427. *Studies in Dielectric Polarisation. Parts II,*
III, and IV.

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PART II. BENZENE SOLUTIONS OF *n*-PROPYL MERCAPTAN,
n-BUTYL MERCAPTAN, THIOPHENOL, AND ACETONITRILE.

THE dipole moment of ethyl mercaptan (1·39) is greater than that
of hydrogen sulphide (1·01), while the moment of ethyl alcohol
(1·70) is smaller than that of water (1·87) (Part I; J., 1931, 2062).
The present paper describes the dipole moments of two further
members of the mercaptan series and of thiophenol.   The moments
of ethyl, *n*-propyl, and *n*-butyl mercaptans (methyl mercaptan is
a gas, b. p. 6°) are equal within the limits of experimental error,
thus resembling those of the corresponding alcohols, and thiophenol
has a moment little different from that of an aliphatic mercaptan,
thus resembling phenol, the moment of which (1·70) is equal to
that of the aliphatic alcohols (1·65—1·70).

Apparatus.—The electrical apparatus used in Part I has been redesigned
as shown in Fig. 1.   The three independent circuits are contained in earthed

Cu screens, through the sides of which the battery leads and connexions enter by means of plug and socket connexions. The two oscillators A and B are coupled to the rectifier by means of the "floating grid" method of Zahn (*Physical Rev.*, 1924, **24**, 300). Other methods of coupling gave less satisfactory zero points on the standard variable condenser (C_S). In the circuit adopted, the coupling between the oscillators is very light and free from damping, the coupling with the older apparatus being much tighter. The
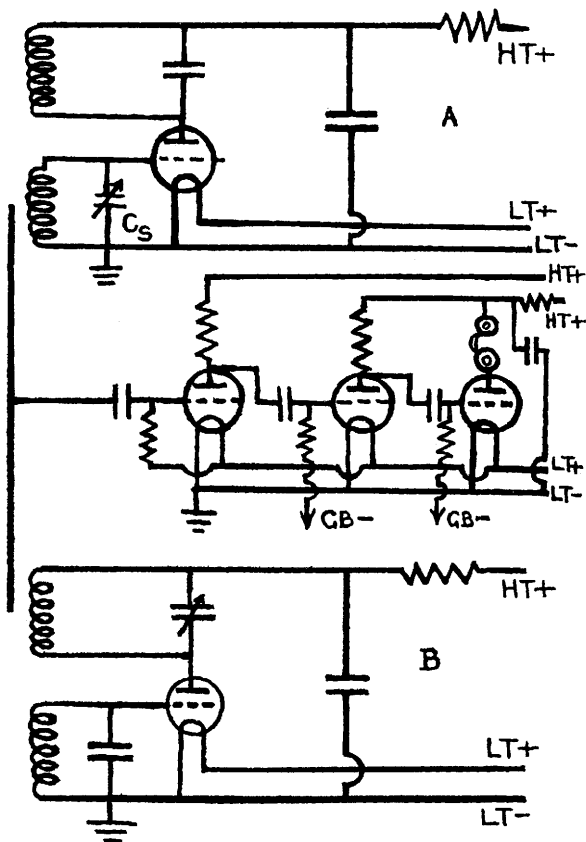

Fig. 1.

high tension was obtained from a 120-volt accumulator battery, frequently charged, and low tension from separate 2-volt accumulators. The leads to the dielectric cell were about 6 cm. long and 4 cm. apart. Increasing the length of the leads did not affect the value of the dielectric const. of C_6H_6 beyond the exptl. error, which is estimated as 0·1—0·2%. The small cell was discarded, all measurements being made with the larger cell. The methods of measuring the dielectric const., refractivities, and densities are described in Part I, and all determinations, as before, were at 20°. If the

valves had been running for 1 hr. before measurements were begun, the frequency remained quite steady, and there was practically no sign of creep.

Preparation of Materials.—n-Propyl and n-butyl mercaptans were purchased from Kodak Ltd., thiophenol from Boots Ltd., and acetonitrile from British Drug Houses Ltd. The mercaptans were dried over anhyd. Na_2SO_4 and fractionated; the acetonitrile was distilled from P_2O_5 five times and fractionated.

	B. p.	$D_4^{20°}$.	$n_D^{20°}$.
n-Propyl mercaptan	63·7°/763 mm.	0·8391	1·4348
n-Butyl mercaptan	97·2°/758 mm.	0·8397	1·4411
Thiophenol	167·4°/759 mm.	1·0791	1·5895
Acetonitrile	81·8°/766 mm.	0·7827	1·3420

Results.—The method of calculation employed is described in Part I, the mol. polarisation P_2 being obtained from measurements of dil. C_6H_6 solutions of the substances, and the electron polarisation P_E from measurements on the refractivity and density of the pure compounds. The dipole moment μ is then given by $\mu = 0.0127 \times 10^{-18} \sqrt{(P_2 - P_E) \cdot T}$, where T is the abs. temp.

f_1.	f_2.	ϵ.	$D_4^{20°}$.	P_{12}, c.c.
		n-*Propyl mercaptan.*		
1	—	2·275	0·8782	26·50
0·9800	0·0200	2·318	0·8767	27·16
0·9566	0·0434	2·374	0·8757	27·97
0·9279	0·0721	2·458	0·8742	29·13
		n-*Butyl mercaptan.*		
1	—	2·277	0·8785	26·52
0·9778	0·0222	2·326	0·8771	27·37
0·9607	0·0393	2·357	0·8757	28·00
0·9462	0·0538	2·395	0·8754	28·54
0·9266	0·0734	2·441	0·8744	29·29
0·9095	0·0905	2·491	0·8729	30·10
		Thiophenol.		
1	—	2·281	0·8788	26·57
0·9912	0·0088	2·304	0·8805	26·97
0·9812	0·0188	2·333	0·8832	27·39
0·9619	0·0381	2·381	0·8877	28·15
0·9401	0·0599	2·436	0·8921	28·97
		Acetonitrile.		
1	—	2·281	0·8788	26·57
0·99184	0·00816	2·407	0·8785	28·18
0·98956	0·01044	2·434	0·8784	28·59
0·98437	0·01563	2·514	0·8781	29·59
0·97418	0·02582	2·665	0·8776	31·35
0·96546	0·03454	2·838	0·8773	33·24

Substance.	P_2, c.c.	P_E, c.c.	$P_2 - P_E$, c.c.	$\mu \times 10^{18}$, e.s.u.
n-Propyl mercaptan	61	23·7	37·3	1·33
n-Butyl mercaptan	65	28·4	36·6	1·32
Thiophenol	72	34·4	37·6	1·33
Acetonitrile	224	11·0	213·0	3·16

DISCUSSION OF RESULTS.

The results, together with relevant results of other workers (all in e.s.u. $\times 10^{-18}$, as throughout), are summarised below.

H_2O	1·87 [1]			H_2S	1·10 [6]	0·93 [7]
$CH_3\cdot OH$ ...	1·66 [2]	1·68 [3]	1·65 [4]	$CH_3\cdot SH$	—	
$C_2H_5\cdot OH$...	1·71 [2]	1·70 [3]	1·74 [4]	$C_2H_5\cdot SH$	1·39 (Part I)	
$C_3H_7\cdot OH$...	1·66 [2]	1·66 [3]		$C_3H_7\cdot SH$	1·33	
$C_4H_9\cdot OH$...	1·66 [2]	1·66 [3]		$C_4H_9\cdot SH$	1·32	
$C_6H_5\cdot OH$...	1·70 [5]			$C_6H_5\cdot SH$ ...	1·33	
$CH_3\cdot CN$ ...	3·11 [8]	3·40 [9]		$CH_3\cdot CN$	3·16	

[1] Jona, *Physikal. Z.*, 1919, **20**, 14.
[2] Wolf and Gross, *Z. physikal. Chem.*, 1932, *B*, **14**, 305.
[3] Miles, *Physical Rev.*, 1929, **34**, 964.
[4] Stranathan, *ibid.*, 1928, **31**, 653.
[5] Williams and Allgeier, *J. Amer. Chem. Soc.*, 1927, **49**, 2416.
[6] v. Braunmühl, *Physikal. Z.*, 1927, **28**, 141.
[7] Miles and Zahn, *Physical Rev.*, 1928, **32**, 497.
[8] Werner, *Z. physikal. Chem.*, 1929, *B*, **4**, 371, 391.
[9] Williams, *ibid.*, 1928, **138**, 75.

It was concluded in Part I that the mercaptans have a V-shaped molecule, and, in order to calculate the moment of Et_2S from those of hydrogen sulphide and ethyl mercaptan, it was assumed, on the basis of calculation of Hund (*Physikal. Z.*, 1925, **31**, 81), that the valency angle of H_2S was 62°. Dadieu and Kohlrausch (*Physikal. Z.*, 1932, **33**, 168) have, since Part I was published, calculated the valency angle to be 90°, from the moments of inertia as determined from the Raman spectrum, and this value, which appears to us more probable than that of Hund, is adopted in the present communication.

The dipoles m_1, m_2, of a V-shaped molecule may affect each other by mutual induction on account of lack of molecular rigidity, since each group is subjected to the electric field of the other. This action will set up induced moments in each group so as to lessen the resultant dipole (Smallwood and Herzfeld, *J. Amer. Chem. Soc.*, 1930, **52**, 1919). In addition to the deformation of the polar group, there will also be induction of moments by each dipole along each hydrocarbon chain, but the effect so produced by each dipole will be much reduced by the field of the other. If the two permanent moments are perpendicular they will not interact, and each dipole will produce the maximum possible induction. If we assume that the valency angle of 90° for hydrogen sulphide is preserved in the simple mercaptans and sulphides, and that the group moment C–S in the mercaptan is the same, 0·66, as that of H–S in H_2S (which will probably not be far wrong, since the carbon atom contains a shell of fully shared electrons), the values of μ calculated for $CH_3\cdot SH$ and $(CH_3)_2S$ by a method closely similar to that used by Smallwood and Herzfeld (*loc. cit.*) are 1·45 and 1·84, respectively. The value

for $CH_3 \cdot SH$ is not known, but that for $(CH_3)_2S$ is distinctly lower than the calculated value, *viz.*, 1·40 (see Part III). We must, it seems, conclude that, in addition to the induction effects which are allowed for in the calculation, there may be some distortion of the valency bonds caused by the field of the C–S dipole.

The group moments H–S, CH_3S–, and C_2H_5S– calculated from the experimental moments of the three sulphides, *viz.*, 0·93, 1·40, and 1·57 respectively, the valency angle being taken as 90° as before, are : H–S = 0·66, CH_3S– = 0·99, C_2H_5S– = 1·11, and the moments of methyl and ethyl mercaptans can be obtained by combining the group moment of HS with those of CH_3S, and C_2H_5S, respectively, to give μ $CH_3 \cdot SH$ = 1·2, and μ $C_2H_5 \cdot SH$ = 1·3. The group moments so calculated include the effects of induction, since they are derived from experimental values. The calculated moment of methyl mercaptan lies between those of hydrogen sulphide and ethyl mercaptan. The moments of the aliphatic alcohols are approximately constant and lower than that of water. This difference between the mercaptans and alcohols is probably due to the difference in the deformabilities of the sulphur ($\alpha = 3·66 \times 10^{-24}$ c.c.) and the oxygen atom ($\alpha = 1·27 \times 10^{-24}$ c.c.), as calculated from the octet refraction (Smyth, " Dielectric Constant and Molecular Structure," 1931, p. 151). Debye (" Polar Molecules," 1929, Chap. iv) calculates from the moments of inertia that the valency angle of water may be either 60° or 110°. Either value leads to a structure in which the two dipoles would interact. The lower values for the alcohols, as compared with water, may thus be due to the lowering of the resultant moment, owing to interaction of the two dipoles.

It is of interest to compare these homologous series with the normal aliphatic chlorides and nitriles :

n-Aliphatic chlorides.

HCl	1·03	Zahn, *Physical. Rev.*, 1924, **24**, 300.
CH_3Cl	1·86	Fuchs, *Z. Physik*, 1930, **63**, 824.
C_2H_5Cl	2·05	,, ,, ,, ,,
C_3H_7Cl	1·94	Parts, *Z. physikal. Chem.*, 1931, B, **12**, 312.
C_4H_9Cl	1·97	Parts, *ibid.*, 1930, B, **7**, 327.

n-Aliphatic nitriles.

HCN	2·65	Werner, *loc. cit.*
$CH_3 \cdot CN$	3·11	,, ,,
	3·40	Williams, *Z. physikal. Chem.*, 1928, **138**, 75.
$C_2H_5 \cdot CN$	3·34	Werner, *loc. cit.*
	3·40	Williams, *loc. cit.*
$C_3H_7 \cdot CN$	3·46	Werner, *loc. cit.*

The increase in moment on passing from methyl to ethyl chloride indicates that induction occurs, but the comparison of ethyl and *n*-propyl chloride is not so satisfactory, since they were measured

by different experimenters. The increase in moment on passing from hydrogen chloride to methyl chloride has been accounted for satisfactorily by Smyth (*op. cit.*, p. 64) by means of a calculation similar to the one we have used for methyl mercaptan. In the nitrile series, the discrepancy in the values for acetonitrile makes it difficult to decide if induction occurs. For this reason we have redetermined the moment of acetonitrile, and have obtained 3·16, in satisfactory agreement with the value of Werner. Induced moments are therefore present in the aliphatic nitriles, which, on account of the larger value of the C–CN dipole, extend at least as far as the third carbon atom, whereas in the case of the chlorides this induction only proceeds as far as the second carbon atom. Werner (*loc. cit.*) has shown that the moments of hydrogen cyanide and the nitriles can be represented by the empirical formula :

$$\mu \ C_nH_{2n+1} \ CN = a + b + b/2 + b/2^2 + .. + b/2^{n-1}$$

in which a is the moment of hydrogen cyanide, b the increment in moment on passing from hydrogen cyanide to acetonitrile, and n the number of carbon atoms in the molecule. This equation agrees with the rapid diminution of the dipole effect on passing along the hydrocarbon chain. The uniform changes in dipole moment and refraction from hydrogen cyanide through the series of normal nitriles, as found by Werner and by Lowry and Henderson (*Proc. Roy. Soc.*, 1932, *A*, **166**, 471), show that if any hydrogen *iso*cyanide molecules are present in hydrogen cyanide (Usherwood, J., 1922, **121**, 1604), their amount must be negligibly small (cf. Partington and Carroll, *Phil. Mag.*, 1925, [vi], **49**, 665 ; Partington, J., 1926, 1559).

Although alcohols and mercaptans are chemically analogous, the important differences in their physical properties indicate that the latter are unassociated in the pure state and in benzene solutions, while alcohols are associated under these conditions, a result confirmed by the measurements of the dipole moments.

Although mercaptans, like alcohols, may contain donor and acceptor groups, these seem incapable of promoting association or solubility in water. This is, at first sight, unexpected, since sulphur in sulphides is capable of co-ordination with oxygen to form sulphoxides and sulphones, while the analogous oxygen compounds are unknown. The case of hydrogen peroxide, for which Smyth (*op. cit.*, p. 86) assumes a semipolar double bond between the oxygen atoms on the basis of the high dielectric constant, does not appear to be certain, on account of the possible effects of intramolecular rotation in the case of formula (I).

(I.)   H–O–O–H   H₂>O→O (II.)

4 x 2
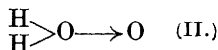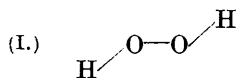
Spectroscopic and viscosity results indicate that in hydrogen halides the proton penetrates somewhat into the electron shell of the halogen, and Debye (*op. cit.*, Chap. iv) considers that penetration occurs into the oxygen of the water molecule. We should expect that ease of penetration would be parallel to the deformability of the central atom, and hence the hydrogen in the S–H group would be screened more completely than in the O–H group, and would show little tendency to association.

The relative insolubility of the mercaptans in water, which is one aspect of this, may be explained in another way. A factor which influences solubility is the relative magnitude of the internal pressures of solute and solvent. When the internal pressures of the mercaptans and alcohols, calculated by Malisoff, Marks, and Hess (*Chem. Rev.*, 1930, **8**, 501), are plotted against the numbers of carbon atoms in the molecule, it is found that the curve for the alcohols lies wholly above that for the mercaptans. The two curves, however, rapidly approach as the higher members of the series are reached, since the effect of the polar group becomes progressively smaller, and the fall in the internal pressures of the higher alcohols, in fact, is followed by a decrease in their solubility in water. The higher internal pressure of the alcohols, as compared with the corresponding mercaptans, is in part due to the larger dipole moments of the former.

In the case of hydrogen compounds the dipole moment is greatest for the compound of the first element in a group in the periodic table :

HF ? ; HCl 1·03 ; HBr 0·79 ; HI 0·38 (Zahn, *loc. cit.*).

H_2O 1·87 ; H_2S 1·01.

NH_3 1·46—51 ; PH_3 0·54 ; AsH_3 0·13—18 (Watson, *Proc. Roy. Soc.*, 1927, *A*, **117**, 43).

Instead of the moment increasing with increase in nuclear separation, as the lighter elements are replaced by heavier ones, a decrease is found. This is almost certainly due to the distortion of the electron shell of the element by the hydrogen, the deformability increasing more rapidly than the atomic volume, and so over-compensating the greater nuclear separation.

SUMMARY.

The dipole moments of ethyl, *n*-propyl, and *n*-butyl mercaptans, and of thiophenol, are approximately constant, and larger than that of hydrogen sulphide. The moment found for acetonitrile is in agreement with that found by Werner and lower than the result of Williams.

The chemical and physical properties of the mercaptans and

alcohols have been discussed, and an explanation offered for the difference in molecular complexity of these compounds.

PART III. BENZENE SOLUTIONS OF METHYL, n-PROPYL, AND n-BUTYL SULPHIDES.

THE dipole moment of ethyl sulphide is higher than that of ethyl mercaptan (Part I, J., 1931, 2062), while that of ethyl ether is lower than that of ethyl alcohol. Measurements of the moments of other members of the sulphide series have been made, and a comparison instituted with the corresponding oxygen compounds. The moments of the sulphides are found to be in all cases higher than those of the corresponding ethers. The previously known values show that this holds also for phenyl ether and phenyl sulphide, and anisole and thioanisole, whilst the moments of benzyl ether and benzyl sulphide were found by the same experimenter to be equal.

Preparation of Materials.—Methyl, n-propyl, and n-butyl sulphides, purchased from Kodak Ltd., were dried over anhyd. Na_2SO_4 and fractionated.

Compound.	B. p.	$D_4^{20°}$.	$n_D^{20°}$.
Methyl sulphide	38—38·5°/763 mm.	0·8476	1·4356
n-Propyl sulphide	140·2—140·5°/762 mm.	0·8444	1·4496
n-Butyl sulphide	188·5—188·9°/762 mm.	0·8450	1·4551

The method of calculation employed has been described in Part I (*loc. cit.*) and the apparatus used was the same as in Part II.

f_1.	f_2.	$D_4^{20°}$.	ϵ.	P_{12}, c.c.
		Methyl Sulphide.		
1	—	0·8790	2·280	26·56
0·9879	0·0121	0·8786	2·310	26·94
0·9804	0·0196	0·8784	2·333	27·23
0·9690	0·0310	0·8780	2·363	27·60
0·9511	0·0489	0·8770	2·404	28·08
0·9416	0·0584	0·8766	2·434	28·50
		n-*Propyl Sulphide.*		
1	—	0·8790	2·280	26·56
0·9894	0·0106	0·8778	2·313	27·21
0·9763	0·0237	0·8768	2·350	27·97
0·9686	0·0314	0·8765	2·378	28·49
0·9453	0·0547	0·8749	2·454	29·95
		n-*Butyl Sulphide.*		
1	0	0·8790	2·280	26·56
0·9870	0·0130	0·8782	2·321	27·48
0·9835	0·0165	0·8776	2·330	27·71
0·9704	0·0296	0·8767	2·375	28·70
0·9650	0·0350	0·8762	2·392	29·10
0·9523	0·0477	0·8756	2·429	29·96

Substance.	P_2.	P_E.	$P_2 - P_E$.	$\mu \times 10^{18}$.
Methyl sulphide	60·5	19·1	41·4	1·40
n-Propyl sulphide	88·5	37·6	50·9	1·55
n-Butyl sulphide	99·0	46·9	52·1	1·57

DISCUSSION OF RESULTS.

The results are here collated with those of other observers :

Methyl ether	1·32 [1]	1·29 [2]	Methyl sulphide...	1·40	
Ethyl ether	1·10 [1]	1·14 [2]	Ethyl sulphide ...	1·57 [6]	
Propyl ether	1·16 [3]		Propyl sulphide	1·55	
Butyl ether	—		Butyl sulphide ...	1·57	
Phenyl ether	1·13 [4]		Phenyl sulphide...	1·47 [7]	1·56 [8]
Anisole	1·16 [5]		Thioanisole	1·27 [7]	
Benzyl ether	1·38 [7]		Benzyl sulphide...	1·38 [7]	

[1] Sanger and Steiger, *Helv. Phys. Acta*, 1929, **2**, 136.
[2] Stuart, *Z. Physik*, 1928, **51**, 490.
[3] Meyer and Buchner, *Physikal. Z.*, 1932, **33**, 390.
[4] Bergmann and Tschudnowsky, *Z. physikal. Chem.*, 1932, B, **17**, 107.
[5] Højendahl, *Thesis*, Copenhagen, 1928.
[6] Hunter and Partington, J., 1931, 2062.
[7] Bergmann, Engel, and Sandor, *Z. physikal. Chem.*, 1930, B, **10**, 397.
[8] De Vries and Rodebush, *J. Amer. Chem. Soc.*, 1931, **53**, 2888

The moments of the ethers are seen to be lower than those of the corresponding alcohols, while the reverse is true for the mercaptans and sulphides. The moments of the ethers decrease slightly from the methyl to the ethyl and propyl compounds, whilst a corresponding increase in moment is found for the sulphides, which is no doubt due to induction along the hydrocarbon chain (see Part II). The mixed ether, anisole, shows little difference in moment from methyl or phenyl ethers, but the higher moment of benzyl ether as compared with phenyl ether is unexpected. With the exception of benzyl sulphide, the sulphides have higher moments than the corresponding ethers. There are noticeable differences between the results for the ethers and sulphides; thus, thioanisole has a lower moment than methyl or phenyl sulphide, and the same is true for benzyl sulphide.

In the ethers and sulphides, the moments of the aliphatic and aromatic compounds in each group are nearly the same. This is usually found to be the case for molecules with a V-shaped structure, since the inclination of the principal dipole to the hydrocarbon chain lessens its electrostatic effect. When the central element is directly attached to hydrogen, as in water, hydrogen sulphide, alcohols, and mercaptans, the moments decrease on passing from oxygen to sulphur, and this effect, which is general with the hydrogen compounds of the elements of a group in the periodic table, has been discussed in Part II. It is not necessarily found when the central element is attached to elements other than hydrogen. Thus, for fluorobenzene, the moment 1·39 (Walden and Werner, *Z. physikal. Chem.*, 1929, B, **2**, 10) is comparable with that of iodobenzene, 1·38, and smaller than those of chloro- or bromo-benzene, 1·56 and 1·53, respectively (Tiganik, *Z. physikal. Chem.*, 1931, B, **13**, 425). The order of the hydrogen halides is

HCl 1·03, HBr 0·79, HI 0·38, and by analogy with the results for other hydrogen compounds, we may assume that the moment of the *normal* hydrogen fluoride molecule should be greater than that of hydrogen chloride. The effect of replacing the hydrogen atom by an alkyl or aryl group is clearly seen from the ratios of the moments in the accompanying table, in which the ethyl halides have been chosen as representative of alkyl compounds, since their moments are fairly accurately known.

X.	HX/HCl.	$C_6H_5X/C_6H_5Cl.$	$C_2H_5X/C_2H_5Cl.$
Br	0·77	0·98	0·91
I	0·37	0·88	0·79

The decrease in moment from RCl to RI is much less rapid than for the hydrogen halides, probably owing to the more complex structure of the carbon compounds. The resultant dipole is the vector sum of (i) the principal dipole C–X, which will not be very different from that of H–X (Part II); (ii) the moment which this group induces along the hydrocarbon chain; and (iii) the corresponding moment which (ii) induces in the principal dipole, C–X.

The third effect may be fairly large. Smyth ("Dielectric Constant and Molecular Structure," 1931, p. 75) found a value of 0·23 for this effect in the case of methyl chloride, and we have similarly calculated that a moment of 0·19 is induced in the C–S group in methyl mercaptan. The magnitude of this effect is mainly determined by the principal dipole C–X, and the deformability of this group. On passing from a lighter to a heavier element X of the same group in the periodic table, the moment of C–X is found to decrease, but the deformability of the element increases very rapidly and may over-compensate the decrease in the group moment. Thus, we see that fluorobenzene has a lower moment than chlorobenzene or bromobenzene, and the difference between the moments of the last two compounds is much smaller than that between the corresponding hydrogen halides.

The comparison of the halogen compounds is useful because of their simple structures. In the case of the oxygen and sulphur compounds, the comparison is less certain because of the effect of the inclined structures, but it would appear that, when the central element is attached to groups other than hydrogen, the moment of the sulphur compound is higher than that of the oxygen compound. This effect appears to be quite general and will be discussed in a later paper in connexion with the ketone and thioketone groups, for which our measurements are already available.

Bergmann and his collaborators have calculated the valency angles of oxygen and sulphur from measurements on para-substituted phenyl ethers and phenyl sulphides. The angle, ϕ, which the

resultant dipole of an inclined group makes with the produced axis of the benzene ring is given by cos $\phi = (m_1{}^2 + m_2{}^2 - \mu^2)/2m_1m_2$, where m_1 and m_2 are the group moments of the substituents, and μ the experimentally observed moment of the disubstituted molecule. Bergmann and Tschudnowsky (*loc. cit.*, p. 108) find the following angular values for *p*-substituted anisoles and diphenyl ethers :

Compound.	ϕ.	θ.	Compound.	ϕ.	θ.
p-F anisole	78°	156°	*p*·NO₂ diphenyl ether	87°	174°
p-Cl anisole	73	146	*p*·Br diphenyl ether ...	97	166
p-Br anisole	67	134	*p*·CH₃ diphenyl ether	108	144
p-I anisole	66	132			
p-NO₂ anisole	67	134			
p·CH₃ anisole	78	156			

The angle ϕ is that made by the resultant moment of the C–O–C group with the bond joining the O–phenyl groups. If we assume that the resultant is symmetrical with respect to the C–O–C bonds, we find the angle between the bonds, θ, also given in the table. Bergmann and Tschudnowsky thence conclude that the angle made by the resultant moment of the inclined group is dependent on the other substituent in the para-position. It would appear from the above results that the valency angle, θ, of oxygen in the substituted anisoles is smaller than in the substituted diphenyl ethers, yet the moments of the two series are very nearly the same. If the valency angle is greater in the diphenyl ethers, this must be compensated by a greater group moment C–O. In the case of the sulphides, Bergmann, Engel, and Sandor (*loc. cit.*) calculate a valency angle of 142° for phenyl sulphide, obtained from measurements on *p*-chlorodiphenyl sulphide ($\mu = 1.76$). In Part II it was shown that the moments of the mercaptans and the aliphatic sulphides are given in a semi-quantitative form, by assuming the valency angle of sulphur to be the same as in hydrogen sulphide, *viz.*, 90°. An analogous calculation for *p*-chlorodiphenyl sulphide, with the valency angle 90°, gives a moment of 1.1, and we conclude that the valency angle of sulphur in this compound differs from 90°.

Bergmann and Tschudnowsky found for the moment of *pp*'-dichlorodiphenyl sulphide a value of $\mu = 0.89$. They calculated this moment to be 2.65 by using the data from the results for *p*-chlorodiphenyl sulphide. We have recalculated this moment in the following way. The group moment Ph–S, calculated from the moment of Ph₂S ($\mu = 1.47$) and the valency angle of 142°, is $\mu = (1.47 \times 10^{-18})/2 \cos 71° = 2.24 \times 10^{-18}$. The moment of C–Cl can be taken as that of PhCl, 1.56. The moment of the $\overset{-}{S}$—$\overset{+}{\diagdown}\diagup\overset{+}{\diagup}$—$\overset{-}{Cl}$ group is then $(2.24 - 1.56) = 0.68$. Since the moments oppose, the resultant moment for *pp*'-dichlorodiphenyl sulphide is thus 0.44.

Dr. Bergmann, whom we have informed of the results of this calculation, is in agreement with the new value. In spite of the recalculation, the agreement between the observed and experimental values, although much improved, is seen to be far from good.

The moment of diphenyl disulphide has been found to be 1·81, and that of pp'-dinitrodiphenyl disulphide, 3·56 (Bergmann and Tschudnowsky, *loc. cit.*). The S–S bond is capable of free rotation, and thus the moment should vary with temperature, since at higher temperatures, the rotational energy of the PhS– groups will increase and tend to lessen the effect of the electrostatic forces between these groups (Williams, *Z. physikal. Chem.*, 1928, *A*, **138**, 75; Meyer, *ibid.*, 1930, *B*, **8**, 27; Smyth, Dornte, and Wilson, *J. Amer. Chem. Soc.*, 1931, **53**, 4242; Smyth and Walls, *ibid.*, 1932, **54**, 2261).

When the two group moments are so far separated that the rotation can be considered to be free, the moment will be independent of temperature, and the equation of Williams will apply. Since the radius of the sulphur atom is 1 Å.U. the separation of the group moments is only 2 Å.U., so that the electrical forces of the group will cause a hindrance to the motions of the groups. The calculation will, however, set an upper limit to the resultant moment. The group moment Ph–S is resolved along and perpendicular to the direction S–S and the perpendicular component gives rise to a resultant moment. In this resolution of the group moment the valency angle of the sulphur atom must be known. Two calculations have been made for the PhS– group moment from the moment of phenyl sulphide, by taking the valency angle either (1) 142°, or (2) 90°. The moment PhS– corresponding to these values becomes (1) 2·24, and (2) 1·04. The components resolved at right angles to the S–S bond are then (1) 2·24 sin 38°, and (2) 1·04. If all positions of the rotating dipole are equally probable, free rotation will give rise to a moment $\mu = m\sqrt{2}$ where m is the resolved moment perpendicular to the axis of rotation. For cases (1) and (2), $\mu = 1·95$ and 1·47 respectively. In a similar way, for pp'-dinitrodiphenyl sulphide, the group moment S–C_6H_4–NO_2 is found on supposition (1) to be 3·98 (moment of nitrobenzene) — 2·24 (PhS–); and for (2) 3·98 — 1·04, *viz.*, (1) 1·52 and (2) 4·16. Comparison with experiment indicates that neither value is satisfactory, since supposition (1) gives an upper limit of μ for pp'-dinitrodiphenyl disulphide which is only about 30% of the experimental moment. The latter, however, can only in the ideal uncoupled state be as large as the theoretical value so calculated, and can never be greater. Supposition (2) leads to more probable results in the case of pp'-dinitrodiphenyl disulphide, but for diphenyl

disulphide the experimental moment is again greater than the calculated upper limit. Although the calculations show that the moments of the disulphides can be qualitatively explained on the assumption of partially free rotation of the group moments, they do not give any definite information as to the values of the valency angles, but seem to lead to the result that in aromatic sulphur compounds both the valency angles and the group moments are larger than in the aliphatic compounds. There is, however, a serious objection to this conclusion. The valency angle in ethylene oxide must be about 60°, and that in tetrahydrofuran about 110°. Their moments are 1·88 (Stuart, *loc. cit.*) and 1·81 (Smyth, *op. cit.*, p. 202), respectively. It would not be expected that the moments of these cyclic ethers should remain so nearly equal whilst the valency angle of the oxygen atom has altered by such a large amount.

The effect of unsaturated cyclic systems on the moments of ethers and sulphides was commented upon in Part I. Since then more data have become available, which show that in the case of a five-membered ring, the moment is decreased, whilst in a six-membered ring there is an increase of moment, as compared with the open-chain compounds.

The higher deformability of a double bond allows polar influences to be transmitted through the hydrocarbon residue, and so modifies the resultant moment. In the case of heterocyclic ethers and sulphides, a shift of negative charge from the 2 : 2'-positions tends to neutralise the charges on the 1 : 1'-carbon atoms, and so compensates the charges conferred on these due to the polar bond. In the derivatives of pyridine, the effect of the unsaturated ring system is modified by the presence of the CN group, and a formal comparison can be made between these compounds and benzophenoneanil, in which there is a tertiary nitrogen doubly bound to carbon. In these heterocyclic compounds, substitution of hydrogen has only a small influence on the resultant moment, and we have found in work not yet published that this is true for the γ-pyrones.

SUMMARY.

There is an increase in dipole moment from methyl to ethyl sulphide, the moments of the higher sulphides remaining constant. A comparison of the ethers and sulphides seems to indicate that the valency angles of oxygen and sulphur in these compounds are different for the aliphatic and for the aromatic compounds.

PART IV. BENZENE SOLUTIONS OF METHYL AND ETHYL THIOCYANATES AND METHYL, ETHYL, AND ALLYL *iso*THIOCYANATES.

PERSCHKE (*Ber.*, 1929, **62**, 3054), from an examination of the parachors of a series of thiocyanates and *iso*thiocyanates, concludes that these compounds can be represented by formulæ (I) and (II), respectively. Since the triple bond in (I) has the same parachor

$$R{-}S{-}C{\equiv}N \qquad R{-}N{=}C{=}S \qquad R{-}\overset{\oplus}{N}{\equiv}C{\to}\overset{\ominus}{S}$$

(I.) (II.) (III.)
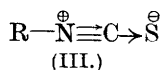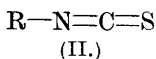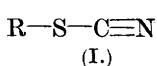
equivalent as the two double bonds in (II), the calculated group parachors are equal. A comparison of the dipole moments of the aromatic thiocyanates and *iso*thiocyanates has been made by Bergmann, Engel, and Sandor (*Z. physikal. Chem.*, 1930, *B*, **10**, 397) and Bergmann and Tschudnowsky (*ibid.*, 1932, *B*, **17**, 100), but no data are available for the aliphatic derivatives. In the present communication the dipole moments of a series of aliphatic thiocyanates and *iso*thiocyanates are reported. The method of calculation and the apparatus have previously been described (Part II).

Preparations of Materials.—Allyl *iso*thiocyanate was from British Drug Houses Ltd., the other compounds from Kodak Ltd. With the exception of methyl *iso*thiocyanate, which is cryst. (m. p. 33—34°), the compounds were dried with anhyd. Na_2SO_4 and fractionated (*cf.* Nasini and Scala, *Gazzetta*, 1887, **17**, 67).

	B. p.	$D_{4°}^{20°}$.	$n_D^{20°}$.
Methyl thiocyanate	130·2—130·4°/757 mm.	1·0750	1·4697
Ethyl thiocyanate	146·0—146·5°/762 mm.	1·0106	1·4641
Ethyl *iso*thiocyanate ...	131·0—131·2°/756 mm.	0·9990	1·5130
Allyl *iso*thiocyanate	150·5—150·9°/764 mm.	1·0152	1·5257

f_1.	f_2.	$D_{4°}^{20°}$.	ϵ.	P_{12}, c.c.
		Methyl iso*thiocyanate.*		
1	—	0·8789	2·280	26·56
0·99113	0·00887	0·8804	2·415	28·40
0·98433	0·01567	0·8815	2·527	29·85
0·97534	0·02466	0·8827	2·664	31·68
0·96833	0·03167	0·8839	2·808	33·14
0·96180	0·03820	0·8849	2·925	34·40
		Ethyl iso*thiocyanate.*		
1	—	0·8789	2·280	26·56
0·98697	0·01393	0·8807	2·512	29·75
0·96980	0·03020	0·8828	2·816	33·38
0·95314	0·04686	0·8847	3·149	37·02
		Allyl iso*thiocyanate.*		
1	—	0·8785	2·281	26·58
0·98952	0·01048	0·8803	2·447	28·93
0·98375	0·01625	0·8813	2·539	30·16
0·97805	0·02195	0·8820	2·626	31·29
0·97654	0·02346	0·8823	2·662	31·74
0·96823	0·03177	0·8830	2·797	33·40

$f_1.$	$f_2.$	$D_{4°}^{20°}.$	$\epsilon.$	P_{12}, c.c.
Methyl thiocyanate.				
1	—	0·8789	2·280	26·56
0·98528	0·01472	0·8811	2·557	30·23
0·98047	0·01953	0·8816	2·663	31·41
0·96816	0·03184	0·8838	2·906	34·24
0·95822	0·04178	0·8851	3·112	36·40
Ethyl thiocyanate.				
1	—	0·8789	2·280	26·56
0·98766	0·01234	0·8800	2·524	29·89
0·98311	0·01689	0·8810	2·623	31·17
0·97531	0·02469	0·8819	2·790	33·17
0·96564	0·03436	0·8833	3·015	35·65

Substance.	$P_2.$	$P_R.$	$P_2 - P_R.$	$\mu \times 10^{18}.$
Methyl thiocyanate ...	287	19	268	3·56
Ethyl thiocyanate ...	305	24	281	3·64
Methyl *iso*thiocyanate	236	21	215	3·18
Ethyl *iso*thiocyanate	257	26	231	3·31
Allyl *iso*thiocyanate ...	260	30	230	3·30

DISCUSSION OF RESULTS.

The foregoing results are discussed in relation to the following data for the aromatic compounds :

Phenyl thiocyanate	3·59 [1]	Phenyl *iso*thiocyanate	3·00 [2]
p-Chlorophenyl thiocyanate	2·93 [1]	p-Chlorophenyl *iso*thiocyanate	1·55 [2]
Phenyl *iso*cyanate	2·34 [3]	p-Bromophenyl *iso*thiocyanate	1·54 [2]
		p-Tolyl *iso*thiocyanate	3·32 [2]

[1] Bergmann, Engel, and Sandor, *Z. physikal. Chem.*, 1930, B, **10**, 397.
[2] Bergmann and Tschudnowsky, *ibid.*, 1932, B, **17**, 100.
[3] Eide and Hassel, *Tids. Kjemi*, 1930, **10**, 93.

The Raman spectrum of allyl *iso*thiocyanate, although difficult to interpret, seems to indicate the presence of a triple bond in the *iso*thiocyanate group (Dadieu and Kohlrausch, *Ber.*, 1930, **63**, 268). Since parachor measurements appear to exclude ring structures, such as that proposed by Dadieu and Kohlrausch, the alternative to formula (II) is (III), proposed by Bergmann and Tschudnowsky, which involves electron transference from nitrogen to sulphur. The distance between the centres of these atoms is about 3 Å.U., and the moment due to electron transference should therefore be about $3 \times 10^{-8} \times 4·77 \times 10^{-10} = 14·4 \times 10^{-18}$. The measured moment is less than one-third of this, and the formula involving semipolar bonds therefore seems unlikely. The stereochemistry of formulæ (I) and (II) indicates that the thiocyanate and the *iso*thiocyanate group should have V-shaped structures, due in the first case to the sulphur, which has this structure in the sulphides, and in the second case to the doubly bound nitrogen. The moments ($\mu \times 10^{18}$) of para-substituted phenyl *iso*thiocyanates, however, agree with those

calculated on the assumption that the –NCS group is linear (Bergmann and Tschudnowsky, *loc. cit.*) :

|	Calc.	Exptl.
p-Tolyl *iso*thiocyanate	3·4	3·32
p-Chlorophenyl *iso*thiocyanate	1·44	1·55
p-Bromophenyl *iso*thiocyanate	1·51	1·54

This result is surprising in view of the usual properties of doubly bound nitrogen, but could be explained on the assumption of electron transference, the triple N≡C bond leading to symmetry in the group. In support of this structure, it is found that the moments of the aliphatic *iso*thiocyanates show an increase from methyl to ethyl and differ from that of the phenyl compound (see Part III). The increase on passing from methyl to ethyl *iso*thiocyanate is almost certainly due to chain induction. Since the moment of allyl *iso*thiocyanate is the same as that of the ethyl compound, the presence of the double bond in the β-position does not affect the moment. The moment of phenyl *iso*thiocyanate is much greater than that of phenyl *iso*cyanate. This may be due to the C=S group moment being greater than that for the C=O group, since the dipole moment of thiobenzophenone, which we find to be 3·4 (unpublished), is also greater than that of benzophenone, 2·95 (Wolf, *Physikal. Z.*, 1930, **31**, 227).

The sulphur atom in a thiocyanate can be compared with that in a sulphide, its atomic refraction in these compounds (and in disulphides) being almost the same, *viz.*, 7·91, whereas in the *iso*thiocyanate group it is 9·4. The higher value in the latter case indicates greater deformation (Price and Twiss, J., 1912, **101**, 1259).

In the thiocyanates, the moments of the *p*-substituted benzene compounds indicate that the group is inclined, and Bergmann, Engel, and Sandor, from measurements on *p*-chlorophenyl thiocyanate, calculate that the resultant moment of the thiocyanate group makes an angle of 127° with the benzene ring. It is to be noted that both the thio- and the *iso*thio-cyanate group have the same sign as that of the C–Cl bond. We can account for the structure of the thiocyanate group if the moment C–S be taken as 0·66 (Part
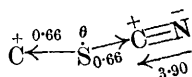

II), and the moment of C≡N as that of phenyl cyanide, 3·90. The resultant moment of the thiocyanate group is taken to be that of the phenyl compound, *viz.*, 3·59, and the angle θ is thus found to be 120°.
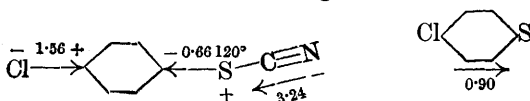
The calculated moment of p-chlorophenyl thiocyanate is similarly found to be 2·9 (2·93 exptl.). The calculation is very approximate, since no account is taken of the mutual interaction of the dipoles composing the thiocyanate group. It accounts, however, for the magnitude of the dipole moment and the stereochemical properties of the molecule. In support of the conclusions that the thiocyanate group is inclined, is the fact that the moments of the alkyl derivatives are almost the same as that of the phenyl compound (see Part II).

The resultant moment of the *iso*thiocyanate group is composed of the group moments

$$\overset{\oplus}{C} \overset{\ominus}{\longleftarrow} \underset{\ominus \rightarrow \oplus}{N} = \overset{\oplus}{C} \overset{\ominus}{\longleftarrow} S$$
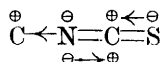
The moment C–N can be taken as 0·6, for $(CH_3)_3N$ (Steiger, *Helv. Phys. Acta*, 1930, **3**, 161), and we assume that μ C=N will be about twice μ C–N, giving $\mu = 1·2$. The moment C=S is taken as that of thiobenzophenone (3·4). Thus, if the groups are in the same straight line the resultant moment would be about 2·8. Bergmann, Engel, and Sandor (*Ber.*, 1930, **63**, 2572) found that azobenzene has zero moment and p-chloroazobenzene has a moment of 1·55 (cf. PhCl, $\mu = 1·56$), which indicates that the two phenyl nuclei in azobenzene have an extended structure, and that the valency bonds of doubly bound nitrogen in these compounds may not be inclined. If nitrogen in the *iso*thiocyanates has this structure, we can account for their dipole moments on the basis of an extended N=C=S group. Although this result is in conflict with the interpretation of the Raman spectrum, which indicates the presence of a triple bond, the latter conclusion is far from established.

SUMMARY.

There is an increase in moment from methyl *iso*thiocyanate to ethyl *iso*thiocyanate, which is probably due to induction along the hydrocarbon chain. The moment of allyl *iso*thiocyanate shows little difference from that of the ethyl compound, indicating that the double bond in the β-position is not influenced by the principal dipole. The *iso*thiocyanate group is best represented by a rod-like structure.

Methyl and ethyl thiocyanates have moments nearly equal to that of the phenyl compound. The absence of inductive effects in this case is no doubt due to the inclination of the polar group to the hydrocarbon chain, and this conclusion finds qualitative support in the calculated angle of the sulphur valencies in the thiocyanate group.

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