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Abstract

Full Text

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REFRACTIONS OF CERTAIN BONDS IN ORGANOARSENIC COMPOUNDS

(Presented by Academician A. E. Arbuzov, December 6, 1962)

In the chemical literature it has repeatedly been pointed out that it is advisable to use bond refractions (b.r.) for calculating molecular refraction (MR). The system of b.r., in comparison with the atomic refractions (AR) previously used for these purposes, reflects to a greater extent the physical essence of the polarizability of a molecule (^{1,2}), is more accurate (¹⁻⁴), and is more convenient to use because of the smaller number of parameters for compounds of polyvalent elements (^{2,3}). The most accurate method for calculating b.r. values in paraffins was proposed by K. Denbigh (¹) and was used by A. Fogel and co-workers (³) to determine these quantities in various organic and organoelement compounds. A. Fogel's data were subsequently supplemented by studies of other authors, chiefly for bonds of various elements with organogens (^{4,5}).

Table 1

B.r. $C_{\text{aliph}}-\text{As}$ in trialkylarsines, cm^3/mol

No.	Compound	d_4^{20}	n_D^{20}	MR_D , found	MR_D , calc. without b.r. $C-\text{As}$	B.r. $C_{\text{aliph}}-\text{As}$	Source
1	$(\text{CH}_3)_3\text{As}$	1,1330	1,4541	28,69	15,08	4,54	(¹¹)
2	$(\text{C}_2\text{H}_5)_3\text{As}$	1,0750	1,4760	42,52	29,03	4,50	(¹³)
3	$(\text{C}_3\text{H}_7)_3\text{As}$	1,0228	1,4750	56,20	42,97	4,41	(¹³)
4	$(\text{C}_4\text{H}_9)_3\text{As}$	0,9854	1,4747	70,31	56,92	4,46	(¹¹)
5	$(\text{C}_6\text{H}_{13})_3\text{As}$	0,9465	1,4745	98,20	84,80	4,47	(¹¹)
6	$(\text{C}_8\text{H}_{17})_3\text{As}$	0,9254	1,4744	126,0	112,79	4,40	(¹¹)
7	(iso- C_3H_7) ₃ As	1,0104	1,4847	56,20	42,97	4,58	(¹¹)
8	(iso- C_4H_9) ₃ As	0,9724	1,4667	70,23	56,92	4,44	(¹¹)
9	$(\text{CH}_3)_2\text{As}(\text{C}_2\text{H}_5)$	1,0160	1,4673	42,61	29,03	4,53	(¹³)
10	$(\text{C}_2\text{H}_5)_2\text{As}(\text{C}_3\text{H}_7)$	1,0193	1,4752	52,52	39,32	4,40	(¹⁴)
11	$\text{CH}_3\text{As}(\text{C}_2\text{H}_5)_2$	1,0103	1,4724	56,62	42,97	4,55	(¹³)
12	$\text{C}_2\text{H}_5\text{As}(\text{C}_3\text{H}_7)_2$	0,9979	1,4730	61,37	47,62	4,58	(¹⁴)
13	$(\text{C}_3\text{H}_7)_2\text{As}(\text{C}_4\text{H}_9)$	0,9945	1,4731	61,54	47,62	4,64	(¹⁴)

No.	Compound	d_4^{20}	n_D^{20}	MR_D , found	MR_D , calc. without b.r. C—As	B.r. $C_{\text{aliph}}-\text{As}$	Source
14	$\text{CH}_3\text{As}(\text{C}_6\text{H}_5)_2$	1,4662	1,4718	75,38	61,56	4,61	(¹⁴)
				Average		$4,51 \pm$ 0,08	

In application to organoarsenic compounds, the b.r. system has hitherto not been used because of the absence of data on the b.r. of arsenic with organogens. Therefore, when calculating MR for organoarsenic compounds with the aid of AR , it is necessary to use specific AR values for arsenic for each narrow class of compounds (⁶⁻¹¹).

In the present work, using literature data, the b.r. of carbon and oxygen with arsenic in its organic derivatives have been determined. The b.r. values of arsenic with other elements were calculated by subtracting from the experimentally found values, according to the Lorentz-Lorenz formula for the sodium D line, the known values (^{3,12}) of the b.r. present in the given compound. The true value of the b.r. was found for each type of compound as an arithmetic mean. From the calculation of the latter, data were excluded for those compounds in which the b.r. found differed from the arithmetic mean by more than 5%. The calculation error was estimated as the root-mean-square error.

For calculating the b.r. $C_{\text{aliph}}-\text{As}$ and $O-\text{As}$, the characteristics of symmetrical derivatives of trivalent arsenic were used: trialkylarsines (Table 1) and esters of arsenous acid (Table 2), respectively. For

For the $C_{\text{aliph}}-\text{As}$ bond in trialkylarsines, the value of the bond refraction was found to be $4.51 \text{ cm}^3/\text{mol}$, and for the $O-\text{As}$ bond in esters of arsenous acid, $3.91 \text{ cm}^3/\text{mol}$. Taking into account the ionic state of carbon in aromatic hydrocarbons (hybridization sp^2 instead of sp^3 in saturated compounds) and the possibility of interaction of the π -electrons of the benzene ring with the unshared pair of p -electrons of the arsenic atom, one might have expected a different polarizability of the $C_{\text{arom}}-\text{As}$ bond as compared with the same property of the $C_{\text{aliph}}-\text{As}$ bond. However, it was impossible to calculate the bond refraction of $C_{\text{arom}}-\text{As}$ from MR_D for symmetrical triarylsines in Ar_3As because of the absence of data on the specific gravity and refractive index of these compounds, which are solids at low temperatures. Therefore, for calculating the bond refraction of $C_{\text{arom}}-\text{As}$, experimentally found MR_D values of dialkylarylsines Alk_2AsAr and alkyldiarylsines AlkAsAr_2 (Table 3), which under the same conditions are liquids, were used. The bond refraction $C_{\text{arom}}-\text{As}$ in both types of compounds is approximately the same and averages $4.94 \text{ cm}^3/\text{mol}$.

Table 2

Bond refraction O–As in trialkyl arsenites, cm³/mol

No.	Compound	d_4^{20}	n_D^{20}	MR_D , found	MR_D , calcd. without r.b. O –As	Bond refrac- tion O –As	Source
1	(CH ₃ O) ₃ As	1.4264	1.4402	31.05	19.70	3.78	(11)
2	(C ₂ H ₅ O) ₃ As	1.4132	1.4360	45.26	33.64	3.87	(11)
3	(C ₃ H ₇ O) ₃ As	1.4277	1.4427	59.21	47.58	3.88	(11)
4	(C ₄ H ₉ O) ₃ As	1.4687	1.44999	73.25	61.52	3.91	(15)
5	(C ₅ H ₁₃ O) ₃ As	1.4120	1.4535	101.10	89.41	3.90	(11)
6	(C ₈ H ₁₇ O) ₃ As	1.4759	1.4569	129.06	117.29	3.92	(11)
7	(iso-C ₃ H ₇ O) ₃ As	1.0937	1.4280	59.32	47.58	3.95	(11)
8	(iso-C ₄ H ₉ O) ₃ As	1.0568	1.4390	73.23	61.52	3.90	(16)
9	(CH ₃ O) ₂ As(O ⁺ C ₂ H ₅) ₂	1.452	1.452	36.1	24.35	3.92	(17)
10	CH ₃ OAs(O ⁺ C ₂ H ₅) ₂	1.434	1.434	41.2	28.99	4.07	(17)
11	C ₂ H ₅ OAs(O ⁺ C ₃ H ₇) ₂	1.4423	1.4423	54.51	42.42	4.03	(16)
12	C ₂ H ₅ OAs(O ⁺ C ₄ H ₉) ₂	1.4542	1.4542	64.03	52.22	3.94	(16)
13	C ₃ H ₇ OAs(O ⁺ C ₄ H ₉) ₂	1.4438	1.4438	68.10	56.69	3.80	(16)
					Average	3.91 ± 0.08	

The bond refractions found were used to check the additivity of MR_D for esters of various arsenic acids. As it turned out, using the values found for the bond refractions C_{aliph}–As and O–As, one can obtain close agreement between the calculated and found MR_D values for esters of alkylarsinous acids. In the case of esters of dialkylarsinous acids, the average deviation between these quantities (0.28) is somewhat beyond the limits of the mean square error of calculation (0.24). Therefore, for accurate calculations of MR_D in esters of dialkylarsinous acids, a correction for molecular exaltation equal to +0.28 cm³/mol should be introduced.

Table 3
Bond refraction C_{arom}–As in dialkylaryl- and alkyldiarylsines, cm³/mol

No.	Compound	d_4^{20}	n_D^{20}	MR_D , found	MR_D , calcd. without r.b. $C_{\text{arom}}-\text{As}$	Bond refrac- tion $C_{\text{arom}}-\text{As}$	Source
1	$\text{C}_6\text{H}_5\text{As}(\text{C}_2\text{H}_5)_2$	—	—	57.72	52.83	4.89	(14)
2	$\text{C}_6\text{H}_5\text{As}(\text{CH}_3)_2$	1.5642	—	53.07	48.18	4.89	(18)
3	$\text{C}_6\text{H}_5\text{As}(\text{C}_2\text{H}_5)(\text{C}_3\text{H}_7)$	1.5492	—	62.47	57.50	4.97	(18)
4	$\text{C}_6\text{H}_5\text{As}(\text{C}_2\text{H}_5)(\text{C}_4\text{H}_9)$	1.5438	—	67.22	62.12	5.10	(18)
5	$\text{C}_6\text{H}_5\text{As}(\text{C}_2\text{H}_5)(\text{C}_5\text{H}_{11})$	1.5371	—	71.80	66.78	5.02	(18)
6	$\text{C}_6\text{H}_5\text{As}(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_{13})$	1.5340	—	76.17	71.39	4.78	(18)
7	$\text{C}_6\text{H}_5\text{As}(\text{C}_2\text{H}_5)(\text{C}_7\text{H}_{15})$	1.5271	—	80.83	76.08	4.75	(18)
8	o- $\text{CH}_3\text{C}_6\text{H}_4\text{As}(\text{CH}_3)_2$	1.1993	1.5690	53.55	48.45	5.10	(14)
9	m- $\text{CH}_3\text{C}_6\text{H}_4\text{As}(\text{CH}_3)_2$	1.1906	1.5645	53.59	48.45	5.14	(14)
10	$(\text{C}_6\text{H}_5)_2\text{AsCH}_3$	—	—	68.23	58.53	4.85	(14)
11	$(\text{C}_6\text{H}_5)_2\text{AsC}_2\text{H}_5$	—	—	73.13	63.18	4.98	(14)
12	$(\text{C}_6\text{H}_5)_2\text{AsC}_3\text{H}_7$	1.5846	—	86.55	77.13	4.71	(14)
13	(n- $\text{CH}_3\text{C}_6\text{H}_4)_2\text{AsCH}_3$	1.2011	1.6097	78.51	68.44	5.03	(14)
					Average	4.94 ± 0.13	

When using the system of bond refractions for calculating MR_D for four types of compounds (trialkylarsines, esters of arsenious acid, alkylarsinous and dialkylarsinous acids), it is sufficient to know six quantities—the bond refractions C—C, C—H, C—O, As—C and As—O, and the correction for molecular exaltation for esters of dialkylarsinous acids. Previously, for these purposes, seven atomic refractions were used—C, H, O and four specific atomic refractions of arsenic for each type of compound^(8,9,11). Therefore, extension of the bond-refraction system to organoarsenic compounds makes it possible—

Table 4

MR_D of esters of alkyl- and dialkylarsinic acids, cm^3/mol

No.	Compound	d_4^{20}	n_D^{20}	MR_D , found	MR_D , calc.	Deviation, Δ	Source
1	$\text{CH}_3\text{As}(\text{OC}_2\text{H}_5)_2$	1.4338	1,4522	58,30	58,38	-0,08	(19)
2	$\text{C}_2\text{H}_5\text{As}(\text{OC}_2\text{H}_5)_2$	1.4417	1,4533	63,07	63,03	+0,04	(20)
3	$\text{C}_3\text{H}_7\text{As}(\text{OC}_2\text{H}_5)_2$	1.4519	1,4509	58,51	58,38	+0,13	(19)
4	$\text{C}_3\text{H}_7\text{As}(\text{OC}_4\text{H}_9)_2$	1.4713	1,4528	67,52	67,68	-0,16	(20)
5	$\text{C}_4\text{H}_9\text{As}(\text{OC}_2\text{H}_5)_2$	1.4559	1,4555	44,39	44,44	-0,05	(8)

No.	Compound	d_4^{20}	n_D^{20}	MR_D , found	MR_D , calc.	Deviation, Δ	Source
6	$C_4H_9As(Cl_2H_7)_2$	1,4496	1,4496	53,86	53,73	+0,13	(8)
7	$C_4H_9As(Cl_2H_7)_2$	1,4570	1,4570	72,46	72,33	+0,13	(8)
8	$C_5H_9As(Cl_2H_7)_2$	1,4603	1,4603	109,43	109,51	-0,08	(8)
						$\Delta_{avg.}$ 0,11	
9	$(C_2H_5)_2AsCl_2H_5$	1,4621	1,4621	43,82	43,50	+0,32	(21)
10	$(C_2H_5)_2AsCl_2H_7$	1,4613	1,4613	48,70	48,17	+0,53	(10)
11	$(C_2H_5)_2AsCl_2H_9$	1,4608	1,4608	52,90	52,79	+0,11	(21)
12	$(C_3H_7)_2AsCl_2H_5$	1,4621	1,4621	52,88	52,79	+0,09	(22)
13	$(C_4H_7)_2AsCl_2H_7$	1,4615	1,4615	57,75	57,44	+0,31	(22)
14	$(C_3H_7)_2AsCl_2H_9$	1,4618	1,4618	62,18	62,09	+0,09	(22)
15	$(C_3H_7)_2AsCl_2H_9$ - iso	1,4606	1,4606	62,48	62,09	+0,39	(22)
16	$(C_3H_7)_2AsCl_2H_{13}$	1,4625	1,4625	71,67	71,39	+0,28	(22)
17	$(C_3H_7)_2AsCl_2H_{19}$	1,4650	1,4650	85,74	85,33	+0,41	(22)
18	$(C_3H_7)_2AsCl_2H_{21}$	1,4603	1,4603	94,34	94,24	+0,10	(22)
19	$(C_4H_9)_2AsCl_2H_3$	1,4653	1,4653	57,49	57,44	+0,05	(9)
20	$(C_4H_9)_2AsCl_2H_5$	1,4613	1,4613	62,38	62,09	+0,29	(9)
21	$(C_4H_9)_2AsCl_2H_9$	1,4627	1,4627	71,59	71,39	+0,20	(9)
22	$(CH_3)(C_4H_9)AsOC_3H_7$	1,4575	1,4575	53,10	52,79	+0,31	(10)
23	$(CH_3)(C_4H_9)AsOC_4H_9$	1,4588	1,4588	57,57	57,44	+0,10	(10)
						$\Delta_{avg.}$ 0,28	

will apparently reduce the number of characteristics required for calculating MR_D of the indicated substances.

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