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Molecular Polarizability of the Organic Substances and Their Complexes: LX.[1] Molecular Volume and Spatial Structure of the Series of Heterocycles, Their Structurally Nonrigid Derivatives, and Chromium Tricarbonyl π-Complexes in Solutions

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Abstract—We have analyzed the molar volumes and structures in solutions of a series of azines, azoles, conformationally nonrigid bis(2-substituted benzimidazol-1-yl)methanes, and chromium tricarbonyl complexes of arenes. For most of the compounds, the rules of molar volume additivity with respect to the bonds and groups increments hold. Molecules of bis(2-substituted benzimidazol-1-yl)methanes exist in the form of conrotatory comformers with aryl fragments being out of the plane of bridging NCN bond angle. Strong linear correlations between the molar volume and molar refraction have been revealed within the studied compounds classes. In the case of chromium tricarbonyl complexes of arenes, the coordination bond polarity has increased with growing π-donor ability of the ligand, the molar volume increment of $Cr(CO)_3$ has increased as well, due to transfer of π-electron density from the ligand. The simplification of dipole moment and Kerr constant determination has been demonstrated.

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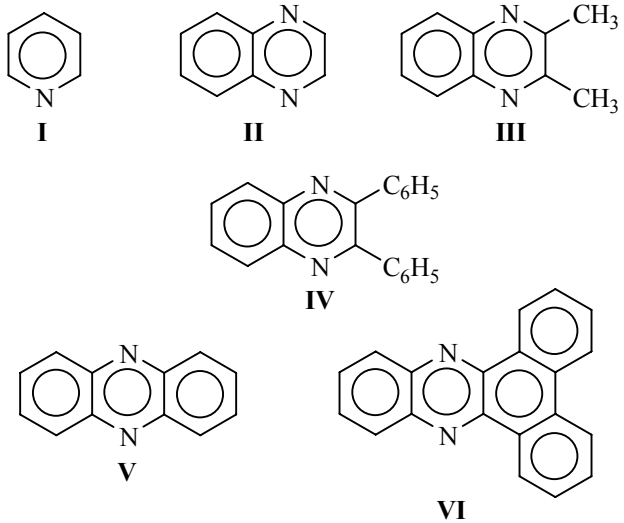
Molar Volumes of a Series of Heterocyclic Compounds

We studied a series of the benzannulated azines (**II–VI**), their structures are presented below. Pyridine **I** was used as a model compound.

The molar volumes of the compounds at the infinite dilution ${}_{\infty}V_2$ were determined in CCl_4 and C_6H_6 solutions; the respective experimental values are given in Table 1.

The additive analysis of the molar volumes of aromatic heterocycles **II–VI** started with determination of the molar volume increment $\Delta V_{C-N=C}$ of the endocyclic fragment C–N=C containing nitrogen atom of the pyridine ring. The calculations revealed that the increment $\Delta V_{C-N=C}$ according to the individual pyridine liquid suited the best in the case of azines [2]. The molar volume of pyridine in solutions [3] was, in our opinion, significantly underestimated, likely, due to the density measurement inaccuracy. Indeed, the molar volume of individual pyridine liquid was of 80.6 $cm^3\ mol^{-1}$, whereas ${}_{\infty}V_2$ of pyridine equaled 68.8 $cm^3\ mol^{-1}$. Most often such difference is on the order of the molar volume determination inaccuracy [4].



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

Table 1. Molar volume of the studied compounds in the infinitely diluted solutions at 25°C and determination of dipole moments and Kerr constant assuming molar volumes additivity[a]

Comp. no.	Solvent	β	${}_{\infty}V_2$, $cm^3\ mol^{-1}$	V_{ind}, $cm^3\ mol^{-1}$	V_{ad}, $cm^3\ mol^{-1}$	ε of ${}_{\infty}V_2$, %	Found in this work via the simplified method		Experimental data		Reference
							μ, D	${}_{\infty}({}_mK_2)\times10^{12}$, ESU	μ, D	${}_{\infty}({}_mK_2)\times10^{12}$, ESU	
						Pyridine					
I	C_6H_6	0.624	68.8	80.6	–	–	–	–	–	–	[2, 3]
						Benzannulated 6-membered heterocycles					
II	C_6H_6	0.251	111.6	–	109.6	1.8	0.46	50.9	0.49	51.0	[4]
III	C_6H_6	0.207	142.8	–	144.4	1.1	0.83	105.8	0.82	105.7	[4]
III	CCl_4	–0.430	143.6	–	144.4	0.6	0.77	107.2	0.76	107.1	[4]
IV	C_6H_6	0.256	240.0	–	231.2	3.7	0.65	179.8	0.75	180.6	[4]
V	C_6H_6	0.288	148.5	–	147.2	0.9	0	193.5	0	193.5	[4]
VI	C_6H_6	0.306	222.6	–	220.3	1.1	0.60	355.4	0.62	355.4	[4]
						Monoheterocycles					
VII	CCl_4	–0.624	67.3	72.7	–	–	–	–	–	–	[5]
VIII	CCl_4	–0.487	78.9	80.6	–	–	–	–	–	–	[5]
IX	CCl_4	–0.708	78.9	78.8	–	–	–	–	–	–	[5]
						Azoles					
X	Dioxane	0.120	58.3	–	60.6	3.0	4.00	195	3.99	231	[6, 7]
XI	″	0.026	78.4	–	74.3	5.2	4.02	275	4.03	318	[7, 8]
XII	″	0.013	79.2	–	74.7	5.7	4.07	102	4.05	115	[7, 8]
XIII	″	0.207	91.2	–	94.2	3.3	4.00	253	3.99	289	[7, 8]
XIV	″	0.075	119.0	–	114.3	4.0	4.23	344	4.08	393	[7, 8]
XV	″	0.061	62.2	–	–	–	–	–	–	–	[6, 7]
XVI	″	0.134	71.8	–	–	–	–	–	–	–	[6, 7]
XVII	″	0.256	50.0	–	50.9	1.8	3.33	133	3.32	155	[6, 7]
XVIII	″	0.072	75.2	–	72.3	3.8	3.37	217	3.37	248	[7, 8]
XIX	″	0.298	48.4	–	52.2	7.8	5.01	343	4.96	382	[6, 7]
XX	″	0.188	95.1	–	88.1	7.4	4.25	386	4.28	432	[7, 8]
XXI	CCl_4	–0.255	107.7	–	107.7	0	1.63	65.4	1.63	84	[7, 8]
XXII	CCl_4	–0.340	100.7	–	104.8	4.1	1.42	64.3	1.42	73	[7, 8]
XXIII	CCl_4	–0.428	119.0	–	117.1	1.6	1.27	28.6	1.29	39	[7, 8]
						Bis(2-substituted benzimidazol-1-yl)methanes					
XXIV	Dioxane	0.145	233.4	–	218.8	6.2	3.93	–789	3.95	–894	[9]
XXV	″	0.103	269.4	–	253.2	6.0	3.89	–689	3.91	–749	[9]
XXVI	″	0.187	288.6	–	315.0	9.1	3.42	–10.5	3.35	–13	[9]

Table 1. (Contd.)

Comp. no.	Solvent	β	$_{\infty}V_2$, $cm^3\ mol^{-1}$	V_{ind}, $cm^3\ mol^{-1}$	V_{ad}, $cm^3\ mol^{-1}$	ε of $_{\infty}V_2$, %	Found in this work via the simplified method		Experimental data		Reference
							μ, D	$_{\infty}(_mK_2)\times10^{12}$, ESU	μ, D	$_{\infty}(_mK_2)\times10^{12}$, ESU	
Chromium tricarbonyl π-complexes of alkylbenzenes											
XXVII	C_6H_{12}	0.464	148.3	–	–	–	–	–	–	–	[10]
XXVIII	C_6H_{12}	0.436	166.3	–	167.7	–	4.82	1376	4.86	1285	[10]
XXIX	C_6H_{12}	0.410	184.6	–	181.1	–	5.07	1352	5.07	1262	[10]
XXX	C_6H_{12}	0.386	203.3	–	197.5	–	5.31	1275	5.31	1189	[10]
XXXI	C_6H_{12}	0.382	215.8	–	213.9	–	5.55	1305	5.55	1218	[10]
XXXII	C_6H_{12}	0.376	229.2	–	230.3	–	5.82	1155	5.82	1076	[10]
XXXIII	C_6H_{12}	0.372	242.1	–	246.7	–	6.03	1345	6.03	1258	[10]
XXXIV	C_6H_{12}	0.385	214.8	–	212.8	–	5.05	1445	5.04	1346	[10]
XXXV	C_6H_{12}	0.338	279.2	–	277.3	–	5.53	1435	5.52	1338	[10]
XXXVI	C_6H_{12}	0.289	351.4	–	341.8	–	5.90	1308	5.91	1218	[10]

[a] β, concentration coefficient; $_{\infty}V_2$, molar volume extrapolated to the infinite dilution; V_{ind}, molar volume of the individual liquid; V_{ad}, additive molar volume; ε, relative difference between the experimental and the calculated valued; μ, dipole moment; $_{\infty}(_mK_2)$, Kerr constant (in electrostatic units).

Molar volume increment of C–N=C. The group increment of that fragment was calculated as the difference between molar volumes of pyridine and benzene.

$$\Delta V_{C-N=C} = V(\mathbf{I}) - {}_{\infty}V_2(C_6H_6),$$

$$\Delta V_{C-N=C} = 80.6 - 87.3 = -6.7\ cm^3\ mol^{-1}.$$

The molar volumes of azines **II–VI** were calculated according to schemes below, taking into account the molecules structure.

Quinoline (II). $V_{ad}(\mathbf{II}) = {}_{\infty}V_2(\text{naphthalene}) + 2\Delta V_{C-N=C} = 123.1 + 2(-6.7) = 109.7\ cm^3\ mol^{-1}$, where $_{\infty}V_2$(naphthalene) was naphthalene molar volume [3].

2,3-Dimethylquinoline (III). $V_{ad}(\mathbf{III}) = {}_{\infty}V_2(\mathbf{II}) + 2V(CH_3) = 111.6 + 2(16.4) = 144.4\ cm^3\ mol^{-1}$, where $V(CH_3)$ was the group molar volume increment of CH_3 substituent [4].

2,3-Diphenylquinoline (IV). To do this calculation, the molar volume increment of the C_6H_5 group was found from molar volumes of biphenyl and of benzene [3].

$$V(C_6H_5) = {}_{\infty}V_2(\text{biphenyl}) - {}_{\infty}V_2(\text{benzene})$$

$$= 147.1 - 87.3 = 59.8\ cm^3\ mol^{-1}.$$

Further calculation followed the structure of **IV**.

$$V_{ad}(\mathbf{IV}) = {}_{\infty}V_2(\mathbf{II}) + 2V(C_6H_5)$$

$$= 111.6 + 2(59.8) = 231.2\ cm^3\ mol^{-1}.$$

Phenazine (V). Molar volume of **V** was calculated taking into account the respective value for anthracene [3] and the increment of $\Delta V_{C-N=C}$.

$$V_{ad}(\mathbf{V}) = {}_{\infty}V_2(\text{anthracene}) + 2\Delta V_{C-N=C}$$

$$= 160.6 + 2(-6.7) = 147.2\ cm^3\ mol^{-1}.$$

2,3,4,5-Dibenzophenazine (VI). Molar volume of **VI** was calculated taking into account the respective value for **V** and the necessary increments.

$$V_{ad}(\text{VI}) = {}_{\infty}V_2(\mathbf{V}) - 2\Delta V_{CC} - 8\Delta V_{CH} + 2_{\infty}V_2(\text{benzene})$$

$$= 148.5 - 2(2.2) - 8(12.3) + 2(87.3) = 220.3\ cm^3\ mol^{-1},$$

where ΔV_{CC} and ΔV_{CH} were bond molar volume increments of the C–C and exocyclic C–H in benzene [3].

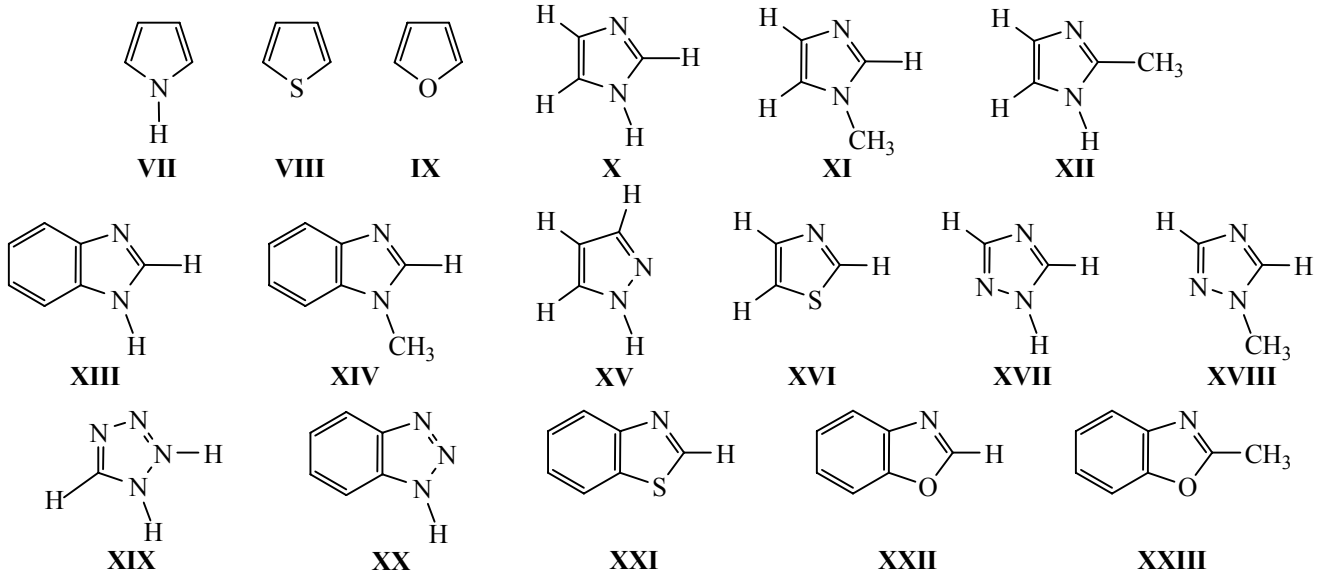
As seen from Table 1, the molar volumes calculated via the additive scheme were in good agreement with the experimental values. The relative difference between the experimental and the calculated values did

not exceed 3.7%. This proved that the molar volume increment of C–N=C as determined from the pyridine and benzene properties was roughly the same as that for other azines, and that the molar volumes of the discussed heterocycles were additive with respect to the constituting fragments and bonds.

Previously, it was shown that in the systematically considered series the molar volume and the molar refraction were linearly correlated [5]. From the experimental data on the molar refraction R_D [6] this strong linear correlation was confirmed in the considered series of azines as well.

Molar Volumes of Azoles

The series of azoles **X**–**XXIII** was studied, their structures are given below. Pyrrole **VII**, thiophene **VIII**, and furan **IX** were used as model compounds.



The molar volumes of those compounds were determined at the infinite dilution of the solutions in dioxane and in CCl_4. The respective experimental data are given in Table 1.

Beforehand, we considered the molar volume group increment of C–N=C in azoles. It was expected that azoles, 5-membered heterocycles, should show the $\Delta V_{C–N=C}$ value differing from that of 6-membered azines heterocycles. The values of $\Delta V_{C–N=C}$ were compared in the pairs: pyrrole–imidazole, *N*-methylpyrrole–*N*-methylimidazole, and thiophene–thiazole. The values of $\Delta V_{C–N=C}$ were calculated as follows.

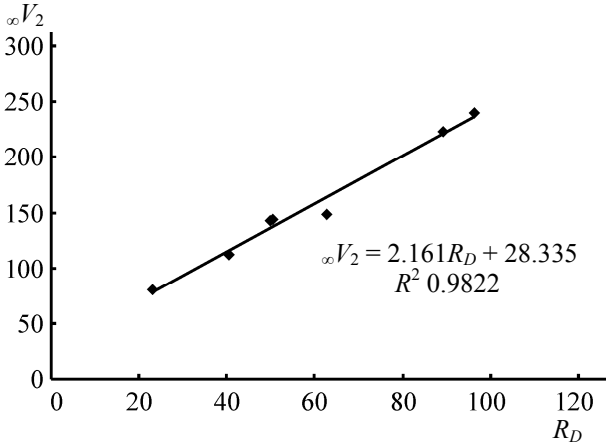


Fig. 1. Linear correlation of $_\infty V_2$ and molar refraction R_D of azines. R^2 is the squared linear correlation coefficient.

Pyrrole–imidazole. $\Delta V_{C–N=C} = {}_\infty V_2$(**X**) – $_\infty V_2$(**VII**) = 58.3 – 68,3 = –10.0 cm^3 mol^{-1}, with $_\infty V_2$ (**X**) and $_\infty V_2$ (**VII**) being molar volumes of imidazole and pyrrole, respectively.

N-Methylpyrrole–*N*-me**thylimidazole.** $\Delta V_{C–N=C} = {}_\infty V_2$(**XI**) – *V*(*N*-methylpyrrole) = 78.4 – 88.7 = –10.3 cm^3 mol^{-1}, with *V*(*N*-methylpyrrole) being *N*-methylpyrrole individual liquid molar volume [2].

As was expected, the values of $\Delta V_{C–N=C}$ from those two pairs were close. Thereafter, the $\Delta V_{C–N=C}$ value calculated for the pyrrole–imidazole pair was considered in the calculations of molar volume of azoles containing C–N=C fragment in the heterocycle and not containing sulfur. For the sulfur-containing heterocycle, the increment calculated for the thiophene–thiazole pair was used.

Thiophene–thiazole. $\Delta V_{C-N=C} = {}_{\infty}V_2$(**XVI**) – ${}_{\infty}V_2$(**VIII**) = 71.8 – 78.6 = –6.8 cm^3 mol^{-1}, with ${}_{\infty}V_2$(**XVI**) and ${}_{\infty}V_2$(**VIII**) being molar volumes of thiazole and thiophene, respectively. Interestingly, the increment $\Delta V_{C-N=C}$ calculated for that pair was very close to that for the pair benzene–pyridine (–6.7 cm^3 mol^{-1}), likely because thiophene was similar to benzene with respect to the aromaticity-related properties [7].

We determined also the pyrazole-type C–N=N molar volume increment for the pyrrole–pyrazole pair.

$$\Delta V_{C-N=N} = {}_{\infty}V_2(\mathbf{XV}) - {}_{\infty}V_2(\mathbf{VII})$$
$$= 62.2 - 68.4 = -6.2 \text{ cm}^3 \text{ mol}^{-1}.$$

Imidazole (X). The additive calculation of **X** molar volume was performed using that of pyrrole, ${}_{\infty}V_2$(**VII**), and the respective increment.

$$V_{ad}(\mathbf{X}) = {}_{\infty}V_2(\mathbf{VII}) + \Delta V_{C-N=C}$$
$$= 67.3 - 6.7 = 60.6 \text{ cm}^3 \text{ mol}^{-1}.$$

***N*-Methylimidazole (XI).** First, the group increment of N–CH_3 was determined.

$$V(\text{N–CH}_3) = V(N\text{-methylpyrrole}) - V(\mathbf{VII})$$
$$= 88.7 - 72.7 = 16.0 \text{ cm}^3 \text{ mol}^{-1}.$$

In that equation, V(*N*-methylpyrrole) = 88.7 cm^3 mol^{-1} was molar volume of *N*-methylpyrrole individual liquid [2]. Then,

$$V_{ad}(\mathbf{XI}) = {}_{\infty}V_2(\mathbf{X}) + V(\text{N–CH}_3)$$
$$= 58.3 + 16.0 = 74.3 \text{ cm}^3 \text{ mol}^{-1}.$$

2-Methylimidazole (XII). V_{ad}(**XII**) = ${}_{\infty}V_2$(**X**) + $V(CH_3)$ = 58.3 + 16.4 = 74.7 cm^3 mol^{-1}, with $V(CH_3)$ – being the group increment of CH_3 in aromatic compounds [4].

Benzimidazole (XIII). V_{ad}(**XIII**) = ${}_{\infty}V_2$(**X**) –ΔV_{CC} – $4\Delta V_{CH}$ + ${}_{\infty}V_2$(benzene) = 58.3 – 2.2 – 4(12.3) + 87.3 = 94.2 cm^3 mol^{-1}, ΔV_{CC} and ΔV_{CH} were the bond molar volume increments of the C–C and exocyclic C–H. The equation above was written according to structure of **XIII** taking into account the benzannulation effect.

***N*-Methylbenzimidazole (XIV).** V_{ad}(**XIV**) = ${}_{\infty}V_2$(**XI**) – ΔV_{CC} – $4\Delta V_{CH}$ + ${}_{\infty}V_2$(benzene) = 78.4 – 2.2 – 4(12.3) + 87.3 = 114.3 cm^3 mol^{-1}.

As was noted above, **XV** and **XVI** were used for estimation of the increments of $\Delta V_{C-N=N}$ and $\Delta V_{C-N=C}$, respectively, thus there was no reason to calculate their molar volume using the additive scheme.

1,2,4-Triazole (XVII). V_{ad}(**XVII**) = ${}_{\infty}V_2$(**VII**) + ΔV_{C-N-N} + $\Delta V_{C-N=C}$ = 67.3 + (–6.2) + (–10.2) = 50.9 cm^3 mol^{-1}.

***N*-Methyl-1,2,4-triazole (XVIII).** V_{ad}(**XVIII**) = V(*N*-methylpyrrole) + ΔV_{C-N-N} + $\Delta V_{C-N=C}$ = 88.7 + (–6.2) + (–10.2) = 72.3 cm^3 mol^{-1}.

As the increments of N–N=N and N–N were not known, the molar volume of **XIX** and **XX** were estimated by using approximating increment $\Delta V_{C-N=C}$.

1,2,3,4-Tetrazole (XIX). V_{ad}(**XIX**) = ${}_{\infty}V_2$(**XV**) + $\Delta V_{C-N=C}$ = 62.2 – 10.0 = 52.2 cm^3 mol^{-1}.

Benzotriazole (XX). V_{ad}(**XX**) = ${}_{\infty}V_2$(**XV**) –ΔV_{CC} – $4\Delta V_{CH}$ + ${}_{\infty}V_2$(benzene) + $\Delta V_{C-N=C}$ = 62.2 –2.2 – 4(12.3) + 87.3 – 10.0 = 88.1 cm^3 mol^{-1}.

Benzotriazole (XXI). V_{ad}(**XXI**) = ${}_{\infty}V_2$(**XVI**) – ΔV_{CC} – $4\Delta V_{CH}$ + ${}_{\infty}V_2$(benzene) = 71.8 – 2.2 –4(12.3) + 87.3 = 107.7 cm^3 mol^{-1}.

Benzoxazole (XXII). V_{ad}(**XXII**) = ${}_{\infty}V_2$(**IX**) – ΔV_{CC} – $4\Delta V_{CH}$ + $\Delta V_{C-N=C}$ + ${}_{\infty}V_2$(benzene) = 78.9 – 2.2 – 4(12.3) + (–10.0) + 87.3 = 104.8 cm^3 mol^{-1}.

2-Methylbenzoxazole (XXIII). V_{ad}(**XXIII**) = ${}_{\infty}V_2$(**XXII**) + $V(CH_3)$ = 100.7 + 16.4 = 117.1 cm^3 mol^{-1}.

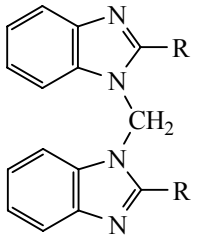
The additive calculation of the azoles molar volumes was essentially similar to the previously suggested vector and additive schemes of azoles dipole moments and polarizability tensors calculation [8–10]. The respective calculation results in comparison with the experimental data are given in Table 1.

From Table 1, in most cases the experimental and the calculated values were in acceptable agreement. The exceptions were 1,2,3,4-tetrazole and benzotriazole, the respective relative errors were of 7.8 and 7.4%. This was expected, as the endocyclic fragments increments used in the molar volume calculation did not completely correspond the molecules structure.

Similarly to the case of azines, the correlation between the molar volumes at the infinite dilution and the molar refractions [8–10] was tested in the case of azoles. The result shown in Fig. 2 proved that the linear correlation was reasonably strong, with R of 0.95.

Molar Volumes of Bis(2-substituted benzimidazol-1-yl)methanes

The experimental values of bis(2-substituted benzimidazol-1-yl)methanes **XXIV–XXVI** molar volumes in dioxane solutions are given in Table 1. The additive calculation of the molar volume was performed as well, according to the molecules structures.



XXIV–XXVI

R = CH_3 (**XXIV**), C_2H_5 (**XXV**), *t*-C_4H_9 (**XXVI**).

$$V_{ad}(\textbf{XXIV–XXVI}) = 2V_{ad}(\text{azole fragment}) - 4\Delta V_{CH}.$$

In that equation, V_{ad}(azole fragment) was the additive molar volume of the respective azole fragment, and ΔV_{CH} was aliphatic C–H bond increment, 13.0 $cm^3\ mol^{-1}$ [4]. The additive molar volumes of the rotating azole fragments were calculated by adding the group increment of the corresponding substituent R to the molar volume ${}_\infty V_2$ of benzimidazole.

$$V_{ad}(\text{azole fragment}) = {}_\infty V_2(\textbf{XIV}) + V(\text{R})$$

with ${}_\infty V_2$(**XIV**) the *N*-methylbenzimidazole molar volume; R = CH_3, C_2H_5, or *t*-C_4H_9. The mentioned groups increments V(R) for the aromatic systems were taken equal to 16.4 [4], 33.6 (from the individual liquid benzene and ethylbenzene data [2]), and 64.5 $cm^3\ mol^{-1}$ [4], respectively.

Bis(2-methylbenzimidazol-1-yl)methane (XXIV). $V_{ad}(\textbf{XXIV}) = 2[{}_\infty V_2(\textbf{XIV}) + V(CH_3)] - 4\Delta V_{CH}$.

Bis(2-ethylbenzimidazol-1-yl)methane (XXV). $V_{ad}(\textbf{XXV}) = 2[{}_\infty V_2(\textbf{XIV}) + V(C_2H_5)] - 4\Delta V_{CH}$.

Bis(2-*tert*-butylbenzimidazol-1-yl)methane (XXVI). $V_{ad}(\textbf{XXVI}) = 2[{}_\infty V_2(\textbf{XIV}) + V(t\text{-}C_4H_9)] - 4\Delta V_{CH}$.

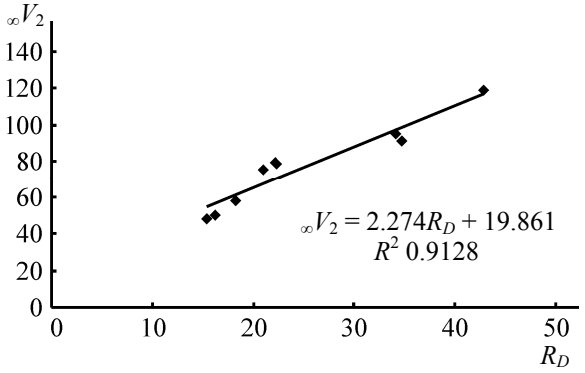


Fig. 2. Linear correlation of ${}_\infty V_2$ and molar refraction R_D of azoles.

The results of additive calculation are compared with the experimental data in Table 1. In the cases of **XXIV** and **XXV,** there was a agreement between the experimental and the calculated values, thus revealing that the hetaryl rings of those compounds were solvated similarly to the respective parent azoles. This corresponded to the conrotatory model of the aryl rings arrangement with respect to the plane of the bridging NCN bond angle [11], as such structure made the aryl rings available to the solvent molecules from any side. In the case of **XXVI,** the noticeable overestimation of the calculated molar volume was seemingly due to presence of bulky *tert*-butyl substituent. Sterically, the *tert*-butyl ring substituents could not be located at the both sides of the CNC bond angle plane, as that would cause the substituents approaching one another [11]. Evidently, the *tert*-butyl groups could be only located at the opposite sides of the NCN bond angle plane; however, that way the *tert*-butyl groups were close to the C–H bonds of the bridging group, and the excluded volume (unavailable to the solvent molecules) appeared, accounting for the observed overestimation of the calculated molar volume. However, we suggested that for **XXVI** molecule the conrotatory model would be the most probable as well. The similar situation of the overestimation of the calculated molar volume due to closely located substituents was revealed in the case of *peri*-substituted naphthalenes [12].

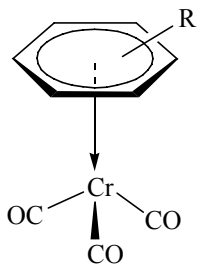
Molar Volumes of the Series of Chromium Tricarbonyl π-Complexes of Alkylbenzenes in Solution

Metal carbonyl π-complexes of arenes and their heterocyclic analogs are extremely interesting coordination compounds, thus the number of known complexes of this type continuously grows [13]. Among such complexes, the $Cr(CO)_3{\cdot}(\eta^6\text{-arene})$ compounds are well known, but the nature of the donor-acceptor bond in those complexes has been still questionable. The electron density should evidently be shifted from the π-aromatic donor system to the $Cr(CO)_3$ group (acceptor).

It was of interest to determine how the formation of donor-acceptor bond arene → $Cr(CO)_3$ influenced the molar volume of the complexes and to check whether the molar volume increment of $Cr(CO)_3$ changed with increasing complexes dipole moment, characterizing the efficiency of π-electron density transfer.

We studied the molar volumes of the series of alkylbenzenes and the respective π-complexes **XXVII–XXXVI** at the infinite dilution of the cyclohexane

solutions. The generalized structure of the complexes is shown below.



R = one or several of CH_3 or $C(CH_3)_3$.

The calculated ${}_{\infty}V_2$ of the complexes are given in Table 1, the values for arenes are collected in Table 2. The simple additive analysis of ${}_{\infty}V_2$ presumed the calculation of the difference between the molar volumes of the complex and of the respective ligand.

$$\Delta({}_{\infty}V_2) = {}_{\infty}V_2(\text{complex}) - {}_{\infty}V_2(\text{ligand}).$$

The results are collected in Table 2 along with other physical properties of the complexes. From Table 2, $\Delta({}_{\infty}V_2)$ (that could be considered the molar volume increment of the $Cr(CO)_3$ group) of the complexes grew with increasing the number of methyl groups in the methyl and *tert*-butyl substituted benzenes, as compared with the chromium tricarbonyl complex of benzene. The π-donor ability of the ligands increased simultaneously. The above-mentioned changes were also accompanied with the coordination arene → $Cr(CO)_3$ bond strengthening, as evidenced by increase of the complex dipole moment and the stretching vibrations frequency ν_{CO} [14].

Table 2 shows the comparison of the molar volume complex increment $\Delta({}_{\infty}V_2)$ with the polarizability along the coordination bond arene → $Cr(CO)_3$ (from [14]).

Generally, strengthening of the coordination bond is accompanied with its shortening. This should result in weakening of the Cr–CO bond as well as in decrease of the CO vibration frequency, both effects were observed experimentally. Evidently, the electron density transfer from the arene π-system to $Cr(CO)_3$ group decreased the strength of the carbonyl binding with chromium, and increased the molar volume of that group.

The above-mentioned conclusions were supported by strong linear correlations of the complexes ${}_{\infty}V_2$ with their dipole moments (R = 0.99) and with the polarizability along the coordination π-bond (R = 0.99). The latter value characterized the lability of the complex electron density distribution along the coordination bond in the external electrical field.

Thus, the major conclusion regarding that class of complexes was that with increasing the ligand π-donor ability, the coordination bond polarity increased, as well as did the molar volume increment of the $Cr(CO)_3$ fragment; those effects being due to π-electron density transfer from the ligand.

Table 2. Molar volume of arenes and the molar volume change upon formation of the π-complex $[Cr(CO)_3(\eta^6\text{-arene})]$ (cyclohexame solution, 25°C)

Comp. no.	Arene (ligand)	β(ligand) [10]	${}_{\infty}V_2$(ligand), $cm^3\ mol^{-1}$	$\Delta({}_{\infty}V_2)$ at complex formation	Polarizability along the coordination bond, 10^{24} cm^3 [10]	Frequency change $\Delta\nu_{CO}$, cm^{-1} [10]
XXVII	Benzene	0.0901	91.8	56.5	24.90	–
XXVIII	Toluene	0.0799	109.5	56.8	26.96	–4.4
XXIX	1,4-Dimethylbenzene	0.0726	127.2	57.4	28.67	–9.1
XXX	1,3,5-Trimethylbenzene	0.0681	144.7	58.6	30.11	–12.9
XXXI	Дурол	0.0915	157.6	58.2	31.37	–17.9
XXXII	Pentamethylbenzene	0.1184	168.9	60.3	32.45	–21.8
XXXIII	Hexamethylbenzene	0.1415	180.0	62.1	33.88	–25.8
XXXIV	*tert*-Butylbenzene	0.0930	157.3	57.5	32.00	–7.4
XXXV	1,4-Di-*tert*-butylbenzene	0.1010	221.1	58.1	38.56	–14.1
XXXVI	1,3,5-Tri-*tert*-butylbenzene	0.0908	289.5	61.9	44.49	–19.8

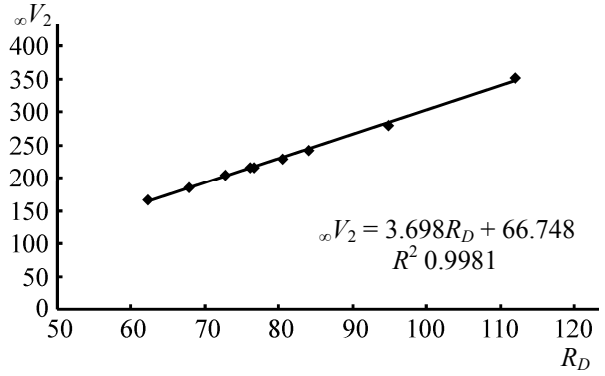


Fig. 3. Linear correlation of $_\infty V_2$ and molar refraction R_D of chromium tricarbonyl π-complexes.

The linear correlation of the same complexes molar volume at the infinite dilution and their molar refraction [14] is shown in Fig. 3, the strong linear correlation was observed.

In the further part of the study, we demonstrated the simplification of methods to determine the dipole moment and the Kerr constant; the method was applicable in the cases of compounds that obeyed the additive scheme of molar volume calculation. We calculated the dipole moments μ and the Kerr constants $_\infty(_mK_2)$ of the considered compounds according to the simplified procedure suggested previously in [4]; the calculation procedure used the modified Fujita [Eq. (1)] and Le Fevre [Eq. (2)] equations as well as the additively calculated V_{ad}.

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

$$_\infty(_mK_2) = {}_sK_1\rho_1{}_\infty V_2 + (\gamma + \delta - H\gamma - J\alpha\varepsilon_1){}_sK_1\rho_1\frac{M_2}{M_1}V_1. \quad (2)$$

The Eqs. (1) and (2) were equivalent to the ones used for determination of the dipole moment and the Kerr constant (see [4] for details and the description of the symbols). The values of V_{ad} (Table 1) were inserted into Eq. (1) and Eq. (2) instead of $_\infty V_2$. In the case of chromium tricarbonyl complexes, the V_{ad} values were calculated via a simplified procedure, by adding the respective number of group increments for CH_3 and *t*-C_4H_9 groups to the molar volume of the chromium tricarbonyl complex with benzene (Table 1). The results of μ and $_\infty(_mK_2)$ calculation in comparison with the experimental values are shown in Table 1.

The calculated μ and $_\infty(_mK_2)$ values were close to the experimental ones [3, 6, 8–11, 14, 15]. The concentration coefficients α, γ, and δ published in the same papers were used to calculate $_\infty V_2$ of the studied compounds.

Thus, in most cases the methods to determine μ and $_\infty(_mK_2)$ could be significantly simplified: instead of the solution density determination, the additive molar volumes could be calculated, and then the modified Le Fevre and Fujita equations were used. The simplifications worked the better, the closer were V_{ad} and $_\infty V_2$.

EXPERIMENTAL

The experimental data on the solutions density as function of the concentration (used to determine the molar volumes at the infinite dilution $_\infty V_2$) were extracted from [3, 6, 8–11, 14, 15]; the values of β were taken from that papers as well. The calculation of $_\infty V_2$ was performed according to the previously derived [4] extrapolation Eq. (3).

$$_\infty V_2 = \frac{M_2(1 - \beta)}{\rho_1}. \quad (3)$$

The dipole moments and Kerr constants were calculated using the additive molar volumes V_{ad}, the necessary parameters α, γ, and δ were taken from the same papers [3, 6, 8–11, 14, 15].

The following solvent properties (25°C) [16] were used to determine the experimental molar volumes of the studied compounds: carbon tetrachloride, ρ_1 = 1.5845 g cm^{-3}, ε_1 = 2.2270; Dioxane, ρ_1 = 1.02687 g cm^{-3}, ε_1 = 2.209; benzene, ρ_1 = 0.87378 g cm^{-3}, ε_1 = 2.2725; and cyclohexane, ρ_1 = 0.77389 g cm^{-3}, ε_1 = 2.0199. Other solvents properties necessary to calculate the Kerr constant were taken from [16] as well. The dipole moments were expressed in Debye units (D), the Kerr constants were given in electrostatic units (ESU). The conversion factors into SI units are as follows: 1 C m = 0.2998×10^{30} D, 1 m^5 V^{-2} mol^{-1} = 0.8988×10^{15} ESU/mol.

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