the aromatic ring and their entropy stabilization [a]

Comp. no.	${}_{\infty}V_2$, $cm^3\ mol^{-1}$	V_{ad1}, $cm^3\ mol^{-1}$	V_{ad2}, $cm^3\ mol^{-1}$	ΔV_1, $cm^3\ mol^{-1}$	ΔV_2, $cm^3\ mol^{-1}$	Δn_1	$T\Delta S_1^0$, kJ mol^{-1}
XVI	208.2	212.0	208.1	3.8	–0.1	0.039	2.5
XVII	189.3	191.7	190.7	2.4	1.4	0.025	1.6
XVIII	185.0	186.9	186.7	1.9	1.7	0.020	1.2
XIX	170.3	171.3	–	1.0	–	0.010	0.6
XX	185.5	189.2	182.4	3.7	–3.1	0.038	2.4
XXI	189.1	193.9	188.5	4.8	–0.6	0.049	3.1
XXII	215.4	203.6	194.1	–11.8	–21.3	–0.114	–7.3
XXIII	179.9	185.8	184.5	5.9	4.6	0.069	4.0
XXIV	180.8	189.2	182.4	8.4	1.6	0.086	5.5
XXV	184.1	189.2	182.4	–5.1	–1.7	0.050	3.2
XXVI	196.3	193.9	188.5	–2.4	–7.8	–0.025	–1.6
XXVII	185.6	186.9	186.7	1.3	1.1	0.013	0.8
XXVIII	219.1	220.5	219.5	1.4	0.4	0.015	1.0
XXIX	183.7	–	–	–	–	–	–
XXX	196.0	–	200.1	–	4.1	0.042 [b]	2.7
XXXI	201.6	–	200.1	–	1.5	–0.015	–1.0
XXXII	197.3	–	198.0	–	0.7	0.007	0.4
XXXIII	188.5	190.7	–	2.2	–	0.023	1.4
XXXIV	216.7	207.2	204.9	–9.5	–11.8	–0.098	–6.3
XXXV	250.1	237.8	–	–12.3	–	–0.144	–8.4
XLVIII	185.3	186.5	–	1.2	–	0.013	0.8
XLIX	206.3	203.0	201.7	–3.3	4.6	–0.038	–2.2

[a] V_{ad1} and V_{ad2} are the molar volumes calculated according to two versions of the additivity scheme; ΔV_1 and ΔV_2 are the reductions in the molar volume due to chelation, calculated according to the two versions: $\Delta V_1 = {}_{\infty}V_2 - V_{ad1}$, ${}_{\infty}V_2 = \Delta V_2 - V_{ad2}$; Δn_1 is the decrease in the number of moles of the solvent, $\Delta n_1 = \Delta V_1/V_1$; and $T\Delta S_1^0$ is the contribution of entropy stabilization, $T\Delta S_1^0 = 298.15 S^0 \Delta n_1$. [b] For compounds **XXX**–**XXXII**: $\Delta n_1 = \Delta V_2/V_1$.

methylazobenzenes (first version), to the molar volume ${}_{\infty}V_2$ of **XLII** and **XLIII** we also added the hydroxy group increment V(OH) and the increment of the methyl group $V(CH_3)$ in the second aromatic ring; in the second version, the increment of the substituent R, V(R), was added to ${}_{\infty}V_2$ of **XLVIII**.

The results of additivity calculations with the use of V(OH) were denoted as V_{ad1}, and those obtained according to the second version, as V_{ad2}. The V_{ad1} and V_{ad2} values are given in Table 3. It is seen that the experimental ${}_{\infty}V_2$ values and calculated V_{ad1} and V_{ad2} values are very similar. As might be expected, the difference between ${}_{\infty}V_2$ and V_{ad2} is almost always smaller than between ${}_{\infty}V_2$ and V_{ad1}. The reason is that the second version more appropriately takes into account intramolecular hydrogen bonding (formation of H-chelate ring). In the first version, the increment V(OH) corresponds to free OH group. It is also interesting that V_{ad1} is almost always greater than ${}_{\infty}V_2$. Insofar as the V_{ad1} values were determined with no account taken of H-chelation using the increment V(OH) for phenol at infinite dilution [33], lower values of ${}_{\circ}V_2$ as compared to V_{ad1} indicate contraction of the molar volume as a result of *H*-chelation.

We believe that the observed contraction of molar volume ${}_{\infty}V_2$ relative to that calculated by the additivity scheme (V_{ad1}) reflects so-called chelate effect [36]. This term was formerly introduced to denote the gain in the Gibbs energy ΔG upon formation of chelate compounds as compared to complexes containing unidentate ligands [37]. Chelation (chelate effect) is possible via not only coordination to a metal but also intramolecular hydrogen bonding. The energy gain $\Delta G = \Delta H - T\Delta S$ depends on both the enthalpy contribution ΔH (which is likely to be always favorable) and the entropy contribution ΔS [37, 38].

We made an attempt to estimate $T\Delta S^0$, i.e., entropy stabilization of *H*-chelates in solution, under standard conditions using molar volumes extrapolated to infinite dilution, ${}_{\infty}V_2$. For this purpose, we calculated

the number of moles of the solvent Δn expelled from the solvate shell of one mole of a compound upon chelation by the formula $\Delta n = \Delta V/V_1$, where ΔV is reduction of the molar volume as a result of chelation, $\Delta V = {}_\infty V_2 - V_{ad}$; and V_1 is the molar volume of the solvent. We thus obtained $T\Delta S^0 = 298.15 S^0 \Delta n$, J mol^{-1} (25°C), where S^0 is the standard entropy of the solvent [39]. The calculated values of ΔV, Δn, and $T\Delta S^0$ for compounds **XVI**–**XXXV** and **XLVIII**–**XLIX** having a hydroxy group in the *ortho* position are given in Table 3.

As follows from these data (Table 3), almost all *N*-salicylideneanilines and about a half of the other *ortho*-hydroxy derivatives are characterized by contraction of the experimental molar volume ${}_\infty V_2$ relative to that calculated by the additivity scheme (V_{ad1}). The difference is attributed to the entropy stabilization via chelation ($T\Delta S^0$). This contribution is fairly small and is similar to the energy of a weak hydrogen bond [40]; this is intrinsic to *ortho*-hydroxy compounds capable of forming intramolecular H-chelates [27].

As in previous studies [1, 34], we also calculated the molar Kerr constants ${}_\infty({}_mK_2)$ and dipole moments μ of compounds **I**–**XLIX** be the new simplified procedure with the use of additive molar volumes V_{ad}. The concentration coefficients α, γ, and δ were taken from [7–10, 29–33]; the data given therein were used by us previously to determine ${}_\infty V_2$ values of the same compounds. The dipole moments and Kerr constants were calculated using modified Le Fevre and Fujita equations (3) and (4) for the Kerr constant ${}_\infty({}_mK_2)$ and molar polarization ${}_\infty P_2$.

$$ {}_\infty({}_mK_2) = {}_sK_1\rho_1 {}_\infty V_2 + (\gamma + \delta - H\gamma - J\alpha\varepsilon_1)K_1\rho_1 \frac{M_2}{M_1}V_1, \quad (3) $$

$$ {}_\infty P_2 = \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} {}_\infty V_2 + \frac{3\alpha\varepsilon_1 M_2}{(\varepsilon_1 + 2)^2 M_1} V_1. \quad (4) $$

Here, V_1 is the molar volume of solvent (for other details, see [34]). The parameter ${}_\infty V_2$ in formulas (3) and (4) was replaced by V_{ad1} from Tables 1 and 3. Following this approach, the reference molecules were only parent ones (R = H). The calculated values of μ and ${}_\infty({}_mK_2)$ are given in Table 1 together with the corresponding values determined previously. A very good agreement between the values calculated by the simplified method and traditional procedure is observed. The differences do not exceed the experimental error in the determination of μ and ${}_\infty({}_mK_2)$ in solution, and in some cases the values calculated by both methods coincide with each other. This means that procedures for the determination of μ and ${}_\infty({}_mK_2)$ can be simplified to a considerable extent by exclusion of determination of the density of solution. Instead, additive molar volumes should be calculated, and modified formulas (3) and (4) should be used. However, a well-adjusted additivity scheme for the calculation of molar volumes is necessary for this purpose.

EXPERIMENTAL

The concentration coefficients β for the linear dependences of solution density ρ_{12} upon weight fraction ω of the dissolved substance [$\rho_{12} = \rho_1(1 + \beta\omega)$, where ρ_1 is the solvent density] were taken from [7–10, 29–33]. The experimental molar volumes ${}_\infty V_2$ were calculated by extrapolation formula (5) [34].

$$ {}_\infty V_2 = \frac{M_2(1 - \beta)}{\rho_1}. \quad (5) $$

The required parameters for the calculation of the dipole moments and Kerr constants from the additive molar volumes V_{ad} were taken from the same sources. In the calculation of the experimental molar volumes, the following solvent parameters were used (25°C): carbon tetrachloride: $\rho_1 = 1.5845$ g cm^{-3}, $\varepsilon_1 = 2.2270$ [41]; dioxane: $\rho_1 = 1.02687$ g cm^{-3}, $\varepsilon_1 = 2.209$ [41]. The dipole moments are given in debyes (D), and the Kerr constants, in CGS units (esu); 1 C m = 0.2998×10^{30} D, 1 m^5 V^{-2} mol^{-1} = 0.8988×10^{15} esu mol^{-1}.

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