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An Electron Diffraction Investigation of Dimethyl Selenide

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The results of an electron diffraction investigation of $(CH_3)_2Se$ are C–H/Se–C, 1.09/1.97 (assumed); Se–C, 1.977 ± 0.012 Å.; Se · · · H, 2.571 ± 0.034 Å.; C · · · C, 2.98 ± 0.23 Å.; ∠C–Se–C, 98 ± 10°; and ∠Se–C–H, 110.5 ± 3.5°. The selenium-carbon distance of 1.98 Å. leads to a single-bond radius for selenium of 1.22 Å., which is considerably larger than the value 1.17 Å. chosen by Pauling.

A selenium–carbon distance of 2.01 ± 0.03 Å. has been reported from an X-ray diffraction investigation of 1,4-diselenane.[1] Smaller values have been reported for other molecules, but none of these molecules is comparable to diselenane. In di-*p*-tolylselenium dichloride[2] (Se–C = 1.93 ± 0.03 Å.), di-*p*-tolylselenium dibromide[2] (1.95 ± 0.03), diphenylselenium dibromide[3] (1.91 ± 0.05), and diphenyl diselenide[4] (1.93 ± 0.05) aromatic groups are conjugated with the empty d orbitals and unshared p electrons of selenium and the coördination of selenium, except in diphenyl diselenide, is fourfold rather than twofold. In perfluorodimethyl selenide[5] (1.958 ± 0.022) and perfluorodimethyl diselenide[5] (1.934 ± 0.018) the situation is exceptional because of the perfluoro substitution.[6] We undertook an electron diffraction investigation of dimethyl selenide in order to provide an additional, more precise value for the Se–C distance in a simple compound of bi-covalent selenium. Our result, 1.977 ± 0.012 Å., is in fair agreement with the diselenane value.

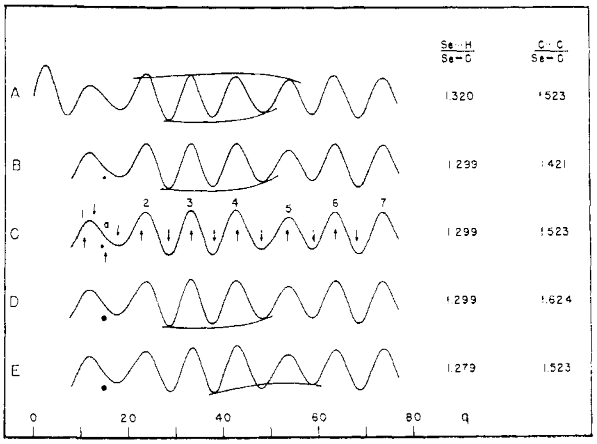

Fig. 1.—Theoretical intensity curves for dimethyl selenide. All curves calculated with Se–C = 1.97, C–H = 1.09, a_{C-H} = 0.0017, $a_{Se...H} = a_{C...C}$ = 0.0041. Best model: Se...H/Se–C = 1.300 and C...C/Se–C = 1.51 (close to curve C). Significant points of comparison with observation are indicated by critical marks. (See W. F. Sheehan, Jr., and V. Schomaker, THIS JOURNAL, **74**, 4468 (1952).)

Experimental

The sample (b.p. 57–59°) was supplied by Mr. Jordan Bloomfield of the Massachusetts Institute of Technology. Electron diffraction photographs were taken on Kodak 50 plates with 40 kv. electrons at 10 cm. distance in a new apparatus recently constructed in these laboratories. The temperature of the sample bulb was about −50°. The photographs were interpreted in the usual way.[7]

Theoretical intensity curves (Fig. 1) were calculated for Se–C = 1.97, C–H = 1.09, 2.52 ⩽ Se · · · H ⩽ 2.62, 2.80 ⩽ C · · · C ⩽ 3.30, with Z_H^{eff} = 1.25, a_{C-H} = 0.0017 and, for most of the curves, $a_{Se...H} = a_{C...C}$ = 0.0041.[8] Reasonable variations of the *a* values and of the ratio C–H/Se–C were tested and found to have only very small effects on our final results.

The weak, rather sharp feature 1*a* is readily visible on the photographs even though it is shown only very weakly by the best curve, C, and but little more strongly by a corresponding curve with (Z–F)'s rather than *Z*'s as coefficients. This, however, is characteristic of the appearance of such features. All other aspects of C, including even the minor differences in the widths, asymmetries, and amplitudes of the maxima and minima, are in exceptionally good agreement with our observations.

TABLE I

COMPARISONS OF OBSERVED AND CALCULATED POSITIONS OF MAXIMA AND MINIMA (CURVE C)

	Minima		Maxima	
No.	$q_{obsd.}$[a]	$q/q_{obsd.}$	$q_{obsd.}$[a]	$q/q_{obsd.}$
1	7.10	(0.986)	10.64	(1.006)
1a	12.95	(1.081)	15.13	(0.991)
2	17.79	(1.016)	22.79	(1.038)
3	28.42	1.009	33.17	1.004
4	37.99	0.998	42.88	0.996
5	48.01	1.006	53.55	1.009
6	58.92	0.999	63.62	1.002
7	68.10	1.010		
	Av. 9 features		1.0037	
	Av. dev.		0.0044	

Se–C = 1.97 × 1.0037 = 1.977 Å.

[a] Measurements of K. H. Check measurements were made by the other authors.

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[1] R. E. Marsh and J. D. McCullough, THIS JOURNAL, **73**, 1106 (1951).

[2] J. D. McCullough and R. E. Marsh, *Acta Cryst.*, **3**, 41 (1950).

[3] J. D. McCullough and G. Hamburger, THIS JOURNAL, **63**, 803 (1941).

[4] R. E. Marsh, *Acta Cryst.*, **5**, 458 (1952).

[5] H. J. M. Bowen, *Trans. Faraday Soc.*, **50**, 452 (1954).

[6] An anomalously short C–O distance is found (ref. 5) for perfluorodimethyl ether, an analog of perfluorodimethyl selenide, and progressive substitution of H by F shortens the C–F distance in the series CH_3F · · · CF_4 (L. O. Brockway, *Acta Cryst.*, **7**, 682 (1954)).

[7] K. Hedberg and A. J. Stosick, THIS JOURNAL, **74**, 954 (1952).

[8] We write $a_{ij} = {}^1/_2(\overline{\delta r_{ij}^2} - \overline{\delta r_{Se-C}^2})$. Approximation of the methyl group vibrations as pure bendings and pure stretchings leads to the somewhat larger value 0.0055 for $a_{Se...H}$. Normal coördinate treatment of the molecule, regarded as triatomic with skeletal frequencies assigned by P. Donzelot, *Compt. rend.*, **203**, 1069 (1936), shows that for reasonable values of the potential constants $a_{C...C}$ varies over the approximate range 0.0006–0.0060; the choice of 0.0041 for $a_{C...C}$ is purely arbitrary.

The phase shift expected for the Se–C interaction (J. A. Ibers and J. Hoerni, *Acta Cryst.*, **7**, 405 (1954)) in effect increases $\overline{\delta r_{Se-C}^2}$ by about 0.0016 Å.² and should have been taken into account in estimating the other a_{ij}. The only appreciable change would be the reduction of a_{C-H} to about 0.0009, and its effect on the theoretical curves would be very small.

Our final parameters and estimated limits of error, as deduced from qualitative comparisons of calculated curves (Fig. 1) and from ratios of calculated to observed positions of maxima and minima (Table I is an example), are the following: C–H/Se–C = 1.09/1.97 (assumed), Se···H/Se–C = 1.300 ± 0.017, (∠Se–C–H = 110.5 ± 3.5°), C···C/Se–C = 1.51 ± 0.11, (∠C–Se–C = 98 ± 10°), Se–C = 1.977 ± 0.012 Å., Se···H = 2.571 ± 0.034 Å., and C···C = 2.98 ± 0.23 Å.

Discussion

It seems appropriate to regard the selenium–carbon bonds in unconjugated compounds of bivalent selenium as normal and, therefore, to take 1.98 Å. as the normal Se–C single bond length. With a small (and perhaps unjustifiable) correction for electronegativity difference, the selenium radius then becomes 1.22 Å. (1.98 = 0.77 + 1.22 – (0.09 × 0.1)). This is appreciably greater than Pauling's value 1.17 Å.,[9] which is supported by the bond lengths of 2.32 Å. in hexagonal selenium[10] and 2.34 Å. in both α- and β-monoclinic selenium.[11,12] It has been pointed out,[13] however, that nominal single bonds in the heavier elements may actually have appreciable double-bond character; our value for the selenium radius is in agreement with this possibility, which, accordingly, may deserve further consideration.

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(9) L. Pauling, "The Nature of the Chemical Bond," 2nd edition, Cornell University Press, Ithaca, N. Y., 1940, p. 165.

(10) A. J. Bradley, *Phil. Mag.*, **48**, 477 (1924).

(11) R. Burbank, *Acta Cryst.*, **4**, 140 (1951).

(12) R. E. Marsh, L. Pauling and J. D. McCullough, *ibid.*, **6**, 71 (1953).

(13) V. Schomaker and D. P. Stevenson, THIS JOURNAL, **63**, 37 (1941).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF LONDON, KING'S COLLEGE]

The Effect of Solvent in Dipole Moment Measurements

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The apparent dipole moments of acetophenone, phenetole, chlorobenzene, nitrobenzene and benzonitrile have been calculated from solution data by the conventional method, and by employment of the solvent effect equations of Sugden, Smith and Goss. The values differ from the true vapor values by amounts which depend on the method of calculation. These differences can be almost completely eliminated by averaging the values obtained by the four different methods.

The purpose of the present paper is to draw attention to the fact that, by suitable combination of three solvent effect equations—those due to Sugden,[1] Smith,[2] and Goss[3]—with the conventional expression for dipole moments in solution,[4] values of the moments can be obtained which, for five compounds at least, agree very reasonably with the true values which the compounds exhibit when in the vapor state. For the purpose of discussion the following notation is employed.

P_{12} is the total polarization of a two component mixture and is given by

$$P_{12} = [(\epsilon_{12} - 1)/(\epsilon_{12} + 2)](M_1c_1 + M_2c_2)/d_{12} \quad (1)$$

ϵ denotes dielectric constant, d density, M molecular weight, c mole fraction, n refractive index, and the subscripts 1, 2, and 12 refer respectively to the solvent, the solute and the mixture. P_1 and P_2 are the partial polarizations of the solvent and of the solute and are calculated on the assumption that P_1 is independent of c. P_{s1} and P_{s2} are the corresponding partial polarizations obtained by the intercept method,[5] in which P_{s1} is assumed a function of c. μP denotes orientation polarization, P_D distortion polarization. These are related by

$$\mu P = P_{2\infty} - P_D \quad (2)$$

where P_D is given by

$$P_D = 1.05(n_2^2 - 1)/(n_2^2 + 2)M_2/d_2 \quad (3)$$

The subscript ∞ indicates the value of the particular parameter at infinite dilution, μ, the dipole moment is calculated from the Debye equation

$$\mu = 0.0128[T(P_{2\infty} - P_D)]^{1/2} \quad (4)$$

The solvent effect equation of Sugden, which is applicable to the particular case of polar solutes dissolved in the non-polar solvent benzene, may be written

$$P_2 = A + \mu P(\epsilon_{12} - 1)/(\epsilon_{12} + 2) \quad (5)$$

In this A is a constant characteristic of the solute and solvent. Plotting P_2 against $(\epsilon_{12} - 1)/(\epsilon_{12} + 2)$ should therefore yield a straight line of slope μP, and from this μ can be calculated by equations 2 to 4.

The second solvent effect equation considered is that due to Smith.[2,6] This is written

$$P_{2\infty} = B + \mu P(\epsilon_1 - 1)/(\epsilon_1 + 2) \quad (6)$$

where again B is a constant. When polar solvents are used it is necessary to correct the measured $P_{2\infty}$ values for the quantity $\partial P_1/\partial c_2$, *i.e.*, for the variation in P_1 with concentration of the solute. Then plotting $P_{2\infty\ \mathrm{cor}}$ against $(\epsilon_1 - 1)/(\epsilon_1 + 2)$ should yield a straight line from which μP and μ can be calculated as before.

The third solvent effect treatment considered is due to Goss,[3,7] and applies strictly only when the isotropic, non-polar solvent CCl_4 is used. The relevant equations are

$$P_{s2} = P_D + Z\{(\epsilon_{12} - 1)/(\epsilon_{12} + 2)\}^4 + Y/\epsilon_{12} \quad (7)$$

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(2) J. W. Smith, *Trans. Faraday Soc.*, **48**, 802 (1952).

(3) F. R. Goss, *J. Chem. Soc.*, 1915 (1937).

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