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Molecular Polarizability of Organic Compounds and Their Complexes: LIX.[1] Molar Volumes, Intrinsic Atomic Solvation Radii, and Spatial Structures of Certain Conformationally Flexible Compounds in Solutions

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Abstract—The molar volumes and structures in individual liquids and solutions of a series of conformationally flexible compounds, such as alkanes and diaryl-substituted systems with sp^3-hybridized bridging atoms, were analyzed in terms of intrinsic solvation radii of atoms constituting the molecule. Intrinsic solvation atomic radii were determined for various molecules to show that they are larger than the van der Waals radii of the same atoms. An approach to parametrization of the intrinsic solvation radii of atoms constituting a molecule, using appropriate model compounds, was proposed. From the resulting values of intrinsic atomic solvation radii, the possible conformations of a series of diphenylmethanes, diphenylsilanes, diphenyl sulfides, diphenyl sulfoxides, and diphenyl sulfones in solutions were assessed.

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The hypothesis of intrinsic solvation radii was first proposed by Burdastykh [2]. Its essence is as follows. The molar volume of a solute at infinite dilution, reduced to one solute particle, is the molecular volume which has the meaning of the volume of a void occupied by this particle in the dynamic structure of the solvent. This volume includes the intrinsic volume of the particle, which can be treated as the van der Waals volume, as well as the so-called free volume [2]. The van der Waals shell is considered to be formed by mutually overlapping rigid atom-centered van der Waals spheres in accordance with the composition and supposed molecular structure [3]. The free volume of the void is equal to the volume occupied by the particle minus the van der Waals volume of this particle. It is assumed that the shape of the dynamic solvent volume accommodating the solute molecule repeats, to a certain extent, the shape of the van der Waals shell of the molecule. This is explained by the thermal motion of solvent molecules and, in the long run, by the solvent isotropy. Naturally, such a shape of the void can be considered to result from averaging over all possible positions of the nearest neighboring solvent molecules around the solute molecule. If the solute molecule undergoes conformational changes, its van der Waals shape will also change, thereby changing the molecular volume, as well as the volume and shape of the molecular void. In a similar way one can consider molecules in individual solvents and also self-solvation phenomena. Note that in due time the concept of van der Waals molecular volume has played a great role in the research in understanding molecular crystal structures [3].

To analyze the molecular volumes of solvated and self-solvated molecules, we have constructed a scheme of intrinsic radii of atoms constituting a molecule, which is analogous to the scheme of van der Waals radii. The additional volume occupied by a molecule in a liquid void is associated with the presence of some free space between the inner surface of the molecular void of the liquid and the surface of the van der Waals shell of the molecule residing in this void. Therefore, the intrinsic solvation radii of atoms should be larger than their van der Van der Waals radii. In the present

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

work the shape and intrinsic volume of the solvation shell of a molecule we consider by analogy with the shape and volume of a van der Waals shell.

According to [4], the molar volumes of compounds in inert solvents at infinite dilution ($_\infty V_2$) and the molar volumes of the corresponding individual liquids (V) are close to each other within the accuracy of determination of $_\infty V_2$. This fact suggests close values of the molar volumes of compounds irrespective of whether they are determined in solutions or in individual liquids [4]. The $_\infty V_2$ values for one and the same compound in different solvents, too, are close to each other [4]. From this it follows that the intrinsic solvation radii should not vary in going from one solvent to another, and to an individual liquid.

The hypothesis of intrinsic solvation radii has not yet received wide acceptance and has in fact been only used by Burdastykh [2] to assess correctly the structure of the transition state of the reaction of pyridine with ethyl iodide under a high pressure. Probably, the approach based on the hypothesis of intrinsic solvation radii is useful for quantitative or at least semiquantitative conformational assessment of organic molecules in solutions or individual liquids. The main goal of the present work was to determine the intrinsic solvation radii of a series of organic and organoelemental molecules in solutions for further analysis of their spacial structure.

The volumes of the van der Waals shells of molecules (V_{vdW}) were calculated using standard van der Waals radii [5] and bond length and angles, set in the ChemCraft program. The shells were designed based on the data on molecular conformations, published in [6–10]. The intrinsic solvation radii of atoms in various molecules were found using our developed special program based on the Monte Carlo method and designed for determination of the volumes of figures comprised of overlapping rigid spheres. The intrinsic solvation radii were considered as unknown values which were found by fitting the calculated molar volumes to experimental value. The fitting procedure involved addition to the van der Waals radius [5] of a certain target value Δ. Thus we determined solvation radii for a series of organic molecules. It must be emphasized that by solvation radius we mean the so-called intrinsic solvation radius. Neither solvent nor individual liquid molecules penetrate inside this radius. The calculated V_{vdW} values and experimental molar volumes of various compounds are listed in Table 1.

The partial molar [4, 11–15] and van der Waals molar volumes of molecules were also used to estimate the fraction of free molecular volume ε (%) by Eq. (1).

$$\varepsilon = 100\% \times (V - V_{\text{vdW}})/V. \quad (1)$$

Here V is the molar volume of a compound at infinite dilution $_\infty V_2$ or molar volume of an individual liquid $V_{\text{ind.l}}$; and V_{vdW}, van der Waals molar volume equal to the product of the van der Waals molecular volume on the Avogadro number.

For saturated hydrocarbon molecules the free void fraction ε was 45−52% and for aromatic hydrocarbons, 33−41%. Obviously, the intrinsic solvation radii of compounds will depend on this fraction. The relative stability of the ε value for organic molecules allows us to write an arbitrary formula for calculation of the the molar volume V from the van der Waals molar volume V_{vdW} [Eq. (2)].

$$V - (1 + \varepsilon/100)V_{\text{vdW}}. \quad (2)$$

Here ε can be can be set at about 36% for aromatic and at 47% for saturated hydrocarbon molecules.

The fact that the ε values for a series of single-type compounds are close to each other (Table 1) allows intrinsic solvation radii for one compounds to be used to calculate molar volumes for other compounds.

Note that as the hydrocarbon chain length in alkanes and the π-system length in unsaturated molecules increase, the ε value tends to decrease (Fig. 1). The $\ln \varepsilon \infty 1/n$ trend was used to estimate ε for the alkane series at $n \rightarrow \infty$ at 39.7% (correlation coefficient 0.99).

In particular, note that carbon tetrachloride in which the most part of partial volumes of substances was determined, as an individual liquid has, according to [16] and our calculations, the free volume comprising 42.6% of its van der Waals volume.

Determination of intrinsic solvation radii for alkanes. In our approximation, the intrinsic solvation atomic radius of an alkane molecule was found by fitting the calculated molar volume of a self-solvation shell to the partial molar volume of the alkane as an individual liquid. The fitting was performed by adding to the van der Waals radii of carbon and hydrogen of a target value Δ which was considered the same for these two atoms. Only sterically accessible staggered conformations were considered under the assumption of their equal populations. In this way we determined

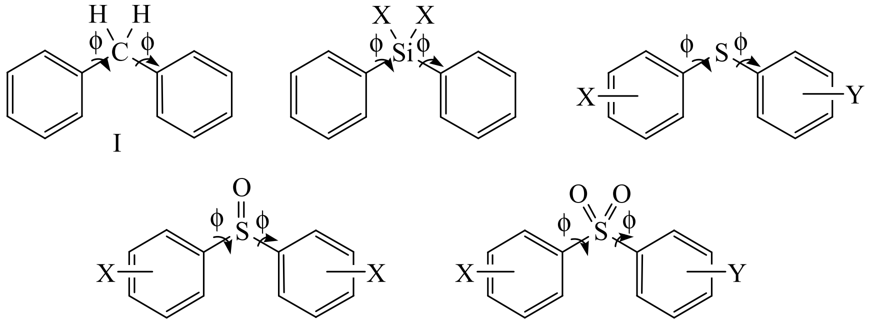
Table 1. Intrinsic molar volumes of molecules and fractions of the molar volume of free void in solutions and individual liquids

Compound	$_{\infty}V_2$ or $V_{\mathrm{ind.l}}$, cm^3 mol^{-1}	V_{vdW}, cm^3 mol^{-1}	ε, %	T, °C	Solvent or individual liquid
Diphenylmethane	163.0	102.7	36.4	25	CCl_4 [4]
Diphenyl sulfone	169.4	111.8	34.0	25	Dioxane [11]
Diphenylsilane	186.0	112.1	39.7	25	CCl_4 [11]
Triphenylphosphine oxide	238.3	149.9	37.1	25	″ [11]
Tris(*p*-methylphenyl)phosphine oxide	271.1	184.8	31.8	25	″ [11]
Triphenylphosphine	229.6	147.2	35.9	25	Benzene [11]
Triphenylsilane	242.0	154.0	36.4	25	CCl_4 [11]
Nitrobenzene	92.24	61.7	33.1	25	″ [12]
p-Nitrodiphenyl	176.8	105.2	40.5	25	″ [13]
p-Chlorodiphenyl	163.6	103.4	36.8	25	″ [13]
Stylbene	170.9	110.8	35.1	25	″ [14]
Benzalaniline	168.6	107.6	36.1	25	″ [14]
p-Chlorobenzalaniline	186.4	117.2	37.1	25	″ [14]
p-Methylbenzalaniline	184.2	117.9	35.9	25	″ [14]
p-Nitrobenzalaniline	183.1	118.7	35.1	25	″ [14]
Benzene	88.9	50.4	43.2	25	″ [12]
Diphenyl	141.7	93.6	33.9	25	″ [13]
Naphthalene	123.1	77.0	37.4	25	″ [13]
Anthracene	160.6	103.3	35.6	25	″ [15]
Toluene	103.8	60.6	41.6	25	″ [12]
Carbon tetrachloride	96.5	55.4	42.6	25	Individual liquid [16]
Butane	100.4	47.6	52.6	20	The same
Pentane	115.2	57.6	50.0	20	″
Hexane	130.5	67.6	48.2	20	″
Heptane	146.6	77.7	47.0	20	″
Octane	162.6	87.7	46.1	20	″
Nonane	178.8	97.8	45.3	20	″
Decane	194.9	108.0	44.5	20	″
Undecane	211.2	118.2	44.0	20	″
Dodecane	227.5	128.4	43.6	20	″
Tridecane	243.8	138.6	43.1	20	″
Tetradecane	260.1	148.1	43.0	20	″
Pentadecane	276.4	158.3	42.2	20	″

intrinsic solvation radii for carbon and hydrogen in linear alkane molecules (Table 2). As would be expected, as the number of atoms in a hydrocarbon molecule increases, the solvation radii of carbon and hydrogen regularly decrease up to decane, after which they tend to decrease only slightly. Figure 2 presents the dependence of the increment Δ to the van der Waals radii of carbon and hydrogen, required to fit corresponding intrinsic solvation radii, on the number *n* of carbon atoms in alkane molecules.

The $\ln \varepsilon \infty 1/n$ trend was used to estimate the Δ limit at $n \to \infty$ at 0.503 Å (correlation coefficient 0.99). This value is reached already for the tenth member of the butane → pentadecane series.

Intrinsic solvation radii and structure of diaryl derivatives of compounds with an *sp*^{3}-hybridized bridging atom. We have analyzed the following diaryl derivatives **I**–**XI** with *sp*^{3}-hybridized bridging atoms:



X = H (**II**); X = Cl (**III**); X = Y = H (**IV**); X = Y = NO$_2$ (**V**); X = Y = H (**VI**); X = H, Y = Cl (**VII**); X = Y = H (**VIII**); X = 4-Cl, Y = H (**IX**); X = Y = 4-Cl (**X**); X = Y = 4-NO$_2$ (**XI**).

Before considering these systems in detail, we would like to advance some speculations concerning the method of molar volumes and intrinsic solvation radii which were planned to be used for assessing the conformations of compounds **I**–**XI** in solutions. As mentioned above, we construct a molecular figure analogous to the van der Waals figure but the intrinsic solvation radii in which are larger than the van der Waals radii. Obviously, in a theoretical consideration of the changes of molar volumes due to ring rotation, at the same torsion angles the intrinsic solvation radii of proximate valence-nonbonded atoms will overlap and, therefore, the calculated molar volumes will depend on these angles. However, beginning with certain large torsion angles, the intrinsic solvation radii will no longer overlap, and, as a result, the calculated molar volumes will no longer depend on torsion angles in their certain range. If the experimental molar volume corresponds to this range, the method of molar volumes becomes structurally insensitive and allows one no more than to judge about the "solvation accessible" range of torsion angles in a molecule and also to say whether the molecule in a liquid is acoplanar with respect to rotating fragments.

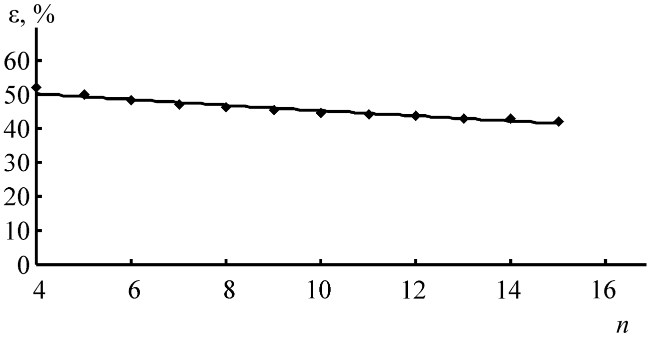


Fig. 1. Dependence of the free void fraction ε of alkanes as individual liquids on the number *n* of carbon atoms in the molecular chain.

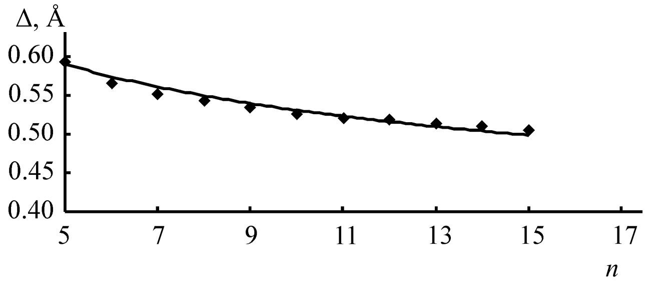
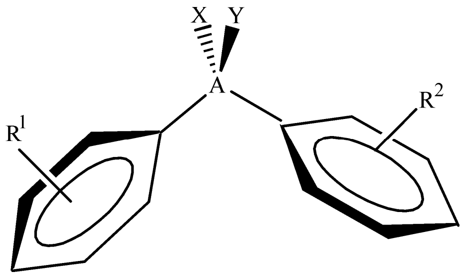
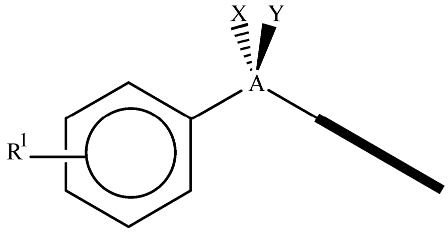


Fig. 2. Dependence of the increments Δ to the van der Waals radii of hydrogen and carbon, required to reach their intrinsic solvation radii, on the number *n* of carbon atoms in the alkane molecules.

(a)



(b)



The conformations of diaryl derivatives **I**–**XI** were previously studied by physical methods in [6–10]. Many of these molecules characteristically prefer two conformaions: (a) both rings are rotated in a controtatory manner with respect to the C_{Ar}–A–C_{Ar} plane (helical or propeller conformation, C_2 symmetry) and (b) one ring is coplanar to the C_{Ar}–A–C_{Ar} plane and the other ring is almost orthogonal to this plane (planar–orthogonal conformation) [17].

Bridging atom A in these structures can be carbon, silicon, and sulfur and substituents X and Y here are hydrogen, chlorine, oxygen, or lone electron pairs (LEPs). In our consideration we assumed that the molecules are present largely in the helical conformation (a), as evidenced by numerous experimental data [17].

We assume that the intrinsic solvation radii of hydrogen and carbon in phenyl rings can be set as parameters obtained from appropriate model compounds. Intrinsic solvation radii for ring substituents in the diaryl derivatives in study can be deduced from data for diphenyl derivatives [13], since in molecular dimensions diaryl derivatives **I**–**XI** are closer to diphenyl than, say, to substituted benzenes. Since the *para* ring substituents do not overlap by their intrinsic solvation radii on ring rotation, we suggested that the dependences of calculated molar volumes on ring torsion angles for the *para*-substituted diaryl derivatives could be obtained from the same dependences for unsubstituted molecules by adding some constant values which are additive increments of the molar volumes of the substituents.

To find the intrinsic solvation radii of substituents in diphenyl, we based on its conformation in the gas phase and in solutions in van der Waals liquids (the dihedral angle between rings is 44° [7]), as well as the molar volumes of diphenyl and substituted diphenyls in solutions [13]. The intrinsic solvation radii of carbon and hydrogen in diphenyl [r_C 2.12 Å, r_H 1.62 Å] were found by adding the same increment Δ to the van der Waals radii of hydrogen and carbon in diphenyl so that to fit the calculated molar volume of the latter molecule to the experimental value. Further on, with fixed values of the intrinsic solvation radii of carbon and hydrogen in the rings, we performed the parametrization of the intrinsic solvation radii of substituents. The same procedure was applied to find the intrinsic solvation radii of substituents in benzene rings from the molar volumes of monosubstituted benzenes in solutions (Table 3).

As seen from Table 3, in most cases the intrinsic solvation radii of the same atoms in substituents in benzene and diphenyl are close to each other within the experimental error in the determination of molar volumes in solutions.

Table 2. Intrinsic solvation radii of carbon and hydrogen in alkanes

Compound	Intrinsic solvation radii, Å[a]	
	r(C), Å	*r*(H), Å
Butane	2.331	1.831
Pentane	2.297	1.797
Hexane	2.281	1.781
Heptane	2.273	1.773
Octane	2.262	1.762
Nonane	2.254	1.754
Decane	2.250	1.750
Undecane	2.245	1.745
Dodecane	2.243	1.743
Tridecane	2.239	1.739
Tetradecane	2.236	1.736
Pentadecane	2.233	1.733

[a] The intrinsic solvation radii were calculated for the molecular conformations where the intramolecular torsion angles around ordinary C–C bonds were equal to 120°.

Table 3. Intrinsic solvation radii R_i of atoms in benzene, diphenyl, and their derivatives

Compound	${}_{\infty}V_2$, cm^3 mol^{-1} in CCl_4	Reference	van der Waals radii of substituents, r_i, Å [5]	Intrinsic solvation radii, R_i, Å
Benzene	87.3	[12]	r_H 1.20, r_C 1.70	R_C 2.18, R_H 1.68
Fluorobenzene	93.7	[12]	r_F 1.35	R_F 2.00
Chlorobenzene	101.6	[12]	r_{Cl} 1.80	R_{Cl} 2.24
Iodobenzene	111.0	[12]	r_I 2.15	R_I 2.45
Nitrobenzene	102.1	[12]	r_N 1.50, r_O 1.40	R_O 1.73, R_N 1.83
Diphenyl	147.1	[13]	r_H 1.20, r_C 1.70	R_C 2.12 Å, R_H 1.62 Å
4-Fluorodiphenyl	154.5	[13]	r_F 1.35	R_F 2.01
4-Chlorodiphenyl	163.6	[13]	r_{Cl} 1.80	R_{Cl} 2.28
4-Iododiphenyl	176.8	[13]	r_I 2.15	R_I 2.34
4-Nitrodiphenyl	185.7	[13]	r_N 1.50, r_O 1.40	R_O 2.15, R_N 2.25

Having found the intrinsic solvation radii of carbon and hydrogen using data for diphenyl, we performed the parametrization of the molar volumes of bridging groups AXY. With fixed values of the intrinsic solvation radii of the aryl rings, we fitted the intrinsic solvation radius of a bridging group to the partial molar volume of the corresponding parent compound **I**, **II**, **IV**, **VI**, or **VIII** at infinite dilution. In all the calculations, we used parameters for the conformations found by the dipole moment and Kerr effect methods (torsion angles of the phenyl rings: diphenylmethane 44º; diphenylsilane 50º; diphenyl sulfone 90º; diphenyl sulfoxide 90º; and diphenyl sulfide 37º) [8, 9]. If the central atom had substituents, the same increment Δ was added not only to the van der Waals radius of the central atom, but also to the van der Waals radii of the other atoms in the bridging group.

The resulting data show that, in general, the diphenyl parameters are well suited for estimating the molar volumes of diaryl derivatives, but sometimes the intrinsic solvation radii estimated by benzene and monosubstituted benzenes are more suitable. The choice depends on the bridging group and on the ring substituents. If a compound in study contains fairly strong electron-acceptor groups ($=SO_2$, $=SO$, NO_2, CN, etc.), it is better to use the intrinsic solvation radii estimated by diphenyl, while if the bridging group cannot be classed with acceptors, the intrinsic solvation radii estimated by benzene are better suited ones. Let us dwell in more detail on different classes of compounds.

Intrinsic solvation radii and possible conformations of diphenylmethane and diphenylsilanes. As shown in different works on the conformational analysis of diphenylmethane and diphenylsilanes, the mutual orientation of the aromatic rings in them is conrotatory [17]. According to the IR spectral data in [7], the torsion angle of the phenyl rings in diphenylmethane in a CCl_4 solution is 51° for the conrotatory conformation. The Kerr effect measurements in different solvents resulted in the following torsion angles of the phenyl rings in diphenylmethane in the conrotatory conformation: CCl_4 41°, chlorodiphenylmethane 33°, bromodiphenylmethane 38°, dichlorodiphenylmethane 50° [7]. Such orientations of the aryl ring imply that the latter are almost eclipsed by the C–H bond plane of the bridging group. The advantage of the arrangement in which the plane is eclipsing the rings π-system is evident from the fact that the electron cloud of the ordinary bond is therewith located in the nodal plane of the bulky benzene π orbitals, thus ensuring a minimal electrostatic repulsion. Moreover, in the conrotatory conformation the *ortho*-hydrogen atoms of different aromatic rings are the most distant from each other, and this, too, decreases their repulsion. Such a location of aryl rings is characteristic of diphenyl derivatives whose bridging groups have atoms rather than LEPs as substituents. In particular, such compounds include diarylsilanes. The phenyl rings in diarylsilanes are turned out of the plane including the CSiC bond angle by 40–60° [7], which allows a contact of the van der Waals spheres of the *ortho*-hydrogen atoms of these rings. Obviously, if the molecule has such a conformation, the phenyl rings in it are accessible for solvation on all sides [11].

The solvation radii obtained in the present work and used in the calculations for the other systems studied are listed in Table 4.

It was found that the intrinsic solvation radii for diphenylmethane (**I**) are consistent with those for diphenyl, both for the rings and for the bridging group. Note that the free void fractions of diphenyl and diphenylmethane are close to each other (Table 1). Figure 3 shows the dependence of the calculated molar volume of diphenylmethane on the ring torsion angle φ at the intrinsic solvation radii parametrized for φ 41°.

As to diarylsilanes, the best suited for parametrization were found to be the intrinsic solvation radii for benzene: r_C 2.175 Å and r_H 1.675 Å. The atomic solvation radii for the bridging group are as follows: r_{Si} 2.5 A and r_H 1.7 Å for для diphenylsilane (**II**) and r_{Si} 2.5 Å and r_{Cl} 2.35 Å for 4,4'-dichlorodiphenylsilane (**III**) at φ 50°. These compounds have a fairly large Δ increments (0.5 Å) to the van der Waals radii: r_{Si} 2.5 Å, r_H 1.7 Å, and r_{Cl} 2.35 Å. This result is also consistent with the data in Table 1, which show that the free void fraction in diarylsilanes is markedly larger than in diphenylmethane.

Figure 4 shows the dependences of the deviation of the calculated molar volumes of diphenylmethane (**I**) and diphenylsilane (**II**) from the calculated molar volumes at φ 0° at the conrotatory ring torsion on the torsion angle φ. The plot for diphenylsilane goes below the plot for diphenylmethane. Since Si–C bonds are longer than C–C, the rings in diarylsilanes are more remote from each other than in diphenylmethane (**I**), and, as a result, mutual orientation of the rings in diphenylsilane (**II**) has a weaker effect of the calculated molar volume.

As seen from the plots in Fig. 4, the deviations from the calculated solvation volumes at φ 50°–90° are quite small (0.5–1.0 cm^3 mol^{-1}). Such a situation was expected in advance, as mentioned above. Exact assessment of molecular conformations on the basis of molar volumes and intrinsic solvation radii is not always possible. We can only speak here about acoplanarity of the molecules. In terms of the method of molar volumes and the concept of intrinsic intrinsic solvation radii, the most probable conformations of systems **I–III** fall in the range 50°–90° of the conrotatory torsion angles of the aryl rings.

Solvation radii and possible conformations of diphenyl sulfides, diphenyl sulfoxides, and diphenyl sulfones. Compounds **IV–XII** have the same bridging atom (sulfur) but different substituents in the bridge and rings. The three classes of compounds are expedient to treat separately. Obviously, the aryl π-system can be conjugated with the LEP and with substituents on the bridging sulfur atom. The rings in diaryl sulfides characteristically prefer a close-to-coplanar arrangement with respect to the $C_{Ar}SC_{Ar}$ bond angle plane [10]; by contrast, diaryl sulfones prefer an orthogonal arrangement of the aryl rings with respect to this plane [18]. Diaryl sulfoxides, being intermediate forms, can, in principle, combine the features of both the above two classes of compounds.

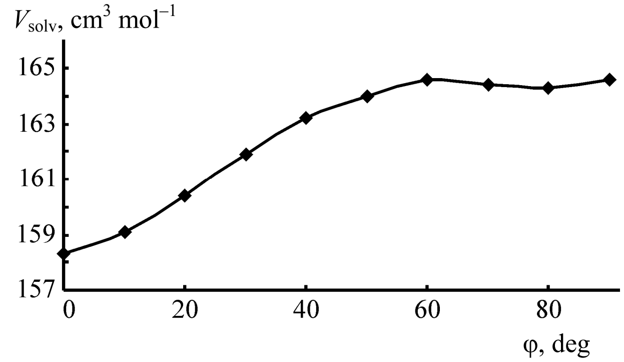


Fig. 3. Dependence of the calculated molar volumes of diphenylmethane on the ring torsion angle φ.

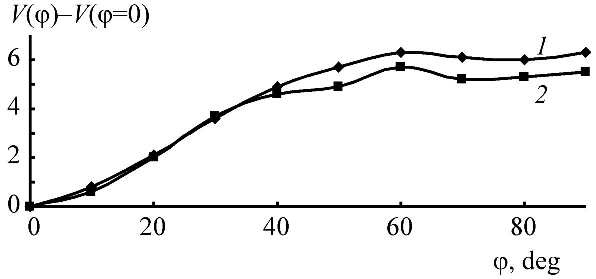


Fig. 4. Dependence of the difference between the calculated molar volumes V(φ)–V(φ=0) on the ring torsion angle φ for (*1*) diphenylmethane and (*2*) diphenylsilane.

Table 4. Intrinsic solvation radii R_i of atoms and groups of atoms in bridging groups and benzene rings[a]

Comp. no.	$_\infty V_2$, cm^3 mol^{-1}	Reference	Compounds whose data were used to estimate the intrinsic solvation radii of aryl rings	Intrinsic solvation radii of atoms in bridging groups R_i, Å
I	163.0	[4]	Diphenyl	r_C 2.12, r_H 1.62
II	186	[11]	Benzene	r_{Si} 2.5, r_H 1.7
III	213.6	[11]	Benzene	r_{Si} 2.5, r_{Cl} 2.35
IV	162.8	[11]	Diphenyl	r_S 2.05
V[b]	195.3	[11]	Diphenyl	r_S 2.05, r_N 1.8, r_O 1.7
VI	162.6	[11]	Diphenyl	r_S 1.75, r_O 1.3
VII	192.8	[11]	Diphenyl	r_S 1.75, r_O 1.3, r_{Cl} 2.24
VIII[b]	169	[11]	Diphenyl	r_O 1.52, r_S 1.72
IX[b]	185.8	[11]	Diphenyl	r_O 1.52, r_S 1.72, r_{Cl} 2.24
X[b]	198.8	[11]	Diphenyl	r_O 1.52, r_S 1.72, r_{Cl} 2.24
XI[b]	190.0	[11]	Diphenyl	r_O 1.52, r_S 1.72, r_N 1.6, r_O 1.5

[a] The partial molar volumes in solutions were determined at 25°C in CCl_4. [b] Solvent dioxane.

The estimates for the φ angles in compound **IV,** obtained by the methods of dipole moments and Kerr effect in the framework of the conrotatory conformation model, are 37° in benzene and 42° in carbon tetrachloride [10]. According to the methods of dipole moments and Kerr effect, diphenyl sulfone (**VIII**) in dioxane has orthogonally arranged rings with respect to the CSO_2C bond angle plane [9]. The same methods were used in [18] to shows than many of sulfones in dioxane are present in the orthogonal or planar–orthogonal forms and as an equilibrium mixture of these two forms. In particular, compound **IX** is characteristically present as an equilibrium mixture of the orthogonal and planar–orthogonal conformations. Compound **XI** is the only one, where a conrotatory ring orientation with φ 51° is observed.

According to the results obtained by the methods of dipole moments and Kerr effect in CCl_4, the ring planes in diphenyl sulfoxide (**VI**) and its *p*-chloro derivative (**VII**) are perpendicular to the C–SO–C plane in dioxane [9].

The above approach was used to parametrize the intrinsic solvation radii of the bridging groups in diphenyl sulfide (**IV**) (φ 42°), diphenyl sulfoxide (**VI**) (φ 90°), and diphenyl sulfone (**VIII**) (φ 90°). The obtained intrinsic solvation radii are listed in Table 3. It is interesting that in going from diphenyl sulfide to diphenyl sulfoxide and diphenyl sulfone the intrinsic solvation radius of the bridging group tends to decrease. The same picture was previously observed in the analysis of additive molar volumes of these compounds [13]: The group increments of the additive molar volumes of the bridging groups, too, decrease in the same direction. The acceptor properties of oxygen as the substituent on the bridging sulfur atom are likely to be too strong that the volume of the sulfur LEPs coordinated to oxygen is much smaller compared to uncoordinated sulfur LEPs, which is responsible for the observed effect.

Figure 5 shows the dependences of the calculated molar volumes of diphenyl sulfone (**VIII**) and (*p*-chlorophenyl) phenyl sulfone (**IX**) on the ring torsion angle φ. Both series of calculated values were fitted by the quadratic trend $y = a\varphi^2 + b\varphi + c$. The a and b coefficients of these functions for compounds **VIII** and **IX** are fairly close to each other, whereas the difference between the free terms are roughly equal to the additive increment of the molar volume of the substituent (16.07 cm^3 mol^{-1}) [12].

Summarizing the aforesaid we can suggest that the dependences of calculated molar volumes on aryl torsion angles for all π-substituted diaryl compounds

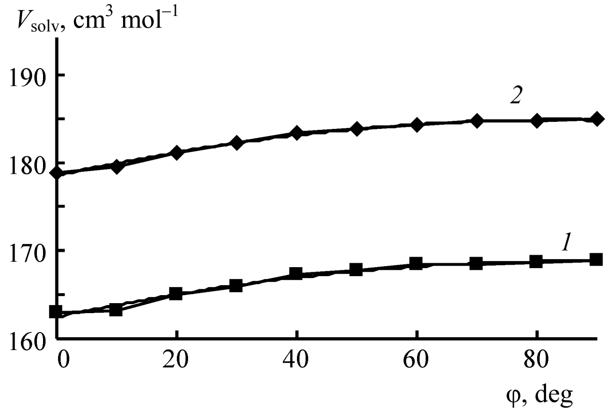


Fig. 5. Dependence of the calculated molar volumes of (*1*) diphenyl sulfone and (*2*) (*p*-chlorophenyl) phenyl sulfone on the ring torsion angle φ.

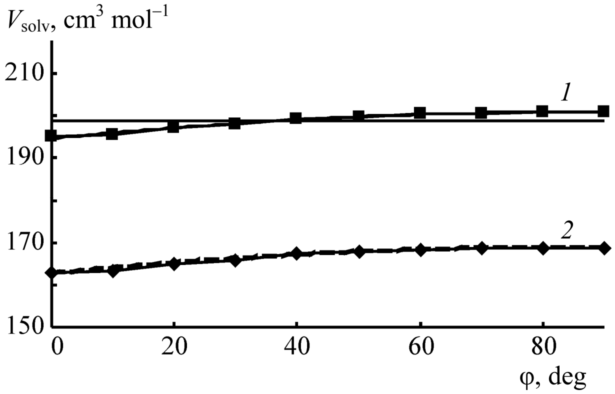


Fig. 6. Assessment of the possible molecular conformation of *p,p'*-dichlorodiphenyl sulfone by the method of solvation radii: (*1*) *p,p*'-dichlorodiphenyl sulfone and (*2*) diphenyl sulfone.

with sp^3-hybridized central atoms can be obtained from the dependences for unsubstituted molecules by adding to them the corresponding substituent increments, like in the additive scheme for the evaluation of molar volumes [4, 12].

Figure 6 presents the application of the developed approach by an example of *p,p*'-dichlorodiphenyl sulfone. The ring torsion angle of 38° corresponds to the experimental molar volume of *p,p*'-dichlorodiphenyl sulfone [9]. Beginning with this torsion angle, the molar volume no longer varies with torsion angle, and, therefore, we can only suggest acoplanarity of these molecules in solutions.

Table 5 lists the ring torsion angles we found for a series of substituted diphenyl sulfones, beginning with which calculated molar volumes become independent of torsion angles; the table also lists the angles found by the method of dipole moments and Kerr effect in [9].

The general conclusion is that diaryl systems **I**–**XI** are acoplanar in solutions. The method of molar volumes only allows confident conclusions on whether aryl rings capable of intramolecular rotation are acoplanar in solutions or not, but it does not provide any definite estimates for the torsion angles of these fragments.

In conclusion we would like to illustrate the correlation between the molar volumes of the studied compounds and their polarizability expressed in terms of molar refraction. Note, by the way, that in the CGS system the molar volume and molar polarizability are measured the same unit: cm^3 mol^{-1}.

There is an excellent correlation between the molar refraction R of alkanes, which is proportional to their molecular polarizability: $R = 4/3\pi N_A b$, where b is the average molecular optical polarizability and N_A, Avogadro number), and the molar volumes $V_{\mathrm{ind.l}}$ of alkanes as individual liquids [16], considered in the present work: $R = [(n^2 - 1)/(n^2 + 2)](M/\rho)$, where n is the refractive index; M, molecular weight; and ρ, density. The following correlation equation was obtained for alkanes: $R = 0.2885\ V_{\mathrm{ind.l}} - 7.8972$ (the correlation coefficient r is 0.99). In the case of diaryl systems, a fair correlation could only be obtained only for sulfoxides and sulfones as a single series, at least because we considered a sufficient number of compounds in these two classes: $R = 0.3458{}_{\infty}V_2 + 3.6292$ (r 0.96). Here R is, too, the molar refraction in solutions. Note that the molar volumes of the studied diaryl systems, which we calculated previously by the additive scheme, well agree with the experimental values reported in the present work and much facilitates determination of the Kerr constants and dipole moments of these compounds without sacrificing the accuracy of the results, as mentioned in [4].

Table 5. Calculated torsion angles φ of the benzene rings in certain *p*-derivatives of diphenyl sulfone and the values φ' of the same angles, found by the methods of dipole moments and Kerr effect [12]

Compound	φ, deg	φ', deg
(*p*-Clorophenyl) phenyl sulfone	90	≈90
p,p'-Dichlorodiphenyl sulfone	38	≈90
p,p'-Dinitrodiphenyl sulfone	10	51

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