obtained by Heldman and Thurmond for $\ln \gamma_1$ at 25° is a result of their failing to take into consideration the change of the heat of fusion with temperature.

It can be concluded from the present study that a solution of aluminum bromide in a normal hydrocarbon becomes more ideal as the number of carbon atoms in the hydrocarbon increases.

From the relationship of the experimental solubility curves for aluminum bromide in *n*-butane and *n*-hexane, it is further concluded that such systems are quite regular in the Hildebrand sense, *i.e.*, the solubility curves for any one solute in a number of different solvents will form a family of curves.

Summary

The solubility of aluminum bromide in *n*-hexane has been measured from 30.6° to the melting point of the salt.

The difference between the actual and the ideal solubility of aluminum bromide in *n*-hexane and *n*-butane is in approximate conformance with the internal pressure characteristics of these hydrocarbons according to the equation of Hildebrand.

Data are still not sufficient to allow the prediction of the solubility of aluminum bromide in a normal paraffin hydrocarbon.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES, AND THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

The Electric Moments of Some Aromatic Selenium Compounds

BY MAX T. ROGERS AND TOD W. CAMPBELL

Very few measurements of the dipole moments of organic compounds of selenium have been made. Since information concerning bond angles, bond moments, and resonance in selenium compounds may be derived from such data, the electric moments of a series of aromatic selenides, diselenides and selenocyanates have been measured in benzene solution.

Experimental

Materials

Benzene.—J. T. Baker C. P. benzene was dried over sodium and filtered before use, $d^{25}{}_4$ 0.87340, $n^{25}{}_D$ 1.4978.

Purification and Analysis of Compounds.—The compounds reported are all solids described in the literature. They were obtained in a high state of purity by repeated fractional crystallization to constant melting point. Most were analyzed for selenium by a flame combustion method.[1]

Dibenzyl diselenide was prepared by allowing benzyl selenocyanate to stand in methanol for ten days. The crude product was purified and analyzed[1]; m. p. 93°.

Diselenides.—Other diselenides were prepared from the corresponding Grignard reagent by addition of purified[2] selenium. The resulting selenophenol was oxidized to the diselenide with a stream of air[2,3]; diphenyl diselenide, m. p. 63°; di-*p*-tolyl diselenide, m. p. 47°; di-*p*-bromophenyl diselenide, m. p. 108°.

Selenides.—These were prepared from the corresponding diazotized amine and potassium selenide[4]; di-*p*-tolyl selenide, m. p. 69.5; di-*p*-chlorophenyl selenide, m. p. 96°. Benzyl selenocyanate was prepared from benzyl chloride and potassium selenocyanate in alcohol,[5] m. p. 72°.

Selenocyanates.—Other selenocyanates were prepared from the corresponding diazotized amine and potassium selenocyanate after the method of Behagel and Rollman[6]; *p*-tolyl selenocyanate, m. p. 70°; *p*-chlorophenyl selenocyanate, m. p. 55°.

Apparatus and Methods

Electric moments were determined in benzene at 25° by the dilute solution method. Dielectric constants were measured to ±0.001 with a heterodyne-beat apparatus previously described[7]; densities to ±0.00005 with a graduated pycnometer[8] of 10-ml. capacity. Refractive indices were determined to ±0.0001 with a Zeiss Abbe refractometer. The mole refractions of the solids were calculated from the refractive indices $n^{25}{}_D$ of the solutions using the equations

$$R_{12} = \frac{(n^2 - 1)\; M_1f_1 + M_2f_2}{(n^2 + 2)\; d}$$

and MR_D (solute) $= R_2 = (R_{12} - R_1)/f_2 + R_1$ where R_1, R_2 and R_{12} are the mole refractions of solvent, solute, and solution, respectively; d the density of a solution containing mole fraction f_2 of solvent of molecular weight M_1. The average of the values of MR_D obtained as above from solutions of different concentration, was used as the sum of the atomic and electronic polarizations in calculating μ.[9] Since the dispersion correction to MR_D and the atomic polarization tend to cancel both have been neglected rather than try to estimate two small uncertain quantities.[10]

The experimental data and molar polarizations are shown in Table I; the derived values of the molar polarization at infinite dilution P_∞, the mole refraction MR_D, and the dipole moment μ,

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[1] J. D. McCullough, T. W. Campbell and N. J. Krilanovich, *Ind. Eng. Chem. Anal. Ed.*, **18**, 638 (1946); the analyses of seven of the compounds used here are given in this article.

[2] T. W. Campbell and J. D. McCullough, THIS JOURNAL, **67**, 1965 (1945).

[3] D. G. Foster, "Organic Syntheses," Vol. XXIV, John Wiley and Sons, New York, N. Y., 1944, p. 89.

[4] H. M. Leicester, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, N. Y., 1943, p. 238.

[5] C. L. Jackson, *Ann.*, **179**, 1 (1875).

[6] O. Behagel and M. Rollman, *J. prakt. Chem.*, **123**, 336 (1929).

[7] M. T. Rogers and J. D. Roberts, THIS JOURNAL, **68**, 843 (1946).

[8] G. R. Robertson, *Ind. Eng. Chem. Anal. Ed.*, **11**, 464 (1936).

[9] For method of calculation, see Smyth, "Dielectric Constants and Molecular Structure," Reinhold Publishing Co., New York, N. Y., 1931.

[10] C. P. Smyth, THIS JOURNAL, **51**, 2051 (1929).

TABLE I

DIELECTRIC CONSTANTS, DENSITIES, REFRACTIVE INDICES AND MOLAR POLARIZATIONS IN BENZENE AT 25°

f_2	ϵ	$n^{25}{}_D$	$d^{25}{}_4$	P_2
	Diphenyl diselenide			
0.00000	(2.2725)		0.87340	(P_1 = 26.636)
.00201	2.2831		.87692	130.3
.00468	2.2966		.88126	130.5
.00580	2.3037		.88321	133.5
.01061	2.3284		.89086	133.0
.01332	2.3408	1.5042	.89515	131.2
.01937	2.3696	1.5067	.90477	129.6
.02516	2.3989	1.5093	.91402	129.5
	Di-*p*-tolyl diselenide			
0.00311	2.2976	1.4993	0.87858	188.2
.00478	2.3123	1.5000	.88119	188.0
.00779	2.3383	1.5013	.88593	190.1
.01221	2.3766	1.5032	.89284	191.1
.01848	2.4286	1.5060	.90256	189.6
.02500	2.4840	1.5089	.91242	189.5
	Dibenzyl diselenide			
0.00304	2.2866	1.4998	0.87865	131.3
.00507	2.2954	1.5004	.88189	131.1
.00716	2.3061	1.5012	.88533	133.8
.01117	2.3234	1.5032	.89181	131.1
.01557	2.3439	1.5057	.89890	132.7
.02214	2.3761	1.5081	.90925	134.7
	Di-*p*-bromophenyl diselenide			
0.00415	2.2820	1.5004	0.88591	101.5
.00869	2.2930	1.5031	.90016	100.1
.01076	2.2976	1.5045	.90630	100.2
	Di-*p*-tolyl selenide			
0.00421	2.2940	1.4990	0.87739	135.1
.01028	2.3268	1.5010	.88271	138.8
.01177	2.3359	1.5015	.88400	140.4
	Di-*p*-chlorophenylselenide			
0.00700	2.2849	1.5008	0.88358	84.5
.01503	2.2985	1.5030	.89510	83.9
.02246	2.3115	1.5059	.90521	84.6
	Benzyl selenocyanate			
0.00365	2.3555	1.4983	0.87665	368.5
.00625	2.4152	1.4994	.87910	364.7
.01264	2.5623	1.5003	.88474	356.7
.02197	2.7818	1.5015	.89199	348.8
.02709	2.9068	1.5027	.89755	342.9
.03311	3.0514	1.5038	.90278	336.4
	p-Tolylselenocyanate			
0.00207	2.3284		0.87537	430.9
.00289	2.3519		.87690	426.9
.00322	2.3571		.87571	424.8
.00429	2.3859		.87662	423.1
.01196	2.5885	1.4993	.88376	403.0
.01562	2.6799	1.5000	.88680	393.4
.02652	2.9680	1.5012	.89593	376.8
	p-Chlorophenyl selenocyanate			
0.00303	2.3199		0.87693	266.1
.00371	2.3307	1.4988	.87755	267.6
.00450	2.3437	1.4990	.87861	267.8
.00937	2.4226	1.5000	.88397	267.7
.01315	2.4839	1.5008	.88827	265.7
.02479	2.6755	1.5029	.90116	260.2

of each compound, are shown in Table II. The probable error in MR_D measured experimentally from the refractive indices of the solutions is about ±2 cc.; the values estimated from empirical constants are probably somewhat better. The probable error in P_∞ is about 5% and in μ roughly ±0.1 for compounds whose moments lie between one and four Debye units; the dipole moment of a compound whose moment is less than one may, however, be in error by 0.3–0.4 since the percentage error in ($P_\infty - MR_D$) is large when the difference is small.

TABLE II

MOLAR REFRACTIONS, MOLAR POLARIZATIONS AND DIPOLE MOMENTS

Substance	MR_D	P_∞, 25°	μ (Debye)
Diphenyl diselenide	75.7	133	1.67
Di-*p*-tolyl diselenide	84.7	192	2.29
Dibenzyl diselenide	84.7[a]	133	1.54
Di-*p*-bromophenyl diselenide	91.8	102	0.70
Di-*p*-tolylselenide	72.6	140	1.81
Di-*p*-chlorophenyl selenide	72.6[a]	84.7	0.77
Benzyl selenocyanate	47.3	372	3.98
p-Tolyl selenocyanate	47.8[a]	434	4.35
p-Chlorophenyl selenocyanate	48.5	269	3.28

[a] Estimated from the empirical constants of Eisenlohr (*Z. physik. Chem.*, **75**, 585 (1910)), along with the value 12.6 for selenium and 26.21 for benzene. The value for selenium is an average calculated from mole refractions of aromatic selenium compounds measured in this Laboratory.

Discussion of Results

The bond moment C_{ar}–Se between the carbon atom of an aromatic ring and a selenium atom, and the angle C–Se–C in aromatic selenides, may be evaluated[11] simultaneously from the observed moments of diphenyl selenide[12] (1.38) and di-*p*-tolyl selenide (1.81). Assuming the bond moments H–C = 0.4 and $C_{aliphatic}$–$C_{aromatic}$ = 0.4, we obtain C_{ar}–Se = 0.88 and ∠C–Se–C = 115°. The moment calculated for di-*p*-chlorophenyl selenide is then 0.30 while the observed value is 0.77. This difference is within the limits of error of the experimental value because of the uncertainty in the correction to be made for atom polarization in solution measurements which becomes relatively

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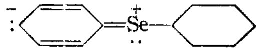
[11] Bond moments and calculations are discussed in the following references: (a) Pauling, "Nature of the Chemical Bond," Cornell University Press, 2nd ed., 1940; (b) C. P. Smyth, *J. Phys. Chem.*, **41**, 209 (1937); (c) Sidgwick, "The Covalent Link in Chemistry," Cornell University Press, Ithaca, N. Y., 1933.

[12] E. Bergmann, L. Engel and S. Sandor, *Z. physik. Chem.*, **B10**, 397 (1930).

important when the observed moment is low; the experimental error is also larger in these cases.

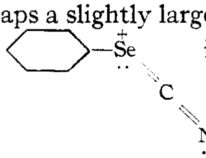
The observed dipole moments[12] of diphenyl sulfide (1.50) and di-*p*-tolyl sulfide (1.93) by a similar calculation lead to a value of the bond moment C_{ar}–S = 1.00 and ∠C–S–C = 115° in aromatic sulfides. These angles are close to those reported for diphenyl ethers from electric moment data[13] and an electron diffraction study.[14] Although the probable error is large in angles determined in this way from dipole moment data, the consistency of the results seems to indicate that the above values are at least approximately correct.

Since the electronegativity of carbon, sulfur and selenium are nearly the same, the comparatively large values of the C–S and C–Se moments indicate that the contribution of structures of the type  to the ground state of the molecule is small; apparently only in diphenyl ether (bond moment C_{ar}–O = 0.65) do these structures contribute appreciably and lower the bond moment.

From the observed moments of the diselenides, we may calculate values of ∠C–Se–Se using the bond moments derived above. If free rotation about the Se–Se bond is assumed, the observed moments of diphenyl diselenide, 1.67, and di-*p*-tolyl diselenide, 2.29, lead to values of ∠C–Se–Se = 114° and 105° 30′, respectively. The average, 110°, is close to the value ∠C–S–S = 107 ± 3° found in an electron diffraction investigation of dimethyl disulfide.[15] The calculated moment of di-*p*-bromophenyl diselenide using ∠C–Se–Se = 110° and the bond moment values previously obtained is 0.31; the observed value, 0.70, is not in disagreement with this since, as mentioned above, the probable error in dipole moments measured in solution is large when the moment is small. The observed electric moment of dibenzyl diselenide, 1.54, leads to a value of bond moment $C_{aliphatic}$–Se = 0.78 (0.10 less than C_{ar}–Se) if ∠C–Se–Se = 110° is used.

The moments of diphenyl disulfide[12] and di-*p*-nitrophenyl disulfide calculated using the bond moment C_{ar}–S = 1.0 and ∠C–S–S = 110° are 1.82 and 3.32, respectively; the observed values are 1.81 and 3.56.

The observed moments of the diselenides and disulfides could also be accounted for by a fixed skew configuration of the molecules as observed for hydrogen peroxide,[16] with the two C–Se bonds lying in planes making a dihedral angle of about 90°.

The experimental values of the moments of *p*-tolyl selenocyanate and *p*-chlorophenyl selenocyanate may be used to calculate simultaneously the magnitude and direction of the moment of the selenocyanate group. Assuming free rotation about the C–Se bond, and using the same bond moments as before, it is found that the group moment C_{ar}–SeCN = 3.83, in a direction inclined 126° 30′ to the line through the axis of the benzene ring and the Se atom. Since ∠C–Se–C might be expected to be near 125°, the group dipole is largely along the SeCN direction as would be anticipated. The C_{ar}–SCN moment calculated from Bergmann's data[17] by the above method is 3.36, 0.47 less than the C_{ar}–SeCN moment, indicating perhaps a slightly larger contribution of the structure  in the selenium compound.

The bond moment calculated for $C_{aliphatic}$–SeCN from the observed dipole moment of benzyl selenocyanate (assuming tetrahedral angles for carbon) is 3.74; this is equal, within experimental error, to the value for C_{ar}–SeCN so no attempt has been made to calculate a mesomeric moment for the selenocyanate group.

Summary

The electric moments of nine aromatic selenides, diselenides and selenocyanates have been measured in benzene solution at 25°.

Assuming additivity of bond moments and constancy of bond moments and of bond angles within a given series, the bond moments $C_{aromatic}$–Se = 0.88 and $C_{aliphatic}$–Se = 0.78, and the angle ∠C–Se–C in aromatic selenides = 115°, have been calculated. If free rotation about the Se–Se bond of diselenides is further assumed, ∠C–Se–Se = 110° is obtained. From the electric moments of the selenocyanates, the group moment C–SeCN = 3.83, in a direction making an angle of 126° 30′ with the C–Se bond, has been derived. The bond angles agree, within their rather large probable errors, with available data on analogous oxygen and sulfur compounds.

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