# 367. *Physical Properties and Chemical Constitution. Part XXI. Aliphatic Thiols, Sulphides, and Disulphides.*

By Arthur I. Vogel.

New determinations have been made of the refractivities at 20° and the parachors of a series of alkylthiols. By subtracting the constants for alkyl groups (Part XI, this vol., p. 611) the undermentioned values for the SH group are obtained; the constants for S (in thiols) are derived by subtracting the constants for H in $CH_2$ (Part IX, *J.*, 1946, 133):

| | *P.* | $R_C$. | $R_D$. | $R_F$. | $R_{G'}$. | $Mn_D^{20°}$. |
|---|---|---|---|---|---|---|
| SH | 66·4 | 8·691 | 8·757 | 8·919 | 9·057 | 50·20 |
| S (in thiols) | 50·7 | 7·665 | 7·729 | 7·876 | 8·017 | 52·76 |

The data for aliphatic sulphides and disulphides of Part VII (*J.*, 1943, 16) lead to the following values for S (in sulphides) and $S_2$ (in disulphides):

| | *P.* | $R_C$. | $R_D$. | $R_F$. | $R_{G'}$. | $Mn_D^{20°}$. |
|---|---|---|---|---|---|---|
| S (in sulphides) | 48·6 | 7·852 | 7·921 | 8·081 | 8·233 | 52·86 |
| $S_2$ (in disulphides) | 97·2 | 15·914 | 16·054 | 16·410 | 16·702 | 106·52 |

New experimental data for phenyl alkyl sulphides are provided; subtraction of the corresponding figures for alkylbenzenes (Part X, this vol., p. 607) leads to constants for S which are generally higher than those in alkyl sulphides.

Price and Twiss (*J.*, 1912, **101**, 1259), utilising Auwers and Eisenlohr's constants for carbon, hydrogen, and oxygen, have deduced the following values for the refractivities of S from their measurements upon dithio-esters of the type $S_2(CHR{\cdot}CO_2R')_2$: $R_C$ 8·07, $R_D$ 8·13, and $R_F$ 8·31. They have also computed *inter alia* from the results of earlier investigators the constants for S in thiols ($R_C$ 7·63, $R_D$ 7·69, $R_F$ 7·83 and $R_{G'}$ 7·98) and in sulphides ($R_C$ 7·85, $R_D$ 7·97, $R_F$ 8·13, $R_{G'}$ 8·28). The parachor for sulphur has been computed by Sugden, Reed, and Wilkins (*J.*, 1925, **127**, 1533) from experimental data described in the literature for sulphur monochloride, carbon disulphide, ethylthiol, and phenylthiol: Sugden's own constants, based upon $CH_2 = 39{\cdot}0$, were used throughout and a mean value for S of 48·2 was obtained. It would appear that the compounds selected for the deduction of such a fundamental constant, although perhaps inevitable at the time, cannot be regarded as altogether satisfactory in view of their heterogeneous character.

New determinations have been made of the refractivities at 20° and the parachors of a number of thiols, and the contributions of the SH group calculated by direct subtraction of the values for the alkyl groups (Part XI, *loc. cit.*). The results are shown in Table I. The constants for $Bu^t$ were computed from $Bu^tCl$ (VIII, **55**) − Cl (Part XIV, this vol., p. 644). The surface-tension results for *n*-heptyl- and *n*-octyl-thiols determined by the method of capillary rise require confirmation by the method of maximum bubble pressure since these compounds appear to be on the border line of applicability of the former procedure. In consequence, the parachor values may be slightly in error and have not been employed in the calculation of the mean; if the parachors for these two thiols are included, the mean parachor is reduced to 65·9. The constants derived from thiophenol, utilising the values for Ph of Part XV (this vol., p. 654) are given for purposes of reference.

Table I.

*Values for* SH *from alkylthiols.*

| | *P.* | $R_C$. | $R_D$. | $R_F$. | $R_{G'}$. | $Mn_D^{20°}$. |
|---|---|---|---|---|---|---|
| Et·SH | 66·5 | 8·65 | 8·72 | 8·89 | 9·04 | 50·23 |
| $Pr^n$·SH | 66·9 | 8·68 | 8·74 | 8·91 | 9·05 | 50·11 |
| $Pr^i$·SH * | 68·0 | 8·46 | 8·52 | 8·67 | 8·81 | 49·10 |
| $Bu^n$·SH | 66·1 | 8·73 | 8·79 | 8·95 | 9·10 | 50·28 |
| $Bu^i$·SH | 65·9 | 8·69 | 8·76 | 8·91 | 9·05 | 50·16 |
| $Bu^t$·SH * | 66·1 | 8·81 | 8·88 | 9·06 | 9·20 | 50·32 |
| $Am^n$·SH | 66·1 | 8·69 | 8·75 | 8·90 | 9·06 | 50·29 |
| $Am^i$·SH | 66·8 | 8·68 | 8·76 | 8·91 | 9·05 | 50·21 |
| $C_6H_{13}{}^n$·SH | 66·2 | 8·68 | 8·75 | 8·93 | 9·04 | 50·26 |
| $C_7H_{15}{}^n$·SH | [64·2] | 8·64 | 8·70 | 8·86 | 8·97 | 50·07 |
| $C_8H_{17}{}^n$·SH | [64·0] | 8·78 | 8·84 | 9·01 | 9·15 | 50·23 |
| Mean SH (excluding *) | 66·4 | 8·691 | 8·757 | 8·919 | 9·057 | 50·20 |
| Ph·SH | 67·6 | 9·08 | 9·16 | 9·66 | — | 53·12 |

The constants for S in dialkyl sulphides have been calculated with the aid of the experimental data recorded in Part VII (*J.*, 1943, 16; compare Strecker and Spitaler, *Ber.*, 1926, **59**, 1754, who give refractivity data for dimethyl, diethyl, and di-*n*-propyl sulphides which are in moderate agreement with the author's results) and the hydrocarbon values given in Part XI (*loc. cit.*). The results are summarised in Table II; the compounds marked with an asterisk have not been used in the evaluation of the mean values. If all the sulphides containing a methyl group in addition to those marked with an asterisk be omitted from the calculation of the mean values, the mean constants for S (in sulphides) are: $P$ 47·9, $R_C$ 7·888, $R_D$ 7·955, $R_F$ 8·122, $R_G$ 8·260, $Mn_D^{20°}$ 52·86.

TABLE II.

*Values for* S *from dialkyl sulphides.*

| | $P$. | $R_C$. | $R_D$. | $R_F$. | $R_{G'}$. | $Mn_D^{20}$ |
|---|---|---|---|---|---|---|
| $SMe_2$ | 52·4 | 7·75 | 7·82 | 7·97 | 8·12 | 52·94 |
| $SMeEt$ | 51·1 | 7·72 | 7·80 | 7·93 | 8·12 | 52·83 |
| $SEt_2$ | 50·8 | 7·87 | 7·93 | 8·12 | 8·29 | 52·64 |
| $SMeBu^n$ | 48·3 | 7·76 | 7·82 | 7·98 | 8·21 | 52·95 |
| $SMeBu^i$ | 50·4 | 7·82 | 7·90 | 8·04 | 8·19 | 52·74 |
| $SMeBu^t$ * | 48·3 | 7·71 | 7·79 | 7·94 | 8·10 | 54·05 |
| $SPr^n_2$ | 48·0 | 7·80 | 7·86 | 8·03 | 8·17 | 52·81 |
| $SPr^i_2$ * | 50·3 | 8·07 | 8·17 | 8·30 | 8·47 | 52·29 |
| $SEtBu^n$ | 49·4 | 7·89 | 7·96 | 8·13 | 8·28 | 52·80 |
| $SEtBu^t$ * | 47·6 | 7·92 | 7·97 | 8·15 | 8·31 | 53·76 |
| $SBu^n_2$ | 47·7 | 7·82 | 7·89 | 8·04 | 8·20 | 52·93 |
| $SBu^i_2$ * | 47·9 | 7·98 | 8·05 | 8·22 | 8·34 | 52·58 |
| $SBu^s_2$ * | 52·7 | 8·24 | 8·30 | 8·49 | 8·64 | 51·77 |
| $SAm^n_2$ | 47·1 | 7·81 | 7·88 | 8·03 | 8·18 | 52·96 |
| $SAm^i_2$ | 47·8 | 7·99 | 8·08 | 8·24 | 8·38 | 52·66 |
| $S(C_6H_{13}{}^n)_2$ | 46·5 | 7·96 | 8·02 | 8·19 | 8·33 | 53·02 |
| $S(C_7H_{15}{}^n)_2$ | 47·0 | 7·93 | 7·99 | 8·15 | 8·25 | 53·08 |
| $S(C_8H_{17}{}^n)_2$ | 47·0 | 7·93 | 7·99 | 8·15 | 8·25 | 53·08 |
| Mean S (excluding *) | 48·6 | 7·852 | 7·921 | 8·081 | 8·233 | 52·86 |

New measurements of the refractivities at 20° and the parachors for phenyl alkyl sulphides have been made; the constants for S in these compounds have been computed by direct subtraction of the experimental figures for the alkylbenzenes (Part X, this vol., p. 607). The results are collected in Table III; it will be noted that the refractivities for S are consistently higher than those deduced from dialkyl sulphides.

TABLE III.

*Values for* S *from phenyl alkyl sulphides.*

| | $P$. | $R_C$. | $R_D$. | $R_F$. | $R_{G'}$. | $Mn_D^{20°}$. |
|---|---|---|---|---|---|---|
| $SPhMe$ | 50·2 | 8·23 | 8·32 | 8·64 | 8·92 | 59·26 |
| $SPhEt$ | 50·1 | 8·32 | 8·44 | 8·71 | 8·92 | 57·72 |
| $SPhPr^n$ | 48·3 | 8·33 | 8·43 | 8·79 | 9·00 | 57·32 |
| $SPhPr^i$ | 51·1 | 8·48 | 8·59 | 8·90 | 9·15 | 56·25 |
| $SPhBu^n$ | 48·5 | 8·40 | 8·49 | 8·83 | 9·10 | 57·52 |
| $SPhAm^n$ | 47·3 | 8·39 | 8·50 | 8·81 | 9·08 | 57·00 |
| $SPhC_6H_{13}{}^n$ | 51·6 | 8·55 | 8·67 | 9·01 | 9·24 | 56·66 |
| $SPh_2$ | 51·4 | 8·92 | 9·05 | 9·48 | 9·89 | 60·18 |

The constants for $S_2$ in aliphatic disulphides have been computed from the experimental data of Part VII (*J.*, **1943**, 16) by subtraction of the values for alkyl groups (Part XI, *loc. cit.*) and are collected in Table IV. In the calculation of the mean values, the constants for $S_2Pr^i_2$ and of $S_2Me_2$ (which, unlike $SMe_2$, appears to be abnormal) have been omitted.

TABLE IV.

*Values for* $S_2$ *from aliphatic disulphides.*

| | $P$. | $R_C$. | $R_D$. | $R_F$. | $R_{G'}$. | $Mn_D^{20°}$. |
|---|---|---|---|---|---|---|
| $S_2Me_2$ * | 103·2 | 15·70 | 15·84 | 16·18 | 16·51 | 107·47 |
| $S_2Et_2$ | 100·4 | 15·92 | 16·07 | 16·42 | 16·74 | 106·77 |
| $S_2Pr^n_2$ | 97·6 | 15·84 | 15·97 | 16·33 | 16·64 | 106·66 |
| $S_2Pr^i_2$ * | 100·5 | 16·09 | 16·23 | 16·58 | 16·89 | 106·28 |
| $S_2Bu^n_2$ | 97·2 | 15·92 | 16·04 | 16·39 | 16·69 | 106·58 |
| $S_2Am^n_2$ | 94·7 | 15·93 | 16·09 | 16·44 | 16·75 | 106·40 |
| $S_2Am^i_2$ | 96·1 | 15·96 | 16·12 | 16·47 | 16·79 | 106·19 |
| Mean $S_2$ (excluding *) | 97·2 | 15·914 | 16·054 | 16·410 | 16·702 | 106·52 |

The results for sulphur monochloride ($P$ 96·0, $R_D$ 17·67, $Mn_D^{20°}$ 112·00) give a reasonable value for the parachor of $S_2$, but $R_D$ seems high; the latter may be partly due to the difficulty of measurement of the refractive index.

It is of interest to employ the experimental data for the evil-smelling dithio-esters $S_2\{[CH_2]_x{\cdot}CO_2R\}_2$ (Price and Twiss, *loc. cit.*) for the calculation of $S_2$; these can be obtained directly by subtraction of the refractivities of the appropriate carboxylic esters (Part XIII, this vol., p. 624) and are given below.

$S_2$ *from Dithio-esters* (Price and Twiss).

| | $R_C$. | $R_D$. | $R_F$. |
|---|---|---|---|
| $S_2(CH_2{\cdot}CO_2Me)_2$ .................. | 16·04 | 16·17 | 16·52 |
| $S_2(CH_2{\cdot}CO_2Et)_2$ .................. | 15·88 | 16·02 | 16·37 |
| $S_2(CH_2{\cdot}CH_2{\cdot}CO_2Et)_2$ ............ | 15·88 | 16·01 | 16·34 |

If the constants for H (Part IX, *loc. cit.*) are subtracted from those found for SH, the following values for S (in thiols) are obtained:

| | $P$. | $R_C$. | $R_D$. | $R_F$. | $R_{G'}$. | $Mn_D^{20°}$. |
|---|---|---|---|---|---|---|
| S (in thiols) ........................ | 50·7 | 7·665 | 7·729 | 7·876 | 8·017 | 52·76 |

It will be noted that, apart from the molecular refraction coefficient, they differ from the constants for S deduced from dialkyl sulphides. Whether the constants for H in SH are identical with those for H in $CH_2$ must be regarded as a very open question and would serve to emphasise the great danger attending any attempt to assign constants for S independently of its mode of combination as Sugden has done for the parachor [compare oxygen where the constants for O (ethers), O (acetals), O (carbonyl), and O (hydroxyl) all differ].

## Experimental.

*Commercial Alkyl Thiols.*—25—50 G. samples of the following thiols, supplied by Eastman Kodak, were carefully fractionated, and middle fractions collected for the physical measurements. Ethyl, b. p. 35·0°/768 mm. *n*-Propyl, b. p. 67·3°/755 mm. *iso*Propyl, b. p. 50·5°/753 mm. *n*-Butyl, b. p. 98°/765·5 mm. *iso*Butyl, b. p. 88°/764 mm. *tert.*-Butyl, b. p. 64°/749 mm. *n*-Amyl, b. p. 125°/771 mm. *iso*Amyl, b. p. 118·2—118·7°/765 mm. Thiophenol, b. p. 168°/758 mm.

n-*Hexylthiol.* The following modification of the method of Backer, Terpstra, and Dijkstra (*Rec. Trav. chim.*, 1932, **51**, 1166; compare *Org. Synth.*, 1941, **21**, 36) was employed. In a 500-ml. three-necked flask, equipped with a glycerol-sealed stirrer and a reflux condenser, was placed a mixture of 62·5 g. of *n*-hexyl bromide and a solution of 38 g. of thiourea in 25 ml. of water; the top of the condenser was connected by means of a glass tube to an inverted funnel just dipping into potassium permanganate solution. The mixture was refluxed with vigorous stirring for 2 hours: it became homogeneous after 30 minutes. A solution of 30 g. of sodium hydroxide in 30 ml. of water was added and the reaction mixture was refluxed with vigorous stirring for a further 2 hours. After cooling, the upper layer of crude thiol (35 g.) was separated: the aqueous layer was treated with a solution of 7 ml. of concentrated sulphuric acid in 50 ml. of water, extracted with ether, the extract combined with the crude thiol, dried ($CaSO_4$) and the solvent removed. Distillation yielded pure *n*-hexylthiol, b. p. 152·5°/762 mm.

n-*Heptylthiol.* This was prepared as for the the *n*-hexyl compound from 62 g. of *n*-heptyl iodide and a solution of 26·2 g. of thiourea in 16 ml. of hot water. The yield of crude thiol, b. p. 173—175°, was 38 g.: redistillation gave the pure thiol, b. p. 174°/766 mm.

n-*Octylthiol.* A highly purified sample was kindly supplied by the Connecticut Hard Rubber Co. and was fractionally distilled; b. p. 195°/761 mm.

*Sulphur Monochloride.*—Commercial "redistilled" sulphur monochloride was first redistilled from pure powdered sulphur and then fractionated in an all-glass apparatus; b. p. 135°/748 mm.

*Phenyl Methyl Sulphide.*—To a solution of 10 g. of sodium hydroxide in 100 ml. of water contained in a 500-ml. three-necked flask, equipped with a dropping funnel, mechanical stirrer, and reflux condenser, were added 27·5 g. of thiophenol during 30 minutes and the vigorous stirring was continued for a further 30 minutes. 31·6 G. of methyl sulphate were introduced during 1 hour and the mixture was refluxed, with constant stirring, for 7 hours. The sulphide layer was separated, washed thrice with 10% sodium hydroxide solution and then with water until the washings were neutral to litmus, dried, and distilled. The yield of phenyl methyl sulphide, b. p. 192—192·5°/761 mm., was 24 g.

*Phenyl Ethyl Sulphide.*—This was prepared exactly as detailed for the methyl compound except that 38·5 g. of ethyl sulphate replaced the methyl sulphate. The yield of phenyl ethyl sulphide, b. p. 204·5°/760 mm., was 32 g. This was redistilled under reduced pressure for the physical measurements; b. p. 69°/6 mm.

*Phenyl* n-*Propyl Sulphide.*—To a solution of sodium ethoxide, prepared from 5·75 g. of sodium and 150 ml. of absolute ethyl alcohol, were added 27·5 g. of thiophenol, followed by 64 g. of *n*-propyl iodide during 1 hour. The mixture was refluxed for 4 hours and then most of the alcohol was distilled off; the residue in the flask was diluted with water, the crude sulphide extracted with ether, the ethereal extract washed successively with 10% sodium hydroxide solution, water, dilute sulphuric acid and water, dried ($CaCl_2$), the solvent removed, and the residue distilled under reduced pressure. The yield of phenyl *n*-propyl sulphide, b. p. 74·5°/3·0 mm., was 25 g. In this and subsequent preparations, it is probably better to use the equivalent quantity of the alkyl halide.

*Phenyl* iso*Propyl Sulphide.*—This was prepared as for the *n*-propyl compound with the substitution of the *n*-propyl iodide by 64 g. of *iso*propyl iodide and the mixture was refluxed for 5 hours. The yield of sulphide, b. p. 70°/4 mm., was 32 g.

*Phenyl* n-*Butyl Sulphide.*—This was prepared as detailed for *n*-propyl sulphide with the substitution of 62 g. of *n*-butyl iodide for the *n*-propyl iodide. The yield of phenyl *n*-butyl sulphide, b. p. 104°/6 mm., was 34 g.

*Phenyl* n-*Amyl Sulphide.*—This sulphide was prepared from 5·75 g. of sodium in 150 ml. of absolute ethyl alcohol, 27·5 g. of thiophenol, and 74 g. of *n*-amyl iodide; the mixture was refluxed for 7 hours, and the compound isolated as above. The yield of *phenyl* n-*amyl sulphide*, b. p. 111·5°/5 mm., was 31 g. (Found: S, 17·8. $C_{11}H_{16}S$ requires S, 17·8%).

*Phenyl* n-*Hexyl Sulphide.*—To a solution of 5·25 g. of sodium in 150 ml. of absolute alcohol were added successively 25 g. of thiophenol and 37 g. of *n*-hexyl bromide. The mixture was refluxed for 6 hours and the *phenyl* n-*hexyl sulphide*, b. p. 124·5°/2·0 mm. (36 g.), isolated as usual (Found: S, 16·7. $C_{12}H_{18}S$ requires S, 16·5%).

**483**. *Ethylthiol.* B. p. 35·0°/768 mm.; $M$ 62·13; $n_C$ 1·42875, $n_D$ 1·43168, $n_F$ 1·43900, $n_{G'}$ 1·44465; $R_C$ 18·91, $R_D$ 19·02, $R_F$ 19·30, $R_{G'}$ 19·52; $Mn_D^{20^\circ}$ 88·95. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8468, $d_{4^\circ}^{7\cdot4^\circ}$ 0·8536. Apparatus A = *. Apparatus $B$ = **.

(These headings apply to all the following tables in this paper.)

| $t$. | $H$. | $d_{4^\circ}^{t^\circ}$. | $\gamma$. | $P$. | $t$. | $H$. | $d_{4^\circ}^{t^\circ}$. | $\gamma$. | $P$. |
|---|---|---|---|---|---|---|---|---|---|
| 9·4° | 15·22 | 0·8525 | 24·30 | 162·0* | 16·5° | 12·00 | 0·8487 | 23·88 | 162·1** |
| 17·2 | 14·85 | 0·8484 | 23·59 | 161·7* | | | | Mean | 161·9 |

**484**. n-*Propylthiol.* B. p. 67·3°/755 mm.; $M$ 76·15; $n_C$ 1·43333, $n_D$ 1·43610, $n_F$ 1·44302, $n_{G'}$ 1·44830; $R_C$ 23·58, $R_D$ 23·71, $R_F$ 24·04, $R_{G'}$ 24·29; $Mn_D^{20^\circ}$ 109·36. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8398, $d_{4^\circ}^{40\cdot9^\circ}$ 0·8181. Apparatus $C$.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 18·4° | 12·56 | 0·8415 | 25·09 | 202·6 | 40·8° | 11·43 | 0·8182 | 22·20 | 202·3 |
| 23·5 | 12·25 | 0·8362 | 24·32 | 202·4 | | | | Mean | 202·4 |

**485**. iso*Propylthiol.* B. p. 50·6°/753 mm.; $M$ 76·15; $n_C$ 1·41618, $n_D$ 1·41886, $n_F$ 1·42551, $n_{G'}$ 1·43057; $R_C$ 23·37, $R_D$ 23·50, $R_F$ 23·82, $R_{G'}$ 24·07; $Mn_D^{20^\circ}$ 108·05. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8182, $d_{4^\circ}^{44\cdot2^\circ}$ 0·7899. Apparatus $B$.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 17·1° | 11·55 | 0·8216 | 22·25 | 201·5 | 40·1° | 10·49 | 0·7947 | 19·55 | 202·0 |
| | | | | | | | | Mean | 201·8 |

**486**. n-*Butylthiol.* B. p. 98·1°/765·5 mm.; $M$ 90·18; $n_C$ 1·43977, $n_D$ 1·44255, $n_F$ 1·44932, $n_{G'}$ 1·45457; $R_C$ 28·23, $R_D$ 28·38, $R_F$ 28·75, $R_{G'}$ 29·05; $Mn_D^{20^\circ}$ 130·09. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8417, $d_{4^\circ}^{40\cdot9}$ 0·8218, $d_{4^\circ}^{59\cdot7^\circ}$ 0·8036. Apparatus $A$.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 21·9° | 16·28 | 0·8399 | 25·57 | 241·5 | 60·9° | 14·03 | 0·8025 | 21·08 | 241·1 |
| 41·2 | 15·22 | 0·8215 | 23·41 | 241·6 | | | | Mean | 241·4 |

**487**. iso*Butylthiol.* B. p. 88°/764 mm.; $M$ 90·18; $n_C$ 1·43547, $n_D$ 1·43822, $n_F$ 1·44491, $n_{G'}$ 1·45011; $R_C$ 28·22, $R_D$ 28·38, $R_F$ 28·75, $R_{G'}$ 29·04; $Mn_D^{20^\circ}$ 129·70. Densities determined: $d_D^{20^\circ}$ 0·8346, $d_{4^\circ}^{41\cdot7^\circ}$ 0·8126, $d_{4^\circ}^{62\cdot9^\circ}$ 0·7916. Apparatus $B$.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 16·4° | 12·36 | 0·8382 | 24·29 | 239·0 | 62·1° | 10·53 | 0·7924 | 19·57 | 239·7 |
| 41·5 | 11·56 | 0·8128 | 22·03 | 240·4 | | | | Mean | 239·7 |

**488**. tert.-*Butylthiol.* B. p. 64°/749 mm.; $M$ 90·18; $n_C$ 1·41973, $n_D$ 1·42246, $n_F$ 1·42918, $n_{G'}$ 1·43419; $R_C$ 28·56, $R_D$ 28·73, $R_F$ 29·13, $R_{G'}$ 29·43; $Mn_D^{20^\circ}$ 128·28. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·7985, $d_{4^\circ}^{40\cdot8^\circ}$ 0·7774. Apparatus $B$.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 18·4° | 11·03 | 0·8001 | 20·69 | 240·4 | 40·9° | 10·01 | 0·7774 | 18·25 | 240·2 |
| | | | | | | | | Mean | 240·3 |

**489**. n-*Amylthiol.* B. p. 125°/771 mm.; $M$ 104·21; $n_C$ 1·44385, $n_D$ 1·44656, $n_F$ 1·45328, $n_{G'}$ 1·45846; $R_C$ 32·83, $R_D$ 33·00, $R_F$ 33·42, $R_{G'}$ 33·76; $Mn_D^{20^\circ}$ 150·75. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8431, $d_{4^\circ}^{41\cdot1^\circ}$ 0·8229, $d_{4^\circ}^{61\cdot2^\circ}$ 0·8053, $d_{4^\circ}^{85\cdot5^\circ}$ 0·7826. Apparatus $A$.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 10·9° | 17·10 | 0·8515 | 27·26 | 279·7 | 61·7° | 14·76 | 0·8048 | 22·24 | 281·2 |
| 41·1 | 15·74 | 0·8229 | 24·25 | 281·0 | 87·3 | 13·54 | 0·7809 | 19·80 | 281·5 |
| | | | | | | | | Mean | 281·1 |

**490**. iso*Amylthiol.* B. p. 118·2—118·7°/765 mm.; $M$ 104·25; $n_C$ 1·44096, $n_D$ 1·44365, $n_F$ 1·45022, $n_{G'}$ 1·45529; $R_C$ 32·78, $R_D$ 32·96, $R_F$ 33·37, $R_{G'}$ 33·70; $Mn_D^{20^\circ}$ 150·51. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8398, $d_{4^\circ}^{40\cdot8^\circ}$ 0·8211, $d_{4^\circ}^{60\cdot1^\circ}$ 0·8035, $d_{4^\circ}^{85\cdot7^\circ}$ 0·7799. Apparatus $C$.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 19·7° | 12·76 | 0·8401 | 25·45 | 278·7 | 66·5° | 11·21 | 0·7977 | 21·23 | 280·3 |
| 41·1 | 12·12 | 0·8208 | 23·62 | 280·0 | 89·4 | 10·00 | 0·7765 | 18·43 | 278·7 |
| | | | | | | | | Mean | 279·4 |

**491**. n-*Hexylthiol*. B. p. 152·5°/762 mm.; $M$ 118·23; $n_C$ 1·44659, $n_D$ 1·44937, $n_F$ 1·45599, $n_{G'}$ 1·46074; $R_C$ 37·41, $R_D$ 37·61, $R_F$ 38·09, $R_{G'}$ 38·43; $Mn_D^{20°}$ 171·36. Densities determined: $d_{4°}^{20°}$ 0·8438, $d_{4°}^{40·2°}$ 0·8268, $d_{4°}^{59·5°}$ 0·8109, $d_{4°}^{86·7°}$ 0·7874. Apparatus $E$.

| $t$. | $H$. | $d_{4°}^{t°}$. | $\gamma$. | $P$. | $t$. | $H$. | $d_{4°}^{t°}$. | $\gamma$. | $P$. |
|---|---|---|---|---|---|---|---|---|---|
| 14·3° | 14·22 | 0·8485 | 28·10 | 320·8 | 61·2° | 12·43 | 0·8095 | 23·43 | 321·3 |
| 16·9 | 14·13 | 0·8464 | 27·85 | 320·9 | 87·4 | 11·50 | 0·7868 | 21·07 | 322·0 |
| 40·8 | 13·19 | 0·8263 | 25·38 | 321·2 | | | | Mean | 321·2 |

**492**. n-*Heptylthiol*. B. p. 174°/766 mm.; $M$ 132·26; $n_C$ 1·44766, $n_D$ 1·45207, $n_F$ 1·45672, $n_{G'}$ 1·46128; $R_C$ 42·04, $R_D$ 42·25, $R_F$ 42·77, $R_{G'}$ 43·14; $Mn_D^{20°}$ 191·82. Densities determined: $d_{4°}^{20°}$ 0·8417, $d_{4°}^{40·2°}$ 0·8260, $d_{4°}^{62·1°}$ 0·8087, $d_{4°}^{85·5°}$ 0·7900. Apparatus $E$.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 16·0° | 14·16 | 0·8449 | 27·86 | 359·7 | 61·3° | 12·57 | 0·8093 | 23·69 | 359·7 |
| 40·9 | 13·08 | 0·8254 | 25·14 | 358·8 | 86·7 | 11·84 | 0·7891 | 21·76 | 362·0 |
| | | | | | | | | Mean | 359·9 |

Consistent results for the surface tensions can only be obtained if the compound is freshly redistilled.

**493**. n-*Octylthiol*. B. p. 195°/761 mm.; $M$ 146·28; $n_C$ 1·45112, $n_D$ 1·45377, $n_F$ 1·46021, $n_{G'}$ 1·46498; $R_C$ 46·74, $R_D$ 46·98, $R_F$ 47·55, $R_{G'}$ 47·98; $Mn_D^{20°}$ 212·66. Densities determined: $d_{4°}^{20°}$ 0·8429, $d_{4°}^{40·0°}$ 0·8282, $d_{4°}^{61·4°}$ 0·8120, $d_{4°}^{85·9°}$ 0·7930. Apparatus $E$.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 19·2° | 14·18 | 0·8435 | 27·86 | 398·4 | 61·1° | 12·89 | 0·8122 | 24·38 | 400·1 |
| 40·8 | 13·52 | 0·8276 | 26·06 | 399·4 | 86·5 | 12·12 | 0·7925 | 22·37 | 401·4 |
| | | | | | | | | Mean | 399·8 |

**494**. *Thiophenol*. B. p. 168°/758 mm.; $M$ 110·18; $n_C$ 1·58325, $n_D$ 1·58973, $n_F$ 1·61201, $n_{G'}$ very faint; $R_C$ 34·22, $R_D$ 34·52, $R_F$ 35·57; $Mn_D^{20°}$ 175·15. Densities determined: $d_{4°}^{20°}$ 1·0766, $d_{4°}^{40·6°}$ 1·0583, $d_{4°}^{59·8°}$ 1·0406, $d_{4°}^{85·7°}$ 1·0168. Apparatus $A$.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 18·9° | 19·46 | 1·0776 | 39·27 | 256·0 | 41·1° | 18·39 | 1·0577 | 36·42 | 255·9 |
| 25·3 | 19·07 | 1·0718 | 38·27 | 255·7 | 64·8 | 17·34 | 1·0361 | 33·64 | 256·1 |
| | | | | | | | | Mean | 255·9 |

**495**. *Phenyl methyl sulphide*. B. p. 192—192·5°/761 mm.; $M$ 124·19; $n_C$ 1·58101, $n_D$ 1·58747, $n_F$ 1·60443, $n_{G'}$ 1·61871 (line faint); $R_C$ 39·09, $R_D$ 39·42, $R_F$ 40·34, $R_{G'}$ 41·11; $Mn_D^{20°}$ 197·15. Densities determined: $d_{4°}^{20°}$ 1·0594, $d_{4°}^{42·3°}$ 1·0397, $d_{4°}^{61·3°}$ 1·0215, $d_{4°}^{85·9°}$ 0·9996. Apparatus $A$.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 20·4° | 20·33 | 1·0590 | 40·31 | 295·5 | 60·3° | 18·44 | 1·0224 | 35·30 | 296·0 |
| 41·4 | 19·33 | 1·0405 | 37·66 | 295·7 | 86·4 | 17·18 | 0·9991 | 32·14 | 296·0 |
| | | | | | | | | Mean | 295·6 |

**496**. *Phenyl ethyl sulphide*. B. p. 204·5°/759 mm.; $M$ 138·22; $n_C$ 1·56070, $n_D$ 1·56656, $n_F$ 1·58115, $n_{G'}$ 1·59442 (line faint); $R_C$ 43·81, $R_D$ 44·19, $R_F$ 45·12, $R_{G'}$ 45·95; $Mn_D^{20°}$ 216·54. Densities determined: $d_{4°}^{20°}$ 1·0211, $d_{4°}^{40·2°}$ 1·0028, $d_{4°}^{60·4°}$ 0·9858, $d_{4°}^{87·3°}$ 0·9614. Apparatus $B$.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 22·5° | 15·44 | 1·0189 | 36·89 | 334·3 | 60·2° | 14·01 | 0·9860 | 32·39 | 334·4 |
| 40·5 | 14·72 | 1·0025 | 34·60 | 334·4 | 86·9 | 13·11 | 0·9618 | 29·57 | 335·3 |
| | | | | | | | | Mean | 334·4 |

**497**. *Phenyl* n-*propyl sulphide*. B. p. 74·5°/3·0 mm.; $M$ 152·25; $n_C$ 1·54978, $n_D$ 1·55521, $n_F$ 1·56938, $n_{G'}$ 1·58115; $R_C$ 48·46, $R_D$ 48·85, $R_F$ 49·88, $R_{G'}$ 50·72; $Mn_D^{20°}$ 236·78. Densities determined: $d_{4°}^{20°}$ 1·0006, $d_{4°}^{40·4°}$ 0·9830, $d_{4°}^{60·2°}$ 0·9671, $d_{4°}^{85·6°}$ 0·9458. Apparatus $D$.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 19·9° | 14·31 | 1·0007 | 35·36 | 371·0 | 61·1° | 12·98 | 0·9663 | 30·98 | 371·7 |
| 26·3 | 14·17 | 0·9953 | 34·83 | 371·6 | 86·4 | 12·21 | 0·9451 | 28·50 | 372·2 |
| 40·6 | 13·65 | 0·9828 | 33·13 | 371·7 | | | | Mean | 371·6 |

**498**. *Phenyl* iso*propyl sulphide*. B. p. 70°/4 mm.; $M$ 152·25; $n_C$ 1·54114, $n_D$ 1·54641, $n_F$ 1·56006, $n_{G'}$ 1·57135; $R_C$ 48·59, $R_D$ 48·98, $R_F$ 50·00, $R_{G'}$ 50·82; $Mn_D^{20°}$ 235·44. Densities determined: $d_{4°}^{20}$ 0·9848, $d_{4°}^{40·6°}$ 0·9677, $d_{4°}^{61·4°}$ 0·9505, $d_{4°}^{85·7°}$ 0·9298. Apparatus $D$.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 17·4° | 13·89 | 0·9870 | 33·86 | 372·1 | 60·7° | 12·42 | 0·9511 | 29·17 | 372·0 |
| 23·9 | 13·60 | 0·9815 | 32·97 | 372·0 | 86·5 | 11·55 | 0·9291 | 26·50 | 371·8 |
| 41·1 | 13·03 | 0·9673 | 31·13 | 371·8 | | | | Mean | 371·9 |

**499**. *Phenyl* n-*butyl sulphide*. B. p. 104°/6 mm.; $M$ 162·27; $n_C$ 1·54145, $n_D$ 1·54658, $n_F$ 1·55994, $n_{G'}$ 1·57102; $R_C$ 53·18, $R_D$ 53·59, $R_F$ 54·68, $R_{G'}$ 55·57; $Mn_D^{20°}$ 257·14. Densities determined: $d_{4°}^{20}$ 0·9831, $d_{4°}^{40·5°}$ 0·9674, $d_{4°}^{62·1°}$ 0·9500, $d_{4°}^{86·6°}$ 0·9304. Apparatus $D$.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 18·4° | 14·26 | 0·9843 | 34·67 | 409·9 | 61·3° | 12·98 | 0·9506 | 30·47 | 411·0 |
| 24·3 | 14·12 | 0·9797 | 34·16 | 410·3 | 86·5 | 12·20 | 0·9305 | 28·04 | 411·2 |
| 41·0 | 13·53 | 0·9670 | 32·31 | 409·9 | | | | Mean | 410·5 |

**500.** *Phenyl* n-*amyl sulphide.* B. p. 111·5°/5 mm.; $M$ 180·30; $n_C$ 1·53498, $n_D$ 1·53990, $n_F$ 1·55263, $n_{G'}$ 1·56300; $R_C$ 57·79, $R_D$ 58·23, $R_F$ 59·37, $R_{G'}$ 60·29; $Mn_D^{20°}$ 277·64. Densities determined: $d_{4°}^{20°}$ 0·9713, $d_{4°}^{40·8°}$ 0·9557, $d_{4°}^{60·8°}$ 0·9408, $d_{4°}^{86·2°}$ 0·9207. Apparatus *A*.

| *t.* | *H.* | $d_{4°}^{t°}$. | $\gamma$. | *P.* | *t.* | *H.* | $d_{4°}^{t°}$. | $\gamma$. | *P.* |
|---|---|---|---|---|---|---|---|---|---|
| 17·6° | 18·82 | 0·9731 | 34·29 | 448·4 | 61·2° | 17·14 | 0·9405 | 30·20 | 449·4 |
| 25·9 | 18·68 | 0·9668 | 33·82 | 449·7 | 86·6 | 16·17 | 0·9204 | 27·87 | 450·1 |
| 41·6 | 17·87 | 0·9551 | 31·96 | 448·8 | | | | | Mean 449·3 |

**501.** *Phenyl* n-*hexyl sulphide.* B. p. 124·5°/2·0 mm.; $M$ 194·32; $n_C$ 1·52894, $n_D$ 1·53358, $n_F$ 1·54577, $n_{G'}$ 1·55552; $R_C$ 62·50, $R_D$ 62·96, $R_F$ 64·16, $R_{G'}$ 65·10; $Mn_D^{20°}$ 298·01. Densities determined: $d^{20°}$ 0·9588, $d_{4°}^{41·0°}$ 0·9432, $d_{4°}^{60·2°}$ 0·9287, $d_{4°}^{86·0°}$ 0·9094. Apparatus *D*.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 22·1° | 18·55 | 0·9572 | 43·85 | 522·4 | 58·3° | 17·22 | 0·9301 | 39·55 | 523·9 |
| 26·9 | 18·33 | 0·9536 | 43·17 | 522·3 | 85·1 | 16·12 | 0·9101 | 36·23 | 523·8 |
| 40·7 | 17·86 | 0·9434 | 41·61 | 523·1 | | | | | Mean 523·1 |

**502.** *Sulphur monochloride.* B. p. 135°/748 mm.; $M$ 135·04; $n_D$ 1·6500; $R_D$ 29·36; $Mn_D^{20°}$ 222·82. Densities determined: $d_{4°}^{20°}$ 1·6776, $d_{4°}^{40·5°}$ 1·6467, $d_{4°}^{60·6°}$ 1·6157, $d_{4°}^{85·7°}$ 1·5778. Apparatus *C*.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 16·3° | 10·98 | 1·6832 | 43·88 | 206·5 | 85·1° | 9·04 | 1·5787 | 33·88 | 206·4 |
| 62·0 | 9·66 | 1·6136 | 37·00 | 206·4 | | | | | Mean 206·4 |

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