136°); $[\alpha]^{25}_{5893}$ +40.7° initial, changing to a final value of +7.1° (c, 4; CHCl₃).

The mutarotation, observed in alcohol-free chloroform, is shown by the curve in Fig. 1.

Anal. Calcd. for C₁₇H₂₆O₁₂: alkoxyl, 18.06. Found: alkoxyl, 18.1.

Ethylmercaptal Ethyl-d-galacturonate.—This compound was prepared from d-galacturonic acid in the same manner as the methyl ester. A dry hydrogen chloride–ethanol solution (approx. 1 N) was used as the solvent. The ethyl ester did not crystallize as readily as the methyl ester. By the repeated addition of absolute ethanol and removal under reduced pressure crystallization was induced. The concentrate was placed in a refrigerator for twenty-four hours to permit more complete crystallization.

From 10 g. of d-galacturonic acid, the yield was 9.6 g. (57%). Recrystallization from absolute ethanol gave a pure product; m. p. 128–129°; $[\alpha]^{25}_{5893}$ +15.7° (c, 2; EtOH).

Anal. Calcd. for C₁₂H₂₄O₆S₂: S, 19.53. Found: S, 19.62.

Ethylmercaptal Tetraacetyl Ethyl-d-galacturonate.—This acetyl derivative was prepared by the same method used for the corresponding methyl ester. From 9.6 g. of crude ethyl mercaptal ethyl ester the yield after one recrystallization was 11.5 g. (79%); m. p. 80–81°; $[\alpha]^{25}_{5893}$ +11.0° (c, 4; CHCl₃).

Anal. Calcd. for C₂₀H₃₂O₁₀S₂: S, 12.92. Found: S, 12.93.

Aldehydo Tetraacetyl Ethyl-d-galacturonate.—The preparation is similar to that of the corresponding methyl ester. The compound is quite soluble in toluene; m. p. 95–97°; $[\alpha]^{25}_{5893}$ −24.0° (c, 4; CHCl₃).

The rotations obtained in the study of the rotatory dispersion with a comparison to the values calculated from the two-term Drude equation, are given in Table II.

Anal. Calcd. for C₁₆H₂₂O₁₁: —OEt, 11.54. Found: —OEt, 11.7.

β-Ethylhemiacetal Tetraacetyl Ethyl-d-galacturonate.—The hemiacetal was prepared by both of the methods which were used for the methyl ester. The resulting compounds were apparently identical and could not be fractionated; m. p. 105–106°; $[\alpha]^{25}_{5893}$ −14.4° initial, reaching equilibrium at −1.6° (c, 4; CHCl₃). The course of the mutarotation, observed in alcohol-free chloroform, is shown by the curve in Fig. 2.

Anal. Calcd. for C₁₈H₂₈O₁₂: —OEt, 20.70. Found: —OEt, 20.8.

Summary

1. The α- and β-ethyl hemiacetals of aldehydo tetraacetyl methyl-d-galacturonate have been prepared. The mutarotation of the two compounds in chloroform indicates an interconversion over the aldehydo form.

2. The ethyl ester of ethyl mercaptal, ethyl mercaptal tetraacetyl, aldehydo tetraacetyl and ethyl hemiacetal tetraacetyl d-galacturonic acid have been prepared. Through mutarotation studies the ethyl hemiacetal tetraacetyl ethyl-d-galacturonate obtained is characterized as a β-hemiacetal.

3. The rotatory dispersions of the aldehydo tetraacetyl methyl- and ethyl-d-galacturonate have been shown to be complex but normal. Two-term Drude equations have been calculated for the dispersions to obtain a qualitative interpretation of the results.

MADISON, WISCONSIN　　　　RECEIVED MARCH 1, 1940

The Dipole Moments and Structures of Certain Compounds of Sulfur, Selenium and Phosphorus

BY C. P. SMYTH, G. L. LEWIS, A. J. GROSSMAN AND F. B. JENNINGS, III

The dipole moments of hydrogen disulfide and sulfur and selenium monochlorides have been measured with a view to obtaining evidence as to the two possible structures, the Y-shaped or irregular tetrahedral such as S—SCl₂ and the more extended structures such as Cl—S—S—Cl, as well as getting some information bearing on the magnitudes of the bond moments. Selenium oxychloride and phosphoryl and thiophosphoryl chlorides have been investigated for the sake of the bond moments involved. Indeed, bond moment values obtained from the measurements on the two latter compounds already have been

published,[1] and electron diffraction measurements have been made upon the more volatile of these several substances. The moments were obtained with the apparatus and methods previously described,[2,3] the dielectric constants and densities of solutions of the substances in benzene or heptane being determined.

Preparation of Materials.—Benzene and heptane were purified as in previous work.[4]

Hydrogen Disulfide.—The material was prepared from sodium polysulfide and purified in the manner described

(1) Smyth, THIS JOURNAL, **60**, 183 (1938).

(2) Lewis and Smyth, *J. Chem. Phys.*, **7**, 1085 (1939).

(3) Lewis and Smyth, THIS JOURNAL, **61**, 3063 (1939).

(4) Smyth and Walls, *ibid.*, **54**, 1854 (1932).

by Butler and Maass[5]; d^{25}_4 1.3279, $n^{25}D$ 1.62635, $n^{22}D$ 1.63237.

Sulfur Monochloride.—Material previously prepared in this Laboratory was fractionally distilled at 10 mm. over sulfur; b. p. (10 mm.) 39°.

Selenium Monochloride.—The material was prepared from selenium and purified by methods described in the literature.[6,7] In spite of all precautions, it could not be regarded as very pure.

Selenium Oxychloride.—Material from the Eastman Kodak Company was vacuum distilled seven times in a glass apparatus which had been acidified with dry hydrogen chloride and completely sealed except for the outlet to the pump. It was then recrystallized and the third recrystallization crop was quickly filtered through a sintered glass crucible. After another vacuum distillation, this material was used for the measurements; $n^{20}D$ 1.65159.

Phosphoryl Chloride.—Material from the Baker and Adamson General Chemical Company was fractionally distilled twice; b. p. 107.0–107.1°, $n^{25}D$ 1.45816, d^{25}_4 1.6659. As this fractionation did not alter the boiling point and raised the refractive index by only 0.0001, a second sample of refractive index 1.45797 was used without purification for a second series of measurements, which agreed well with the first.

Thiophosphoryl Chloride.—Material from the Eastman Kodak Company was dried with calcium chloride and fractionally distilled twice; b. p. 125.0°, $n^{25}D$ 1.5432, d^{25}_4 1.6271.

Experimental Results.—The dielectric constants ϵ and the densities d of benzene or heptane solutions containing mole fraction c_2 of solute are given in Table I, the polarizations P_2 being listed in the last column. The polarization of the pure solvent is given as P_1. The measurements were carried out at 25° with the exception of those on a second set of solutions of phosphoryl chloride in benzene at 10, 40 and 60°, which agreed well with the results on the first set measured at 25°. Table II lists in the second column the values of MR_D, the molar refraction for the D sodium line, calculated for the colored sulfur monochloride and selenium monochloride as the sums of the atomic refractions given in the literature,[8] and for the other substances from the data in the present paper, the density of selenium oxychloride being taken from the literature.[9] A value obtained from the data of Lenher and Kao[7] for selenium monochloride is practically identical with that calculated for the corresponding sulfur compound and is, therefore, to be regarded as too

(5) Butler and Maass, THIS JOURNAL, **52**, 2184 (1930).

(6) Blanchard, Phelan and Davis, "Synthetic Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1936, p. 335.

(7) Lenher and Kao, THIS JOURNAL, **47**, 772 (1925); **48**, 1550 (1926).

(8) Eisenlohr, "Spektrochemie organischer Verbindungen," F. Enke, Stuttgart, 1912.

(9) Henby and Sugden, J. Chem. Soc., 1058 (1929).

TABLE I

DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS

c_2	ϵ	d	P_2
Benzene–Hydrogen Disulfide (25°)			
0.00000	2.276	0.87344	(26.667 = P_1)
.04962	2.380	.88572	44.5
.10021	2.485	.89825	43.3
.14604	2.581	.90959	42.3
.19871	2.691	.92263	41.3
Benzene–Sulfur Monochloride (25°)			
.0580	2.509	.9218	76.6
.1097	2.711	.9624	73.6
.2415	3.256	1.0666	69.3
.3392	3.559	1.1382	64.2
Benzene–Selenium Monochloride (25°)			
.0760	2.838	1.0188	115
.1711	3.543	1.2060	102
.2596	4.251	1.3840	93.7
.3783	5.280	1.6218	85.8
Benzene–Selenium Oxychloride (25°)			
.00743	2.349	0.88158	165
.01265	2.400	.88730	163
.02013	2.474	.89550	160.8
.03467	2.616	.91144	156.0
.04380	2.706	.92145	153.5
Benzene–Thiophosphoryl Chloride (25°)			
.01815	2.324	.8888	73.1
.03091	2.362	.8998	73.3
.05691	2.432	.9219	71.6
.07938	2.499	.9418	70.9
.1175	2.603	.9741	69.9
.1698	2.749	1.0178	69.0
Heptane–Thiophosphoryl Chloride (25°)			
.00000	1.922	0.67944	(34.64 = P_1)
.02445	1.958	.6960	72.9
.04330	1.990	.7089	72.1
.07316	2.043	.7296	71.2
.1012	2.089	.7496	70.1
.1468	2.174	.7826	69.6
.1675	2.215	.7979	69.5
Benzene–Phosphoryl Chloride (25°)			
.00000	2.278	.87339	(26.693 = P_1)
.01937	2.433	.8893	140.9
.03925	2.599	.9056	139.0
.09528	3.087	.9514	132.3
.19205	3.994	1.0294	121.5

c_2	0	0.01950	0.03930	0.07046	0.09712	0.1961
t, °C.				ϵ		
10	2.309	2.473	2.655	2.941	3.198	4.201
40	2.242	2.390	2.545	2.794	3.012	3.877
60	2.199	2.330	2.470	2.698	2.890	3.669
				d		
10	0.88880	0.9044	0.9216	0.9475	0.9696	1.0511
40	.85693	.8728	.8888	.9138	.9352	1.0142
60	.83520	.8508	.8665	.8912	.9123	.9900
	P_1			P_2		
10	26.678	143.4	143.0	138.6	135.3	123.1
40	26.669	138.3	136.4	132.6	129.3	119.1
60	26.680	131.0	130.2	127.8	124.4	115.7

MOLAR REFRACTIONS, POLARIZATIONS AND DIPOLE
MOMENTS

Substance	MR_D	P_∞	$\mu \times 10^{18}$
H_2S_2	17.64	45.8(25°)	1.17
S_2Cl_2	28	80.9(25°)	1.60
Se_2Cl_2	36	126(25°)	2.1
$SeOCl_2$	25.0	168(25°)	2.62
$POCl_3$	25.13	147.0(10°)	2.36
		143.4(25°)	2.39
		140.0(40°)	2.41
		133.4(60°)	2.42
		Mean value =	2.40
$PSCl_3$	32.8	74.3(25°)	1.41 (in benzene)
		74.4(25°)	1.41 (in heptane)

low. The difference of 7.9 in the two values makes a difference of only 0.09 in the moment values. The last two columns of Table II give the polarization P_∞ obtained by extrapolation to $c_2 = 0$ of the values of P_2 in Table I and the dipole moments.

Discussion of Results

The moment of diphenyl disulfide,[10] which is apparently an extended structure C_6H_5—S—S—C_6H_5, is 1.81. The C–S bond moment was calculated[1] on the reasonable assumption of an 112° C–S–C angle. If it is assumed that the greater separation of the attached groups in the disulfide prevents widening of the C–S–S angle by repulsion, this may be taken as 90°. Complete freedom of rotation around the S–S bond would then give a calculated moment[11] = 1.414 × 1.3 = 1.84 in excellent agreement with the observed 1.81. If the C–S–C angle used in calculating the bond moment were really less than 112° or if the C–S–S angle were much widened by repulsion, the calculated moment would be lower than the observed. It would appear, however, that the observed moment is consistent with the extended structure with all positions of rotation around the S–S bond equally probable. A 90° azimuthal angle as suggested in the case of hydrogen peroxide[12] would lead to the same calculated value.

An analogous extended structure, H–S–S–H, for hydrogen disulfide, which is indicated by the electron diffraction measurements made in this Laboratory,[13] leads to a calculated moment value 1.41 × the H–S bond moment 0.68, if the H–S–S valence angle is 90°, as seems highly probable, and

if all positions of rotation around the S–S bond are equally probable or if the azimuthal angle is 90°. The value thus calculated 0.96 is 0.21 lower than the observed value 1.17, which cannot be more than 0.05 high because of neglect of atomic polarization. The discrepancy might arise from differences in the inductive effects in this molecule from those in the hydrogen sulfide molecule, from the moment of which the H–S bond moment is calculated. It would, however, be accounted for if the hydrogen disulfide contained a small proportion of Y-shaped molecules $H_2S^+ - S^-$, in which the large moment of the semipolar bond between the sulfur atoms could easily raise the mean moment to the observed value. It appears highly probable, however, that the largely predominant structure is H–S–S–H.

The problem of the structures of sulfur and selenium monochlorides is analogous to that of the disulfides. Raman spectra investigations have led Matossi and Aderhold[14] to ascribe a Y-shaped structure $SSCl_2$ to sulfur monochloride, while Morino and Mizushima[15] have concluded the structure to be Cl–S–S–Cl. Palmer's[16] electron diffraction measurements are interpreted as indicating an extended Cl–S–S–Cl structure. The dipole moment 1.0 found by Morino and Mizushima[15] for sulfur monochloride in heptane solution is much lower than the value 1.60 found here in benzene solution. If the bond moment value 0.5 calculated[1] from a somewhat doubtful moment value for SCl_2 but consistent with the sulfur and chlorine electronegativities is correct, the two chlorines would have to be on the same side of the extended structure of the molecule $\begin{matrix} Cl & Cl \\ | & | \\ S & —S \end{matrix}$ with a 90° Cl–S–S angle and a zero azimuthal angle to account for the moment value observed by Morino and Mizushima. Even this structure would fail to account for the much higher moment found in benzene solution. If the molecule had the bent Y-shaped or tetrahedral structure ^-S—$^+SCl_2$, the large moment of the semipolar bond between the sulfurs should exceed the small opposing S–Cl moments by an amount sufficient to give a resultant moment, at least, as large as 1.6. The moment 1.6 found for thionyl chloride,[17] which has been shown by electron

(10) Bergmann and Tschudnowsky, Z. physik. Chem., 17B, 107 (1932).

(11) Smyth, Dornte and Wilson, THIS JOURNAL, 53, 4242 (1931).

(12) Penney and Sutherland, Trans. Faraday Soc., 30, 898 (1934).

(13) Stevenson and Beach, THIS JOURNAL, 60, 2872 (1938).

(14) Matossi and Aderhold, Z. Physik, 68, 683 (1931).
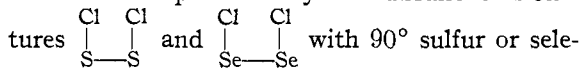
(15) Morino and Mizushima, Sci. Papers Inst. Phys. Chem. Research, Tokyo, 32, 220 (1937).

(16) Palmer, THIS JOURNAL, 60, 2360 (1938).

(17) Smith, Proc. Roy. Soc., London, 138, 154 (1932).

diffraction[16] to have a similar bent Y-shaped or irregular tetrahedral structure is identical with that here found for S_2Cl_2, although the more accurate vapor value 1.44 found by Coop and Sutton[18] is slightly lower.

The moment of selenium monochloride is 0.5 higher than that of the corresponding sulfur compound and the moment of selenium oxychloride is 1.0 higher than that reported for thionyl chloride. An increase in moment is to be expected from the more positive character of selenium as compared to sulfur, but, as in the cases of other bonds involving atoms of considerable size,[19] the increase is greater than would be anticipated from the difference 0.1 in the electronegativities of the two elements.[1,20] If moments 1.1 and 1.55 are assigned to the S—Cl and Se—Cl bonds, respectively, the moments of the two monochlorides can be reproduced by the unbranched structures $\begin{smallmatrix} Cl & Cl \\ | & | \\ S & S \end{smallmatrix}$ and $\begin{smallmatrix} Cl & Cl \\ | & | \\ Se & Se \end{smallmatrix}$ with 90° sulfur or selenium valence angles and freedom of rotation around the S–S or Se–Se bond when the molecules are surrounded by benzene but with much reduced freedom when the molecules are in heptane, somewhat as observed in the case of the ethylene halides.[11,21] However, this necessitates the assumption of the incorrectness of the SCl_2 moment value from which the S–Cl moment was previously calculated and gives a value higher than those of the P–Cl and I–Cl bonds, than which it should be lower. Also, the Se–Cl value is closer to that of As–Cl, 1.6, than the electronegativity difference 0.4 between Se and As would lead one to expect. If the Cl–S–S angle in S_2Cl_2 were 103° as reported by Palmer[16] instead of 90° as roughly assumed here, a still higher value would have to be assigned to the S–Cl moment. The moments of the monochlorides can be accounted for without the assumption of these seemingly too high bond moments if the molecules have the branched structures with semipolar bonds or if the substances, under the conditions of measurement, contained a considerable proportion of the branched molecules. The coexistence of the extended and the branched structures would thus be consistent with the moments observed for hydrogen disulfide as well

as for the two monochlorides. If this is the correct explanation of the moments, a moment of about 0.8 is to be assigned to the Se–Cl bond.

Coop and Sutton[18] have used the moments of thionyl chloride 1.44 and sulfuryl chloride 1.795 together with the assumption of tetrahedral structures to calculate approximate moment values, 0.61 for the S–Cl bond and 2.16 for the S–O bond. Use of the bond moment 0.5 for S–Cl together with the valence angles of the somewhat distorted tetrahedral structures reported by Palmer[16] for these two molecules gives an S–O value 1.64 in thionyl chloride and 2.36 in sulfuryl chloride. All of these values are lower than the value 2.5 for S–O calculated by Coop and Sutton from the moments of dimethylsulfone and dimethyl sulfide, but are not far from the S–O bond values calculated previously by one of the writers[1] from earlier values of the moments of these compounds. In this previous work the moment of the semipolar S$^+$—O$^-$ bond was concluded to be about 3.0, of the magnitude usually found for semipolar bonds. While the discrepancies in the values calculated above arise in part from uncertainties in the valence angles used, it appears fairly certain that the S—O bond moment in thionyl chloride is lower than the usual semipolar S$^+$—O$^-$ moment. Palmer attributes the abnormally short S–O bond distance found in these compounds to contributions from triply-bonded structures. The contributions from such structures as $^-S\equiv{}^+O$ would, of course, oppose the normal bond moment and reduce the value observed for it. Lister and Sutton[22] regard the bond as predominantly double in character, which would involve a moment lower than that of a semipolar bond. In either case, a moment lower than that of the usual hybridized semipolar bond is to be expected.

If it is assumed that the valence angles in selenium oxychloride are identical with those in thionyl chloride and the Se–Cl moment is taken as 0.8, the Se–O moment obtained is 2.95. Raising of the Se–Cl value to 1.5 would increase the Se–O value obtained only to 3.04. The Se–O bond value 3.0 thus obtained is typical of the somewhat hybridized semipolar bond. The more positive character of the selenium evidently reduces the contributions from the doubly-bonded and the much less probable triply-bonded structures.

(18) Coop and Sutton, Trans. Faraday Soc., 35, 505 (1939).

(19) Smyth, Grossman and Ginsburg, THIS JOURNAL 62, 192 (1940).

(20) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 64.

(21) Stearn and Smyth, THIS JOURNAL, 56, 1667 (1934).

(22) Lister and Sutton, Trans. Faraday Soc., 35, 495 (1939).

The data on phosphoryl chloride and thiophosphoryl chloride have already been used[1] to calculate the moments of the semipolar $P^+\!\!-\!\!O^-$ and $P^+\!\!-\!\!S^-$ bonds. As each of these bonds lies in the axis of symmetry of its molecule[23,24] with its moment acting in the opposite direction to the resultant of the three P–Cl bond moments, the semipolar bond moment was calculated by adding the moment of the PCl_3 molecule 1.1 to the moment observed for the whole molecule. A slight revision of the data on thiophosphoryl chloride raises the $P^+\!\!-\!\!S^-$ moment value from 2.4 to 2.5, the $P^+\!\!-\!\!O^-$ value 3.5 remaining unchanged. It was recognized that, as usual in the case of such bonds, neither of these was a pure semipolar bond as other resonating forms, particularly double-bonded structures, contributed to the structures of the molecules. The difference 1.0 between the $P^+\!\!-\!\!S^-$ and $P^+\!\!-\!\!O^-$ bonds appears surprisingly large, especially in view of the fact that the $C\!\!=\!\!S$ bond moment is greater by 0.3 than the $C\!\!=\!\!O$ moment.[1] Coop and Sutton[18] suggest that their low value for thiophosgene 0.28 as compared to 1.18 for phosgene[25] may be due to the inductive effects of the two C–Cl moments upon the very polarizable sulfur. In $PSCl_3$, the three P–Cl dipoles are farther from the S than are the two C–Cl dipoles in $CSCl_2$, but there are three of them instead of two. It appears quite reasonable, therefore, to attribute the lower moment value obtained for the $P^+\!\!-\!\!S^-$ bond as compared to the $P^+\!\!-\!\!O^-$ bond less to any inherent structural difference or even to the lower electronegativity of sulfur as compared to oxygen, than to the greater opposing moments induced by the P–Cl dipoles in the sulfur atom, which is much more polarizable than the oxygen.[26] The inherent moment of the $P^+\!\!-\!\!S^-$ bond is presumably not appreciably different from that of the $P^+\!\!-\!\!O^-$, the two lying in the neighborhood of 3.5, where most of the more or less hybrid semipolar bonds seem to lie.

Summary

The dielectric constants and densities of solutions of hydrogen disulfide, sulfur monochloride, selenium monochloride, selenium oxychloride, phosphoryl chloride and thiophosphoryl chloride in benzene or heptane have been measured and used to calculate the dipole moments of the molecules of the solutes.

The hydrogen disulfide moment may be explained by an extended structure H–S–S–H, but may be best explained if the substance contains also a small proportion of branched molecules $H_2S\!-\!S$. The sulfur monochloride and selenium monochloride moments may be explained with difficulty by extended structures, Cl–S–S–Cl and Cl–Se–Se–Cl, but correspond better to branched structures, $S\!-\!SCl_2$ and $Se\!-\!SeCl_2$, in the form of an irregular tetrahedron like that of $SOCl_2$ and $Se\!-\!OCl_2$, or to a mixture of the extended and the branched structures.

The value 3.0 is calculated for the moment of the Se–O bond in selenium oxychloride which has more polar character than the S–O bond in thionyl chloride. The moments of phosphoryl chloride and thiophosphoryl chloride have been used to calculate the values 3.5 and 2.5 for the moments of the semipolar bonds $P^+\!\!-\!\!O^-$ and $P^+\!\!-\!\!S^-$, the latter of which is lowered more than the former by induction.

(23) Brockway and Beach, THIS JOURNAL, **60**, 1836 (1938).
(24) Beach and Stevenson, *J. Chem. Phys.*, **6**, 75 (1938).
(25) Smyth and McAlpine, THIS JOURNAL, **56**, 1697 (1934).

(26) Smyth, *Phil. Mag.*, **50**, 361 (1925).