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Molecular Polarizability of Organic Molecules and Their Complexes: LIV.[1] Molar Volumes of Polyaryl Organoelement Compounds in Solutions, Extrapolated to Infinite Dilution, and Steric Structure of the Molecules

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Abstract—Molar volumes in various solvents were determined for organic derivatives of silicon, phosphorus, arsenic, sulfur, and tellurium, containing aryl nuclei capable to internal rotation about single bonds between them and bridging groups. Additive analysis of the molar volumes of these compounds showed that the aryl nuclei are acoplanar with respect to the bridging groups. Most probable is a conrotatory mutual orientation of the aromatic rings. Molar volumes were also determined for a series of compounds with two bridging groups, which can serve as models of an extreme case of mutual proximity of aryl ring planes in diaryl systems with one bridging group. A possibility for considerably simplifying the methods for determination of dipole moments and Kerr constants for compounds whose molar volumes can be calculated by our developed additive scheme is demonstrated.

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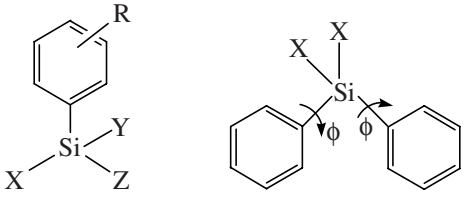
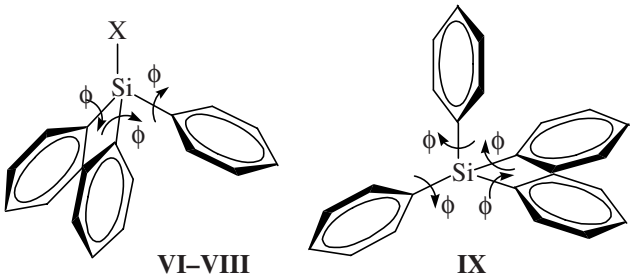
The present work is a continuation of our research on the molar volumes of compounds whose aromatic rings can rotate about formally single bonds between them and bridging groups [1, 2]. We determined molar volumes at infinite dilution ($_{\infty}V_2$) for compounds **I–LXXI**.

Arylsilanes **I–IX**



I–III **IV, V**

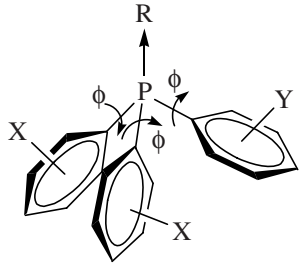
X = CH_3, Y = CH_3, Z = CH_3, R = H (**I**); X = CH_3, Y = Cl, Z = Cl, R = H (**II**); X = CH_3, Y = CH_3, Z = Cl, R = 4-Cl (**III**); X = H (**IV**); X = Cl (**V**).



VI–VIII **IX**

X = H (**VI**); X = Cl (**VII**); X = Br (**VIII**).

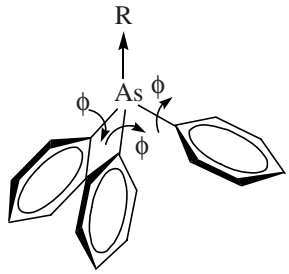
Derivatives of triphenylphosphine and its oxide and sulfide, and phosphazobenzenes **X–XXXIII**



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

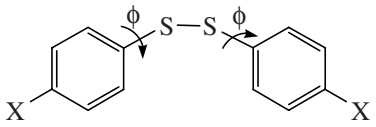
R = LEP: X = H, Y = H (**X**), X = H, Y = 4-CH_3 (**XI**), X = H, Y = 4-Br (**XII**), X = H, Y = 4-$COOCH_3$ (**XIII**), X = = H, Y = 4-CN (**XIV**), X = H, Y = 3-CN (**XV**), X = 4-CH_3, Y = 4-CH_3 (**XVI**), X = 4-$COOCH_3$, Y = 4-$COOCH_3$ (**XVII**), X = 4-CN, Y = 4-CN (**XVIII**); R = O: X = 4-CH_3, Y = 4-CH_3 (**XIX**), X = H, Y = H (XX), X = 4-Cl, Y = 4-Cl (XXI), X = 3-CH_3, Y = 3-CH_3 (**XXII**), X = 3-Cl, Y = 3-Cl (**XXIII**), $(CH_3)_2C_6H_5PO$ (**XXIV**); R = S: X = 4-OCH_3, Y = 4-OCH_3 (**XXV**), X = 4-CH_3, Y = 4-CH_3 (**XXVI**), X = H, Y = H (**XXVII**), X = 4-Cl, Y = 4-Cl (**XXVIII**), X = 3-CH_3, Y = 3-CH_3 (**XXIX**), X = 2-CH_3, Y = 2-CH_3 (**XXX**); R = NC_6H_4Br-4, X = H, Y = H (**XXXI**); R = NC_6H_4I-4 X = H, Y = H (**XXXII**); R = $NC_6H_4NO_2$-4, X = H, Y = H (**XXXIII**).

Triarylphenylphosphine and its oxide and sulfide **XXXIV–XXXVI**



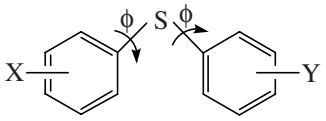
R = LEP (**XXXIV**); R = O (**XXXV**); R = S (**XXXVI**).

Diaryl disulfides **XXXVII, XXXVIII**



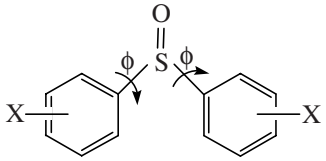
X = H (**XXXVII**); X = 4-Cl (**XXXVIII**).

Diaryl sulfides **XXXIX–XLV**



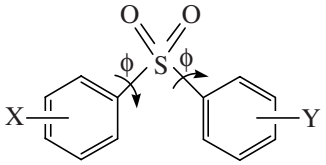
X = H, Y = H (**XXXIX**); X = 4-NO_2, Y = 4-NO_2 (**XL**); X = 4-OCH_3, Y = 4-OCH_3 (**XLI**); X = 4-OCH_3, Y = 4-NO_2 (**XLII**); X = 2-OCH_3, Y = 4-NO_2 (**XLIII**); X = 4-OCH_3, Y = 2-NO_2 (**XLIV**); X = 2-OCH_3, Y = 2-NO_2 (**XLV**).

Diaryl sulfoxides **XLVI, XLVII**



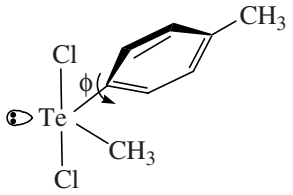
X = H (**XLVI**); X = 4-Cl (**XLVII**).

Diaryl sulfones **XLVIII–LVI**

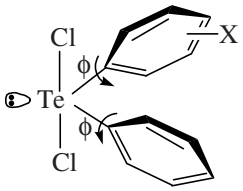


X = H, Y = H (**XLVIII**); X = H, Y = 4-Cl (**XLIX**); X = 4-Cl, Y = 4-Cl (**L**); X = 4-NO_2, Y = 4-NO_2 (**LI**); X = 4-OCH_3, Y = 4-NO_2 (**LII**); X = 2-OCH_3, Y = 4-NO_2 (**LIII**); X = 4-OCH_3, Y = 2-NO_2 (**LIV**); X = 2-OCH_3, Y = 2-NO_2 (**LV**); X = 2,4,6-CH_3, Y = 4-Br (**LVI**).

Organotellurium halides **LVII–LXIII**



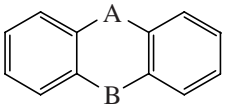
LVII



LVIII–LXIII

X = H, (**LVIII**); X = 4-CH_3, (**LIX**); X = 3-CH_3, (**LX**); X = 4-OCH_3, (**LXI**); X = 4-Cl, (**LXII**); X = 4-Br (**LXIII**).

Compouds with two bridging groups **LXIV–LXXI**



A = CH_2, B = S (**LXIV**); A = S, B = S (**LXV**); A = SO, B = SO (**LXVI**); A = SO_2, B = SO_2 (**LXVII**); A = S, B = O (**LXVIII**); A = S, B = NH (**LXIX**); A = S, B = NCH_3 (**LXX**); A = S, B = NC_6H_5 (**LXXI**).

The resulting molar volumes are listed in Table 1.

Additive analysis of the molar volumes of compounds **I–LXXI** was performed to assess their molecular conformations in solutions.

The additive molar volumes (V_{ad}) of arylsilanes **I-IX** were calculated in the following way. The V_{ad} values for compounds **I–III** were calculated by formula (1):

$$V_{ad} = 0.5\{{}_{\infty}V_2[(C_6H_5)_2SiH_2] - 2\Delta V(SiH)\} + \Delta V(SiX) + \Delta V(SiY) + \Delta V(SiZ) + V(R). \quad (1)$$

Here $0.5\{{}_{\infty}V_2[(C_6H_5)_2SiH_2] - 2\Delta V(SiH)\}$ is the increment of molar volume of the C_6H_5–Si fragment;

Table 1. Additive calculation of the molar volumes of organoelement polyaryl compounds in solutions at infinite dilution. Determination of the dipole moments and Kerr constants from additive molar volumes[a]

Comp. no.	Solvent	β	$_{\infty}V_2$, $cm^3\ mol^{-1}$ (25°C)	V_{ad}, $cm^3\ mol^{-1}$	ε_V, %	Data obtained in the present work by the simplified procedure		Experimental data		References
						μ, D	$_{\infty}(_mK_2)\times10^{12}$, esu	μ, D	$_{\infty}(_mK_2)\times10^{12}$, esu	
Arylsilanes										
I	CCl_4	–0.867	177.1	175.3	1.0	0.36	10.4	0.39	11.9	[3]
II	CCl_4	–0.337	161.3	167.1	3.6	2.5	57.0	1.55	62.4	[3]
III	CCl_4	–0.357	175.7	185.5	5.6	1.89	–16.9	1.85	–19.5	[3]
IV	CCl_4	–0.599	186.0	165.4	11.0	0.62	14.9	0.81	17.5	[3]
V	CCl_4	–0.337	213.6	213.2	0.2	2.58	–42.2	2.55	–50.2	[3]
VI	CCl_4	–0.473	242.1	222.0	8.3	0.28	–0.2	0.7	0.1	[4]
	Benzene	0.193	240.6±1.5		7.7	0.46	–8.0	0.6	–6.7	
VII	CCl_4	–0.350	251.2	235.7	6.2	1.99	–112.1	2.04	–142.1	[3]
	Benzene	0.241	256.0±6.6		7.9	2.06	–141	2.13	–39	[4]
VIII	Benzene	0.340	256.3	241.6	5.7	2.18	–163	2.22	–162	[4]
IX[b]	CCl_4	–0.517	322.2	313.6	2.7	–	55.2	0	16	[3]
				304.4	5.5					
Derivatives of triphenylphosphine and its oxide and sulfide										
X	Benzene	0.235	229.6±2.6	207.8	9.5	1.39	–102	1.50	–100	[5]
XI[c]	Benzene	0.736	250.4	245.3	2.0	1.63	–	1.65	–	[6]
XII	Benzene	1.52	254.6	247.1	2.9	1.74	–	1.77, 2.05	–	[6]
XIII	Benzene	1.08	270.1	266.6	1.3	2.27	–	2.28	–	[6]
XIV	Benzene	0.975	241.6	242.4	0.3	4.22	–	4.22	–	[6]
XV	Benzene	0.970	242.1	242.4	0.1	4.27	–	4.27	–	[6]
XVI	Benzene	0.632	291.8	278.1	4.7	1.79	–	1.8, 2.14	–	[6]
XVII	Benzene	1.42	372.5	342	8.2	2.63	–	2.51	–	[6]
XVIII	Benzene	1.25	274.3	269.4	1.8	3.24	–	3.26	–	[6]
XIX	CCl_4	–0.341	271.1	287.5	6.0	5.0	–1159	5.0	–1159	[7]
XX	CCl_4	–0.357	238.3	198.1	12.4	4.3	–591	4.4	–590	[7]
	Benzene	0.290	226.2±6.8			4.46	–830	4.49	–828	[8]
XXI	CCl_4	–0.123	270.5	281.2	4.0	3.2	–579	3.1	–579	[7]
XXII	CCl_4	–0.331	269.1	287.5	6.8	4.6	–556	4.5	–556	[7]
XXIII	CCl_4	–0.121	270.0	281.2	4.1	4.8	–453	4.7	–453	[7]
XXIV	Benzene	0.24	134.0	126.1	6.0	4.33	–	4.34	–	[9]
XXV	CCl_4	–0.269	307.9	298.2	3.2	5.48	–758	5.49	–758	[10]
XXVI	CCl_4	–0.362	289.2	286.2	1.0	5.17	–492	5.15	–492	[10]
XXVII	CCl_4	–0.276	237.0	212.3	10.3	4.85	–211	4.88	–211	[10]
	Benzene	0.297	236.7±2.7			4.77	–448	4.79	–446	[8]
XXVIII	CCl_4	–0.203	301.9	279.9	7.3	3.16	–392	3.21	–392	[10]
XXIX	CCl_4	–0.333	283.0	286.2	1.1	4.99	–335	4.98	–335	[10]
XXX	CCl_4	–0.280	271.8	286.2	5.3	4.45	–564	4.42	–564	[10]

Table 1. (Contd.)

Comp. no.	Solvent	β	$_{\infty}V_2$, $cm^3\ mol^{-1}$ (25°C)	V_{ad}, $cm^3\ mol^{-1}$	ε_V, %	Data obtained in the present work by the simplified procedure		Experimental data		References
						μ, D	$_{\infty}(_mK_2)\times10^{12}$, esu	μ, D	$_{\infty}(_mK_2)\times10^{12}$, esu	
Triphenylphosphazobenzenes										
XXXI	Dioxane	0.235	322.1	329.5	2.3	6.31	2962	6.44	3232	[11]
XXXII	Dioxane	0.368	295.0	335.1	13.6	6.55	3458	6.50	3780	[11]
XXXIII	Dioxane	0.234	297.2	329.5	10.9	9.65	1373	9.61	1406	[11]
Triphenylarsine and its oxide and sulfide										
XXXIV	Benzene	0.332	234.2±1.9	214.6	8.4	1.11	–38.9	1.23	–37.6	[5]
XXXV	Benzene	0.394	223.4±9.3	197.3	11.7	5.39	–1300	5.41	–1300	[8]
XXXVI	Benzene	0.378	240.6±5.1	212.7	11.6	5.28	–449	5.31	447	[8]
Diaryl disulfides										
XXXVII	CCl_4	–0.298	178.8±1.2	159.4	10.8	1.75	–11.8	1.82	–11.5	[12]
XXXVIII	CCl_4	–0.129	204.7±1.8	207.4	1.3	0.39	64.2	0.33	63.8	[12]
Diaryl sulfides										
XXXIX	CCl_4	–0.385	162.8±0.95	143.2	12.0	1.41	24.5	1.50	24.7	[13]
XL	Dioxane	0.274	195.3	192.4	1.5	3.50	–120	3.50±0.11	–119±8	[14]
XLI	Dioxane	0.159	201.7	203.6	0.9	2.54	–85	2.54±0.09	–85±6	[14]
XLII	Dioxane	0.209	201.3	198.0	1.6	5.04	3811	5.04±0.04	3813±121	[14]
XLIII	Dioxane	0.199	203.8	198.0	2.8	4.82	3440	4.82±0.15	3440±454	[14]
XLIV	Dioxane	0.204	202.6	198.0	2.3	5.87	1678	5.87±0.04	1678±72	[14]
XLV	Dioxane	0.239	193.6	198.0	2.3	5.73	914	5.72±0.05	915±40	[14]
Diaryl sulfoxides										
XLVI	CCl_4	–0.274	162.6±1.56	140.6	13.5	4.05	–165	4.08	–165	[15]
XLVII	Dioxane	0.270	192.8	191.2	0.8	2.43	–126	2.43±0.09	–127±1	[14]
Diaryl sulfones										
XLVIII	Benzene	0.326	168.3±1.9	144.6	14.1	4.95	–1116	4.97	–1115	[15]
	Dioxane	0.203	169.4		14.6	5.10	–1107	5.14±0.02	–1106±35	[16]
XLIX	Dioxane	0.245	185.8	183.7	1.1	4.39	–781	4.39±0.07	–782±24	[16]
L	Dioxane	0.289	198.8	198.0	0.4	3.35	–438	3.35±0.04	–440±14	[16]
LI	Dioxane	0.367	190.0	199.0	4.7	0.87	17.3	0.78±0.14	16±12	[16]
LII	Dioxane	0.279	205.9	204.6	0.6	4.94	1082	4.94±0.05	1083±13	[16]
LIII	Dioxane	0.287	203.6	204.6	0.5	5.51	–710	5.51±0.06	–708±15	[16]
LIV	Dioxane	0.275	207.1	204.6	1.2	6.46	–1213	6.47±0.08	–1211±80	[16]
LV	Dioxane	0.315	184.9	200.6	8.5	7.08	–739	7.07±0.20	–738±57	[16]
LVI	Dioxane	0.263	243.5	236.8	2.8	4.71	–787	4.72±0.15	–788±63	[16]
Organotellurium halides										
LVII	Benzene	0.53	163.9	170.1	3.8	1.97	–	1.91	–	[9]
LVIII	Benzene	0.57	173.6	189.7	9.3	2.16	–	2.06	–	[9]
LIX	Benzene	0.53	197.3	190.0	3.7	2.48	–	2.45	–	[9]
LX	Benzene	0.47	222.4	190.0	14.6	2.46	–	2.31	–	[9]

Table 1. (Contd.)

Comp. no.	Solvent	β	${}_{\infty}V_2$, $cm^3\ mol^{-1}$ (25°C)	V_{ad}, $cm^3\ mol^{-1}$	ε_V, %	Data obtained in the present work by the simplified procedure		Experimental data		References
						μ, D	${}_{\infty}({}_mK_2)\times10^{12}$, esu	μ, D	${}_{\infty}({}_mK_2)\times10^{12}$, esu	
Organotellurium halides										
LXI	Benzene	0.56	192.7	194.0	0.7	3.05	–	2.86	–	[9]
LXII	Benzene	0.50	221.5	187.9	15.2	1.76	–	1.83	–	[9]
LXIII	Benzene	0.52	237.1	191.8	19.1	1.54	–	1.69	–	[9]
Compounds with two bridging groups										
LXIV	CCl_4	–0.291	161.6±0.9	122.6	24.1	1.00	61	1.25	61	[17]
	Benzene	0.280	163.5±1.2		25.0	1.00	42	1.26	45	
LXV	Benzene	0.337	164.2±1.1	111.8	31.9	1.11	–186	1.41	–182	[18]
LXVI	Benzene	0.408	168.3±12.5	106.6	36.7	1.41	–200	1.70	–195	[18]
		0.409	167.8±5.8		36.5	4.80	–1643	4.88	–1640	
LXVII	Benzene	0.502	159.8±20.9	114.6	28.3	5.04	–2811	5.11	–2810	[18]
LXVIII	CCl_4	–0.228	155.3±0.6	105.1	32.3	0.43	–45	0.94	–44	[17]
	Benzene	0.321	155.7±1.53		32.5	0.45	–53	0.97	–49	
LXIX	Benzene	0.337	151.2±2.4	120.5	20.3	2.03	–27	2.14	–25	[19]
LXX	Benzene	0.298	171.5±9.7	130.8	23.7	1.96	19	2.09	22	[19]
LXXI	Benzene	0.294	222.5±9.3	187.5	15.7	2.15	262	2.16	264	[19]

[a] (β) Concentration coefficient; (${}_{\infty}V_2$) molar volume extrapolated to infinite dilution; (ε_V) relative deviation of experimental ${}_{\infty}V_2$ values from additive V_{ad} ; (μ) dipole moment; and [${}_{\infty}({}_mK_2)$] Kerr constant. [b] The V_{ad} values for compound **IX** was calculated in two ways by formulas (3) and (4), respectively. [c] The ${}_{\infty}V_2$ values for compounds **XI–XVIII** were obtained by formula (22) and for the other compounds, by formula (21).

${}_{\infty}V_2[(C_6H_5)_2SiH_2]$, molar volume of diphenylsilane (**IV**) (Table 1); ΔV(SiH), increment of molar volume of the Si–H bond; ΔV(SiX), ΔV(SiY), and ΔV(SiZ), increment of molar volumes of other substituents on silicon; and V(R), group increment of molar volume of the C–R substituent in the aromatic ring (Table 2).

The V_{ad} of diphenylsilane (**IV**) was calculated by formula (2):

$$V_{ад} = {}_{\infty}V_2[(CH_3)_2SiCl_2] - 6\,\Delta V_{CH} - 2\,\Delta V(SiCl) + 2\,\Delta V(SiH) + 2\,V(C_6H_5). \quad (2)$$

Here ${}_{\infty}V_2[(CH_3)_2\ SiCl_2]$ is the molar volume of the model compound $(CH_3)_2SiCl_2$ (Table 3); ΔV_{CH}, increment of molar volume of the alkyl C–H bond, equal to 13.0 $cm^3\ mol^{-1}$; ΔV(SiCl), increment of molar volume of the Si–Cl bond; and $V(C_6H_5)$, increment of molar volume of the phenyl group (Table 2).

The additive molar volume V_{ad} of dichlorodiphenylsilane (**V**) was obtained by subtracting two increments of molar volume of the Si–H bond ΔV(SiH) from and adding two increments of molar volume of the Si–Cl bond ΔV(SiCl) to the molar volume ${}_{\infty}V_2$ of diphenylsilane (**IV**) (Table 2).

The additive molar volume of triphenylsilane (**VI**) was calculated by subtracting nine increments of molar volume of the alkyl CH bond from and adding three increments of molar volume of the phenyl group (Table 2) to the molar volume of trimethylsilane ${}_{\infty}V_2$ (Table 3). The additive molar volumes of chlorotriphenylsilane (**VII**) and bromotriphenylsilane (**VIII**) were obtained by subtracting nine increments of molar volume of the alkyl C–H bond from and adding three increments of molar volume of the phenyl group (Table 2) to the molar volumes ${}_{\infty}V_2$ of chlorotrimethylsilane and bromotrimethylsilane (Table 3).

The V_{ad} of tetraphenylsilane (**IX**) was calculated in two ways by formulas (3) and (4):

$$V_{ad} = 2\,\{{}_{\infty}V_2[(C_6H_5)_2SiH_2] - 2\,\Delta V(SiH)\}, \quad (3)$$

$$V_{ad} = 0.5\,\{{}_{\infty}V_2[(C_6H_5)_2SiH_2] - 2\,\Delta V(SiH)\} + \{{}_{\infty}V_2[(C_6H_5)_3SiH] - \Delta V(SiH)\}. \quad (4)$$

Table 2. Increments of molar volumes of bonds and groups[a]

Bond or group	V, cm^3 mol^{-1}	Reference
Si–H[b]	14.6	–
C–H	13.0	[2]
Si–Cl[b]	28.2	–
Si–CH_3[b]	32.3	–
Si–Br[b]	36.7	–
C_{ar}–H	12.3	[2]
Cl	14.3	[2]
CH_3	16.4	[21]
Br	18.2	[21]
$COOCH_3$	37.7	[21]
CN	13.5	[21]
OCH_3	20.4	[21]
I	23.8	[21]
NO_2	14.8	[21]
C_6H_5	75.0	[20]
C–S–S–C[b]	9.4	–
C–S–C[b]	–6.8	–
C–SO–C[b]	–9.4	–
C–SO_2–C[b]	–5.4	–
C–CH_2–C	–4.0	[1]
C–O–C	–13.5	[1]
C–N(CH_3)–C[b]	12.2	–

[a] (V) Increment of molar volume of bond (ΔV) or group (V).
[b] Determined in the present work.

The increments of molar volume of the Si–Cl and Si–CH_3 bonds, ΔV(SiCl) and $\Delta V(SiCH_3)$, we found from pairs of equations (5), (6), and (7), set up based on the structure of model compounds. The ΔV(SiCl) and $\Delta V(SiCH_3)$ values obtained from each pairs were averaged (Table 2).

$$\left.\begin{aligned} \Delta V(SiCH_3) + 3\,\Delta V(SiCl) &= {}_{\infty}V_2(CH_3SiCl_3), \\ 3\,\Delta V(SiCH_3) + \Delta V(SiCl) &= {}_{\infty}V_2[(CH_3)_3SiCl], \end{aligned}\right\} \quad (5)$$

$$\left.\begin{aligned} 2\,\Delta V(SiCH_3) + 2\,\Delta V(SiCl) &= {}_{\infty}V_2[(CH_3)_2SiCl_2], \\ \Delta V(SiCH_3) + 3\,\Delta V(SiCl) &= {}_{\infty}V_2(CH_3SiCl_3), \end{aligned}\right\} \quad (6)$$

$$\left.\begin{aligned} 2\,\Delta V(SiCH_3) + 2\,\Delta V(SiCl) &= {}_{\infty}V_2[(CH_3)_2SiCl_2], \\ 3\,\Delta V(SiCH_3) + \Delta V(SiCl) &= {}_{\infty}V_2[(CH_3)_3SiCl]. \end{aligned}\right\} \quad (7)$$

Here ${}_{\infty}V_2(CH_3SiCl_3)$, ${}_{\infty}V_2[(CH_3)_3SiCl]$, and ${}_{\infty}V_2[(CH_3)_2 \cdot SiCl_2]$ are the molar volumes of model compounds (Table 3).

The increment for the Si–H bond (Table 2) was calculated by substracting three increments of molar volume of the Si–Cl bond from the molar volume of trichlorosillane ${}_{\infty}V_2(HSiCl_3)$ (Table 3). The increment of molar volume of the Si–Br bond for bromotriphenylsilane (**VIII**) was obtained by formula (8):

$$\Delta V(SiBr) = {}_{\infty}V_2[(CH_3)_3SiBr] - 3\Delta V(SiCH_3). \quad (8)$$

Here ${}_{\infty}V_2[(CH_3)_3SiBr]$ is the molar volume of bromotrimethylsilane (Table 3). The additive molar volumes of triarylphosphines **X–XVIII** and their oxides **XIX–XXIII** and sulfides **XXV–XXX** were calculated by formula (9):

$$V_{ad} = {}_{\infty}V_2[(C_6H_5)_3PR] + 2\,V(X) + V(Y). \quad (9)$$

Here R is lone pair, O, or S; ${}_{\infty}V_2[(C_6H_5)_3PR]$, molar volume of the parent compounds for series **X, XX**, and **XXVII** (Table 1); and V(X) and V(Y), increments of molar volumes of substituent groups in the aromatic rings (Table 2).

The additive molar volumes of the parent compounds in series **X–XVIII, XX–XXIII**, and **XXV–XXX**, viz. triphenylphosphine (**X**), triphenylphosphine oxide (**XX**), and triphenylphosphine sulfide (**XXVII**), were calculated by subtracting nine increments of molar volume of the alkyl C–H bond from (Table 2) and adding three increments of molar volume of the phenyl to the molar volumes of the model compounds trimethylphosphine, trimethylphosphine oxide, or trimethylphosphine sulfide, respectively (Table 3). The additive molar volume of dimethyl(phenyl)phosphine oxide (**XXIV**) was btained by subtracting three increments of molar volume of the alkyl C–H bond from (Table 2) and adding one increment of molar volume of the phenyl group to the molar volume of trimethylphosphine (Table 3).

The additive molar volumes for phosphazo compounds **XXXI–XXXIII** proved to be difficult to evaluate because of the lack of the increment of molar volume of the P–N bond. We also failed to find data for appropriate model compounds, necessary for assessing this increment. We noted that the van der Waals radii of oxygen and nitrogen are close to each other (r_O 1.40 Å, r_N 1.50 Å) [26]. In view of the fact that these atoms have close electronegativities, we took triphenyl-phosphine oxide for the model of the $(C_6H_5)_3P{=}N$ fragment in **XXXI–XXXIII**, under the assumption that the increments of molar volumes of the P=N and P=O bonds, as well as the conformations of the $(C_6H_5)_3P$ fragments in phosphazo compounds

Table 3. Molar volumes at infinite dilution for model compounds

Compound	Solvent	β	${}_\infty V_2$, $cm^3\ mol^{-1}$	Reference
Dichlorodimethylsilane	CCl_4	–0.481	120.6	[22]
Trichloro(methyl)silane	CCl_4	–0.247	117.6	[22]
Chlorotrimethylsilane	CCl_4	–0.829	125.4	[22]
	Benzene	–0.027	127.7±0.3	[4]
Bromotrimethylsilane	Benzene	0.238	133.6±2.2	[4]
Trichlorosilane	CCl_4	–0.16	99.2	[3]
Trimethylphosphine	Dioxane	–0.348	99.8	[23]
Trimethylphosphine oxide	Benzene	0.145	90.1±0.3	[23]
	Dioxane	–0.037	92.9±0.4	
Trimethylphosphine sulfide	Benzene	0.157	104.3±0.8	[23]
	Dioxane	–0.009	106.1	
Triphenylamine	Benzene	0.216	151.9±3.0	[5]
Trimethylarsine	Dioxane	0.087	106.6±2.4	[23]
Trimethylarsine oxide	Benzene	0.426	89.3±3.7	[23]
	Dioxane	0.323	89.6±3.6	
Trimethylarsine sulfide	Benzene	0.399	104.7±6.9	[23]
	Dioxane	0.277	106.9±2.8	
Dimethyl disulfide	CCl_4	–0.470	87.4±0.4	[12]
Dimethyl sulfide	CCl_4	–0.818	71.2±2.2	[13]
Dimethyl sulfoxide	CCl_4	–0.391	68.6±1.2	[15]
Dimethyl sulfone	Benzene	0.326	72.6±0.9	[15]
Dimethyltellurium dichloride	Benzene	0.55	117.7	[9]
Trimethylamine	Benzene	0.334	90.2	[24]
Diphenylamine	Benzene	0.216	151.9±3.0	[25]

and triphenyl-phosphine are close to each other. Moreover, it is obvious that the P=N bond contributes little into the molar volumes of **XXXI–XXXIII**. In this connection the molar volumes of these compounds were calculated by formula (10):

$$V_{ad} = {}_\infty V_2[(C_6H_5)_3PO] + V(R). \quad (10)$$

Here ${}_\infty V_2[(C_6H_5)_3PO]$ is the molar volume of triphenylphosphine oxide (**XX**) (Table 1); V(R), increments of molar volumes of the fragments N–C_6H_5Br-4 in **XXXI**, N–C_6H_5I-4 in **XXXII**, and N–$C_6H_5NO_2$-4 in **XXXIII**, calculated by formula (11):

$$V(R) = 1/3\ {}_\infty V_2[N(C_6H_5)_3] + V(X). \quad (11)$$

Here ${}_\infty V_2[N(C_6H_5)_3]$ is the molar volume of triphenylamine (Table 3); V(X), increment of molar volume of the substituent group in the aromatic ring (Table 2).

The additive molar volumes V_{ad} of triphenylarsine and its oxide and sulfide **XXXIV–XXXVI** were calculated similarly to those of triphenylphosphine and its oxide and sulfide, starting from the molar volumes of trimethylarsine and its oxide and sulfide (Table 2) instead of those of trimethylphosphine, trimethylphosphine oxide, and trimethylphosphine sulfide (Table 3).

The additive molar volumes V_{ad} of the sulfur compounds: diaryl disulfide **XXXVIII**, diaryl sulfides **XL–XLV**, diaryl sulfoxide **XLVII**, and diaryl sulfones **XLIX–LVI** were calculated by a common formula (12):

$$V_{ad} = {}_\infty V_2(model) + nV(X) + V(Y). \quad (12)$$

Here ${}_\infty V_2$(model) are the molar volumes of diphenyl parent compounds **XXXVII, XXXIX, XLVI**, and **XLVIII** (Table 1), respectively; and V(X) and V(Y), increments of molar volumes of the substituent groups in the aromatic ring (Table 2).

The additive molar volumes V_{ad} of compounds **XXXVII, XXXIX, XLVI**, and **XLVIII** were calculated by formula (13):

$$V_{ad} = V(\text{bridge}) + 2V(C_6H_5). \quad (13)$$

Here V(bridge) is the increment of molar volume of the bridging group, calculated as a difference between the ${}_{\infty}V_2$ of model dimethyl derivatives (Table 3) and $6\Delta V_{CH}$. The resulting V(bridge) values are listed in Table 2.

The additive molar volumes V_{ad} of organotellurium halides **LIX–LXIII** were calculated by formula (14):

$$V_{ad} = {}_{\infty}V_2(\textbf{LVIII}) + V(X). \quad (14)$$

Here ${}_{\infty}V_2$(**LVIII**) is the molar volume of diphenyltellurium dichloride (**LVIII**) (Table 1); and V(X), increment of molar volume of the substituent group in the aromatic ring (Table 2).

Methyl(*p*-tolyl)telludium dichloride (**LVII**) was analyzed separately. Its additive molar volume V_{ad} was calculated by subtracting three increments of molar volume of the alkyl C–H bond from and adding the increments of molar volumes of the Ph and CH_3 groups (Table 2) to the molar volume of dimethyltellurium dichloride (Table 3).

The additive molar volume V_{ad} of the parent compound of series **LIX–LXIII,** viz. diphenyltellurium dichloride (**LVIII**), was calculated by formula (15):

$$V_{ad} = {}_{\infty}V_2[Cl_2Te(CH_3)_2] - 6\Delta V_{CH} + 2V(C_6H_5). \quad (15)$$

Here ${}_{\infty}V_2[Cl_2Te(CH_3)_2]$ is the molar volume of dimethyltellurium dichloride (Table 3); the other values were the same.

The additive molar volumes V_{ad} of compounds **LXIV–LXVIII** and **LXX** having two bridging groups were calculated by formula (16):

$$V_{ad} = 2{}_{\infty}V_2(C_6H_6) - 4\Delta V_{C_{ar}H} + V(A) + V(B). \quad (16)$$

Here ${}_{\infty}V_2(C_6H_6)$ is the molar volume of benzene (Table 3); ΔV_{CarH}, increment of molar volume of the C–H bond in the aromatic ring (Table 2); and V(A) and V(B), increments of molar volumes of the corresponding bridging groups: C–CH_2–C, C–S–C, C–SO–C, C–SO_2–C, C–O–C, and C–N(CH_3)–C. The way of calculation of the increments for the C–S–C, C–SO–C, and C–SO_2–C bridging groups is described above (Table 2). The increments for C–CH_2–C and C–O–C we found previously (Table 2). The increment of molar volume of the C–N(CH_3)–C bridging group was calculated by formula (17):

$$V[C–N(CH_3) – C] = {}_{\infty}V_2[(CH_3)_3N] - 6\Delta V_{CH.} \quad (17)$$

Here ${}_{\infty}V_2[(CH_3)_3N]$ is the molar volume of trimethylamine (Table 3).

The additive volume V_{ad} of compound **LXIX** was calculated by formula (18):

$$V_{ad} = {}_{\infty}V_2[NH(C_6H_5)_2] - 2\,\Delta V_{C_{ar}H} + V(C–S–C). \quad (18)$$

Here ${}_{\infty}V_2[NH(C_6H_5)_2]$ is the molar volume of diphenylamine (Table 3); the other detonations are the same.

The additive molar volume V_{ad} of compound **LXXI** was calculated by formula (19):

$$V_{ad} = {}_{\infty}V_2[N(C_6H_5)_3] - 2\Delta V_{C_{ar}H} + V(C–S–C). \quad (19)$$

Here ${}_{\infty}V_2[N(C_6H_5)_3]$ is the molar volume of triphenylamine (Table 3); the other denotations are the same.

The resulting additive volumes V_{ad} and respective experimental ${}_{\infty}V_2$ values are given in Table 1.

The calculated V_{ad} of **arylsilanes I–IX** fairly fit the experimental ${}_{\infty}V_2$ values (Table 1). An especially good fit is observed for compounds **I–III, V, VIII**, and **IX**. Obviously, rotating aromatic rings are fairly well solvated. Probably, molecules **IV, VI**, and **VII** whose experimental ${}_{\infty}V_2$ values are apprwciably higher than V_{ad} involve some molecular volume inaccessible for solvents. Comparison of the experimental and calculated values also suggests that phenylsilanes **IV–IX** acoplanar in solutions. Had such acoplanarity been lacking, the molecular volume inaccessible for solvent molecules would have been much larger.

As seen from Table 1, with **triphenylphosphine, its oxides and sulfide, and phosphazo compound X–XXXIII,** the additive molar volumes calculated on the basis of the parent compounds of series **X–XVIII, XIX–XXIII**, and **XXV–XXX**, viz. compounds **X, XX**, and **XXVII**, respectively, nicely fit the experimental ${}_{\infty}V_2$ values. This fact suggests that the conformation of the aryl nuclei in **XI–XVIII, XIX, XXI–XXIII**, and **XXV–XXVI, XXVIII–XXX** are the same as in triphenylphosphine (**X**), triphenylphosphine oxide (**XX**), and triphenylphosphine sulfide (**XXVII**). However, the experimental values are systematically higher than calculated. The V_{ad} values for the parent compounds of these series (compounds **X, XX**, and **XXVII**), starting from the data for trimethyl derivatives (Table 3), shows that rotating aromatic rings are fairly well solvated but still not so effectively as the starting model compounds which were used for assessing bond and group increments (Tables 2 and 3). The same

relates to dimethyl(phenyl)phosphine oxide (**XXIV**). Probably, these molecules, too, have some volume inaccessible for solvent molecules, which results in that ${}_{\infty}V_2$ are higher than V_{ad}. This evidence allows us to conclude that triarylphosphines and their oxides and sulfides **X–XXIII** and **XXV–XXX** are acoplanar in solutions. The calculated additive molar volumes for the short phosphazaryl series **XXXI–XXXIII** slightly worse fit the experimental values than in the above-considered cases. A probable reason is that the model compound was triphenylphosphine oxide (**XX**) whose aryl nuclei have similar orientations in solutions (C_3 symmetry) [7, 8], whereas the aryl nuclei in triphenylphosphazo derivatives are nonequivalent [11]. Nevertheless, the calculated values are close enough to experimental for us to be safe to state that the aryl rings both in the $P(Ph)_3$ and NAr fragments of **XXXI–XXXIII** are acoplanar.

In **triphenylarsine and its oxide and sulfide XXXIV–XXXVI**, like in the above-considered compounds, the experimental ${}_{\infty}V_2$ values are higher than calculated V_{ad}. Probably, here, too, the rotating aromatic rings are solvated but no strongly as in the starting model compounds–trimethylarsine and its oxide and sulfide, which were used for data for the C_3AsR groups (Tables 2 and 3). Nevertheless, the aryl rings in these compounds are acoplanar, since they are solvated, and the divergence between calculation and experiment is not so large.

As to **diaryl disulfides XXXVII, XXXVIII and diaryl sulfides XXXIX–XLV**, then, as seen from Table 1, the additive molar volume of diaryl disulfide **XXXVIII** with data for diphenyl disulfide (**XXXVII**) nicely fits the experimental value (ε_V 1.3%), implying similar conformations of these two compounds. The additive molar volume of **XXXVII**, calculated on the basis of dimethyl disulfide (Table 3), is slightly higher compared to experiment (ε_V 10.8%). This result suggests that the aryl nuclei in **XXXVII** have some volume inaccessible for solvent molecules. Probably, in the *gauche* structure of this compound [12] the phenyl ring planes are proximate enough to form this inaccessible volume. But the principal conclusion is that the aromatic nuclei in compounds **XXXVII, XXXVIII** are acoplanar to each other.

The additive calculation for diaryl sulfides **XL–XLV** on the basis of the parent compound of the series, diphenyl sulfide **XXXIX**, fairly well reproduces the experimental molar volumes. This result suggests that the aryl rings in these molecules have the same conformations as in **XXXIX**. The calculated molar volume for parent compound **XXXIX** is lower than experimental (ε_V 12.0%), implying the presence of some free volume inaccessible for solvent molecules. However, this divergence is not too large, and, therefore, the aryl nuclei in **XXXIX** and also in the other members of series **XL–XLV** are acoplanar.

Diaryl sulfoxides XLVI and XLVII. The additive calculation for diaryl sulfoxide **XLVII** (Table 1) on the basis of diphenyl dulfoxide **XLVI** results in a good fit of additive and experimental values (ε_V 0.8%), which points to similar molecular conformations. The additive molar volume of **XLVI**, calculated with the dimethyl sulfoxide model (Table 3), is slightly lower than the experimental value (ε_V 13.5%), which suggests that there are some voids between the aryl nuclei, inaccessible for solvent molecules. But here, too, it is safe to state that the aromatic rings in molecules **XLVI** and **XLVII** are acoplanar to each other.

The situation with the additive and experimental molar volumes of **diaryl sulfones XLVIII–LVI** is generally similar to the situation with diaryl sulfides **XXXIX–XLV**. All the additive molar volumes calculated on the basis of diphenyl sulfone (**XLVIII**), except that of compound **LV**, fit well the experimental values (ε_V 0.4–4.7%). From this it follows that the molecular conformation of this series compounds are the same as the conformation of the parent compound of the series, i.e. **XLVIII,** and the aryl nuclei are turned with respect to the bridging group roughly in the same way as in **XLVIII**, i.e., as shown in [15, 16], they are perpendicular to the C–S–C plane of the bridging group. In molecule **LV**, the bridging C–S bond is probably shielded by *ortho* substituents; as a result, the experimental molar volume is lower than additive. Earlier we observed the same effect of shielding of bridging bonds and groups in diphenyls and other systems [2, 20]. The additive molar volume of **XLVIII** with dimethyl sulfone as model (Table 3) is slightly lower than experimental (ε_V 14.1 and 14.6%), which points to the presence of some volume hardly accessible for solvent molecules. Nevertheless, it is still obvious that the aromatic rings in this molecule are acoplanar with respect to the bridging group.

The V_{ad} values for **organyltellurium halides LIX–LXIII** are listed in Table 1. Comparison of ${}_{\infty}V_2$ and V_{ad} shows that the additivity condition of molar volumes in organyltellurium halides in solution is roughly fulfilled, but the relative uncertainty in the additive values compared to experimental reaches 19%. The

calculated molar volumes usually do not diverge so far from experimental, as we showed above. Probably, solvation of the organic groups in dioranyltellurium dihalides is slightly hindered. The aromatic rings in **LVIII–LXIII** reside in the equatorial plane of the tellurium trigonal bipyramid, and the angles between the C–Te–C bonds are between 90° and 100° [9]. The rings are closer to each other than in arylmethanes and silanes. The valent angles in the bridging groups are about 109° (sp^3 hybridization). Probably, because of the mutual proximity between aryls in tellurium compounds, there is some volume between them, which is inaccessible for solvent, and, therefore, their ${}_{\infty}V_2$ values are higher than V_{ad}. This effect is especially pronounced in compounds with two bridging groups.

As seen from Table 1, the experimental ${}_{\infty}V_2$ values in **compounds LXIV–LXXI having two bridging groups** systematically and considerably exceed V_{ad} (ε_V 15.7–36.5%). As described above, the increments of molar volumes of bridging groups we calculated using as models compact molecules readily solvated from all sides. Judging from the structural formulas of compounds **LXII–LXIX**, here such solvation is already impossible and it is clear a priori that these molecules should involve additional intramolecular volumes inaccessible for solvent molecules. Evince for this suggestion is provided by the fact that ${}_{\infty}V_2$ are much higher than V_{ad}. Compounds with two bridging groups can serve as models of an extreme case of mutual proximity of the aryl rings in diaryl systems with one bridging group. Our results suggest that the weaker the aryl ring planes deviate from the C–A–C or C–B–C planes of the bridging groups, the larger is the molecular volume inaccessible for solvating solvent and the more ${}_{\infty}V_2$ values exceed V_{ad}.

The latter conclusion implies that the aryl rings in the studied systems are acoplanar, since their experimental molar volumes not so strongly diverge from those calculated by the additive scheme. This is possible if the aryl ring are sufficiently well solvated, and the additivity of molar volumes is roughly fulfilled.

The conclusion on the acoplanarity of compounds **I–LXXI** is consistent with the results obtained by other physical methods for solutions.

The phenyl rings in **arylsilanes I–IX** deviate from the plane of the CSiC bond angle by 40°–60°, which suggests contacting van der Waals spheres of the *ortho*-hydrogen atoms of these rings. Obviously, such molecular conformation makes the phenyl rings accessible from all sides, and they are well solvated [3]. According to the dipole moments and Kerr effects in CCl_4, the aryl deviation angles in the compounds studied are as follows, deg: **IV**, 40; **V**, 51; **VII**, 53, **IX**, 63; and **II**, the C_{sp3}–Si bond is eclipsed by the aryl ring plane. According to the IR spectra, the deviation angles in compounds **IV** and **V** are 37° and 42°, respectively [3]. According to the dipole moments and Kerr constants in benzene, the orientation of the aryl nuclei in compounds **VI–VIII**, too, are virtually independent of substituent **X**: The deviation angles in **VI, VII**, and **VIII** are 44°, 46°, and 50°, respectively. In symmetrical molecules (symmetry axis C_3), the angle is counted from the position when the ring is eclipsing the C_3 symmetry axes in the molecule [4]. From the dipole moments and Kerr constants in CCl_4 and benzene, measured later, the following aryl deviation angles were obtained in the framework of the conrotatory model, deg: **IV**, 42 ± 3; **V**, 52 ± 1; **VI**, 34 ± 4; and **VII**, 51 ± 3 [27].

The following data were obtained for **tiphenylphosphine, tiphenylphosphine oxide, and tiphenylphosphine sulfide derivatives X–XXXIII.** Bulgarevich et al. [6] showed by vibrational spectroscopy that the phenyl rings in triphenylphosphine (**X**) in melt are equivalent. According X-ray diffraction data in the same work, the aryl rings deviate from the possible C_3 symmetry axis by 24°, 56°, 29° in triphenylphosphine; 12°, 76°, and 14° in triphenylphosphine oxide (**XX**) (monoclinic syngony) and 25°, 59°, and 21° (rhombic syngony); and 50°, 56°, and 11° in triphenylphosphine sulfide (**XXVII**). According to the dipole moments and Kerr constants in benzene, the aryl deviation angles are as follows, deg: **X**, 59 [5]; **XVI**, 68 [6]; **XIX**, 60; **XX**, 55; **XXI**, 65; **XXII** 52; **XXIII**, 49 [7]; **XXV**, 58; **XXVI**, 56; **XXVII**, 61; **XXVIII**, 59; **XXIX**, 59; **XXX**, 60 [10]; **XXXI**, 35; **XXXII**, 16; and **XXXIII**, 90 [11]. Whereas in monoaryl derivatives the aromatic ring and phosphoryl group reside in the same plane, in triaryl derivatives the phenyl rings deviate from this plane, and, therewith, the deviation angle are dependent, to a certain degree, from the substituent in the aryl ring [6]. Aroney et al. [8] reported the following angles obtained from the dipole moments and Kerr constants in the framework of the C_3 symmetry model, deg: **XX**, 61; and **XXVII**, 63.

From the dipole moments and Kerr constants in benzene of **triphenylarsine and its oxide and sulfide** (**XXXIV–XXXVI**), the angle in **XXXIV** was estimated at 53° or 41° [5]. Compounds **XXXV** and **XXXVI** have the same conformation as triphenylarsine **XXXIV** (angle 50°) [8].

Diaryl disulfides XXXVII and XXXVIII has the *gauche* structure. The dihedral angles between the C'–S–S and S–S–C" planes are 68°–85°, and the phenyl nuclei are roughly eclipsing the S'–S bond [12].

With **diaryl sulfides XXXIX–XLV,** the following data were obtained. From the IR spectra the angle in compound **XXXIX** was estimated at 48°. The equivalence of the rings, which is deduced from spectral data, may be associated with either their fast and independent rotation, which is impossible by steric reasons, or with synchronous (conrotatory) torsion. [28]. The dipole moments and Kerr constants give, in the framework of the conrotatory model, for compound **XXXIX** the angle of 37° in benzene and 42° in CCl_4. The angle was counted from the bridging group plane [13]. Bulgarevich et al. [14], based on the dipole moment and Kerr constant data, showed that diaryl disulfide in dioxane are fairly described in terms of the conrotatory model. In compounds containing *ortho* substituents, the ring planes are as distant from each other as possible. In the framework of the conrotatory model, the following angles were obtained, deg: **XL**, 58 or 51; **XLI**, 55; **XLII**, 13; **XLIII**, 35 or 7; **XLIV**, 63 or 52; and **XLV**, 43.

Diaryl sulfoxides XLVI and XLVII were studied by the methods of dipole moments and Kerr constants. It was found that the phenyl rings in diphenyl sulfoxide (**XLVI**) are perpendicular to the C–S–C plane [15], and the rings in compound **XLVII** in dioxane, too, perpendicular to the plane of the bridging C–S–C group [14].

Diphenyl sulfones XLVIII–LVI. According to the dipole moment and Kerr constant in CCl_4, the rings in diphenyl sulfone (**XLVIII**) are perpendicular to the C–S–C plane [15]. As shown in [16], most sulfones in dioxane exist as orthogonal or planar orthogonal conformers, or as an equilibrium mixture of these two conformers. The orthogonal conformation is characteristic of compounds **XLVIII** and **LIII–LV**, and the conformational equilibrium is characteristic of compounds **XLIX** and **LVI**. In compound **LI**, the conrotatory orientation of the rings takes place, torsion angle 51°.

Organotellurium halides LV–LXI were studied by X-ray diffraction. Compounds **LVIII** [29] and **LXIII** [30] are trigonal bipyramids with equivalent axial Te–Hlg bonds; the this, equatorial ligand is the lone electron pair (LEP) of tellurium. The ClTeCl angles are smaller than 180°, which suggests that chlorines are stronger repulsed by the tellurium LEP rather than by the equatorial organic groups.

The following information was obtained about **compounds with two bridging groups LXIV–LXXI**. From the dipole moments and Kerr constants in CCl_4, the dihedral angles between the ring planes were estimated at 135°±8l° for thioxanthene (**LXIV**) and 138°±6° for phenoxathiine (**LXVIII**) [17]. From the dipole moments in benzene, the following angles were obtained, deg: thianthrene (**LXV**) 144±8; α-thianthrene dioxide 139±10; β-thianthrene dioxide 130±10 (**LXVI**); and thianthrene tetroxide (**LXVII**) 140±8. From the dipole moments and Kerr constants in benzene, the angles were estimated at the following values, deg: thianthrene (**LXV**) 140±10; α-thianthrene dioxide 138 and β-thianthrene dioxide 138 (**LXVI**); and thianthrene tetroxide (**LXVII**) 130 [18]. According to the dipole moments and Kerr constants in benzene, the dihedral angles between the benzene ring planes in **LXIX–LXXI** are 150°±7° [19]. As shown in [18], the solid-phase dihedral angles in **LXV** and **LXVIII** are 128° and 138°, respectively.

We demonstrated a possibility of considerably simplifying the methods for determination of dipole moments and Kerr constants for compounds whose molar volumes can be calculated by our developed additive scheme. Table 1 compares the Kerr constants and dipole moments, determined by the simplified scheme, with the experimental data. As seen, the results of the simplified determination are mostly fit the reported experimental values. This fact gives us grounds to conclude that in most cases the methods for determination of μ and ${}_{\infty}({}_{m}K_2)$ can be much simplified by omitting determination of the density of the solution. Instead, additive molar volumes of solutes are calculated, and modified Le Fevre and Fujita formulas are used [21]. The molar polarizabilities ${}_{\infty}P_2$ of compounds **XI–XVIII** were calculated by formula (20), using the coefficients for the concentration scale in molar fractions x, reported in [6].

$$ {}_{\infty}P_2 = \left(\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}\right){}_{\infty}V_2 + V_1\frac{3\alpha_m\varepsilon_1}{(\varepsilon_1 + 2)^2}\cdot \qquad (20) $$

Here ε_1 is the dielectric constant of the solvent; α_m, concentration coefficient; and V_1, molar volume of the solvent.

The simplified formulas for Kerr constants and dipole moments for the contration scale in weight fractions we reported earlier in [21].

EXPERIMENTAL

The experimental concentration dependences of solution densities, required for determination of molar volumes at infinite dilution ${}_\infty V_2$ were taken from [4, 5, 8, 12, 13, 15, 17–19]. Systems containing no less than five concentrations and their corresponding densities and other properties of solutions were chosen. The linear dependences $\rho_{12} = \rho_1(1 + \beta\omega)$ were treated by the least-squares procedures to find β, and the correlation coefficients were no worse than 0.99.

For compounds **I–VII, IX, XIX–XXIII**, and **XXV–XXX** in carbon tetrachloride, **VIII, XI–XVIII, XXIV**, and **LVII–LXIII** in benzene, and **XXXI–XXXIII, XL–XLV**, and **XLVII–LVI** in dioxane we took the author's β values [3, 4, 6, 7, 9–11, 14, 16] because of the lack of concentration dependences of ρ_{12} in their works.

The experimental molar volumes ${}_\infty V_2$ for compounds **I–X** and **XIX–LXXI** were calculated by the extrapolation formula (21) we derived in [21].

$$ {}_\infty V_2 = \frac{M_2(1 - \beta)}{\rho_1} . \qquad (21)$$

Formula (21) corresponds to the concentration dependence in weight fractions ω: $\rho_{12} = \rho_1(1 + \beta\omega)$.

The experimental molar volumes ${}_\infty V_2$ of compounds **XI–XVIII** were calculated by the extrapolation formula (22) which we also derived in [21].

$$ {}_\infty V_2 = \frac{M_2 - M_1\beta_m}{\rho_1} . \qquad (22)$$

Formula (22) corresponds to the concentration dependence in molar fractions x: $\rho_{12} = \rho_1(1 + \beta_m\omega)$.

In calculating the dipole moments and Kerr constants we made use of values that relate to the properties of solvents and solutions in the above-cited works, from which we also determined ${}_\infty V_2$ values for the compounds in hand.

The following solvent parameters were used: carbon tetrachloride, $\rho_1$1.58454 g cm^{-3}, ε_1 2.2270 at 25°C [12]; dioxane, ρ_1 1.02687 g cm^{-3}, ε_1 2.209 at 25°C [14]; benzene, ρ_1 0.87378 g cm^{-3}, ε_1 2.2725 at 25°C [4].

The dipole moments were measured in D and Kerr constants, in CGSE units (esu). The CGSE–SI conversion coefficients were as follows: 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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