791. *The Associating Effect of the Hydrogen Atom. Part XV.* The* S–H–N *Bond. Esters of Thion- and Dithio-carbamic Acids.*

By Arnold A. Burrows and Louis Hunter.

New examples of the S–H–N bond are revealed by molecular-weight measurements of thion- and dithio-carbamic esters, which show a high degree of molecular association provided at least one amino-hydrogen atom remains unsubstituted (I and II); such compounds provide further examples of meso-hydric tautomerism (*J.*, 1945, 806). Association is destroyed, as well as tautomeric character, by the complete replacement of the amino-hydrogen atoms (III and IV). The effect on molecular association of certain *o*-substituents in phenyl-thion- and -dithio-carbamic esters is discussed in the light of steric and other effects.

It has been pointed out in Part XI (*J.*, 1942, 638) that, although hydrogen bonds involving the sulphur atom are usually very weak, such bonds acquire considerable stability in compounds in which the hydrogen atom concerned has tautomeric character. Thus, although thioamides exhibit molecular association involving S–H–N bonds, thiols, thiophenols, and compounds containing cyclic sulphur atoms show no association.

This parallel between tautomeric character and molecular association due to S–H–N bonds has been further substantiated in the present investigation by the behaviour of the esters of thion- and dithio-carbamic acids. Provided these substances contain at least one unsubstituted (amino-)hydrogen atom (as in I and II) they are found to be markedly associated, but complete replacement of the amino-hydrogen atoms by alkyl, aryl, or acyl groups (as in III and IV) destroys their molecular association. Molecular association was assessed

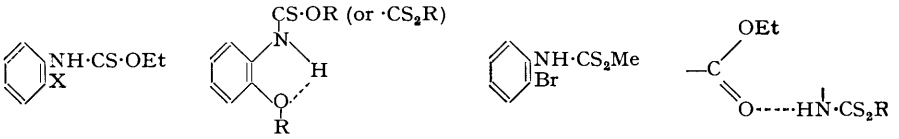
$NHR{\cdot}CS{\cdot}OR'$	$NHR{\cdot}CS_2R'$	$NR_2{\cdot}CS{\cdot}OR'$	$NR_2{\cdot}CS_2R'$	$NHR{\cdot}CO{\cdot}SEt$
(I)	(II)	(III)	(IV)	(V)

cryoscopically for benzene or naphthalene solutions and, as in previous Parts of this series, association is inferred from molecular-weight measurements in all cases in which the factor of association (α) increases substantially with rising concentration; *i.e.*, a steep association–concentration curve is taken to indicate molecular association, whereas a flat or gently sloped curve (in the region of $\alpha = 1$) is interpreted as indicating the absence of association. Association is assessed more from the slopes of these curves than from the absolute values of α, which may have no real significance and in many cases are less than unity. Figs. 1 and 2 provide numerous examples of these two sharply differentiated types, and it seems clear that esters such as (I) and (II) owe their molecular association no less than their tautomeric

* Part XIV, *J.*, 1950, 2857.

character to molecular union through S–H–N bonds, the amino-hydrogen atom of one molecule being shared with the (thion-)sulphur atom of an adjacent molecule. The type of polymer is therefore similar to that proposed for the esters of carbamic acid (Part XIII, *J.*, 1948, 874), and, since factors of association of similar magnitude are observed, it is reasonable to believe that the S–H–N bond in the compounds examined is as strong as the O–H–N bond in carbamic esters or in amides. This conclusion receives strong support from a comparison of the degrees of association of ethyl thioncarbamates (I ; R′ = Et) with the isomeric ethyl thiolcarbamates (V), owing their association respectively to S–H–N and O–H–N bonds. The slopes of the association–concentration curves (Fig. 3) of three pairs of such isomers show no significant differences; nor does the complete replacement of oxygen by sulphur in these compounds, as in the ethyl dithiocarbamates (II ; R′ = Et), cause any considerable change of association, and it seems clear that provided such substances are of tautomeric type the resulting S–H–N bonds are as strong as those exhibited in their oxygen analogues.

A study has been made of the effect of substitution in the phenyl nucleus on the molecular association of phenyl-thion- and -dithio-carbamates. Fig. 3 shows that the high molecular association of ethyl phenylthioncarbamate (VI ; X = H) is completely suppressed on substitution of a methoxyl-group in the *ortho*-position (VI ; X = OMe). Indeed, the slope of the association–concentration curve of ethyl *o*-methoxyphenylthioncarbamate (VI ; X = OMe) is comparable with that of its *N*-benzoyl derivative, which, owing to replacement of its amino-hydrogen atom, cannot possess a hydrogen-bond structure. On the other hand, substitution by methoxyl in the *para*-position, as in methyl and ethyl *p*-methoxyphenylthioncarbamates, does not significantly change the degree of association. Similar effects were observed in the methoxy- and ethoxy-phenyldithiocarbamates (Fig. 4), those having the substituent in the *ortho*-position (VI ; X = OMe or OEt, S in place of O)



(VI) (VII) (VIII) (IX)

being markedly less associated than their *para*-isomers. The origin of this *ortho*-effect was at first supposed to be the tendency of the alkoxy-group to prevent a second molecule's approaching close enough to the amino-hydrogen atom to engage it in intermolecular S–H–N bond formation, thus substantially reducing the proportion of associated molecules. This mainly steric role, however, seems unlikely in view of the fact that other bulky groups, such as methyl and ethyl, when substituted *ortho* to the NH·CS·OR and NH·CS_2R groups, have no such effect. Thus, Figs. 1—3 provide many examples of *o*-tolyl- and *o*-ethylphenyl-substituted thion- and dithio-carbamic esters which possess association factors comparable with those of their *m*- and *p*-isomers. It therefore seems necessary to account for the absence of association in *o*-alkoxyphenyl-thion- and -dithio-carbamic esters by postulating the engagement of the amino-hydrogen atom in chelate-ring formation with the oxygen of the alkoxy-group (VII). The amino-hydrogen atom thus engaged is no longer available to link with the sulphur atom of a second molecule, and the structure thus favours the unimolecular state. The engagement of the oxygen atom of an alkoxy-group in chelate-ring formation with the hydrogen atom of an *ortho*-substituent has previously been suggested to account for the properties of guaiacol (Pauling, " Nature of the Chemical Bond," 2nd Edn., 1948, p. 324; Wulf and Deming, *J. Chem. Physics*, 1938, **6**, 702).

The reason for the reduced association of methyl *o*-bromophenyldithiocarbamate (VIII), compared with that of its *m*- and *p*- isomers (Fig. 5), is obscure. Without further investigation it is impossible to distinguish between a purely steric effect and a hydrogen bond (N–H–Br) similar to those suggested in ethylene bromohydrin, *o*-bromophenol, and tetrabromocatechol (Wulf, Liddel, and Hendricks, *J. Amer. Chem. Soc.*, 1936, **58**, 2287).

Factors other than steric effects must operate in the greatly increased slope of the

FIGS. 1—6.

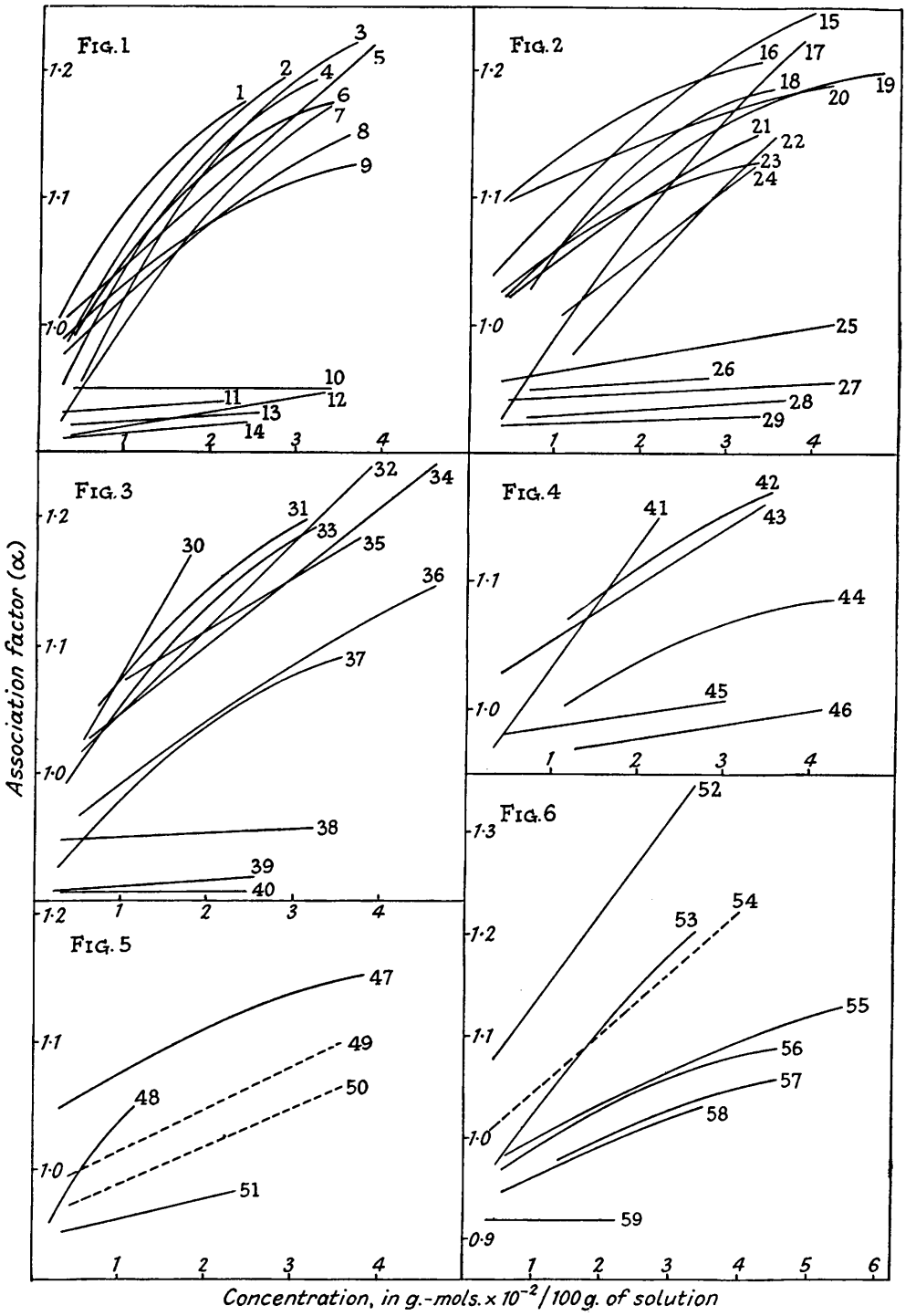


FIG. 1
FIG. 2
FIG. 3
FIG. 4
FIG. 5
FIG. 6
Association factor (α)
Concentration, in g.-mols. × 10⁻²/100 g. of solution

association–concentration curves of the *m*-carbethoxyphenyldithiocarbamates (Fig. 6), and it would appear that, in addition to S–H–N bonds due to association between NH·CS_2R groups, there may exist also heterogeneous association through N–H–O bonds between the carbethoxy-group of one molecule and the amino-hydrogen atom of another (as in IX). Effects of a similar kind have already been reported (Part XIII, *loc. cit.*, p. 877) between nitro- and amino-groups in nitrophenylcarbamates. On the other hand, the reduced association of methyl *cyclo*hexylthioncarbamate (Fig. 6) compared with that of methyl phenylthioncarbamate, is attributed to reduced acidity of the amino-hydrogen atom of the former owing to the absence of a mesomeric effect. Accountable in similar terms is the even more marked reduction in association revealed by comparing phenyl- with benzyl-thion- and -dithio-carbamates (Fig. 6). This dependence of association on the acidity of the hydrogen atom constituting the hydrogen bond has frequently been exemplified in previous Parts of this series.

Experimental

(Microanalyses were by Drs. Weiler and Strauss, Oxford.)

New *compounds* prepared during this investigation are given in the Table.

Thioncarbamic esters, R·NH·CS·OR′.

R′	R	Formula	M. p.	Found, % C	H	N	S	Required, % C	H	N	S
Me	*o*-Tolyl	$C_9H_{11}ONS$	76°	60·4	6·2	8·0	—	59·6	6·1	7·7	—
Me	*m*-Tolyl	$C_9H_{11}ONS$	43	60·0	6·2	8·0	—	59·6	6·1	7·7	—
Me	*p*-Tolyl	$C_9H_{11}ONS$	83	60·0	6·2	8·2	—	59·6	6·1	7·7	—
Et	*o*-MeO·C_6H_4	$C_{10}H_{13}O_2NS$	66	56·9	5·8	6·5	14·9	56·9	6·2	6·6	15·2
Me	*p*-MeO·C_6H_4	$C_9H_{11}O_2NS$	103	55·1	5·3	6·9	15·6	54·8	5·6	7·1	16·2
Et	*p*-MeO·C_6H_4	$C_{10}H_{13}O_2NS$	81	57·0	5·9	6·6	15·0	56·9	6·2	6·6	15·2
Me	CH_2Ph	$C_9H_{11}ONS$	49	—	—	—	18·1	—	—	—	17·7
Me	*cyclo*Hexyl	$C_8H_{15}ONS$	42	—	—	—	18·4	—	—	—	18·5

FIG. 1.

1, Ph·NH·CS·OBu^i
2, Ph·NH·CS·OBu^n
3, *p*-C_6H_4Me·NH·CS·OMe
4, Ph·NH·CS·OPr^i
5, Ph·NH·CS·OMe
6, *p*-C_6H_4Me·NH·CS·OEt
7, Ph·NH·CS·OPr^n
8, *m*-C_6H_4Me·NH·CS·OMe
9, *o*-C_6H_4Me·NH·CS·OMe
10, Ph·NBz·CS·OEt
11, *m*-C_6H_4Me·NBz·CS·OEt
12, *o*-C_6H_4Me·NBz·CS·OMe
13, Ph·NBz·CS·OMe
14, *p*-C_6H_4Me·NBz·CS·OEt

FIG. 2.

15, *o*-C_6H_4Et·NH·CS_2Me
16, 2 : 4 : 1-$C_6H_3Me_2$·NH·CS_2Me
17, Ph·NH·CS_2Me
18, *o*-C_6H_4Me·CS_2Et
19, 2 : 4 : 1-$C_6H_3Me_2$·NH·CS_2Et
20, *p*-C_6H_4Me·NH·CS_2Et
21, *m*-C_6H_4Me·NH·CS_2Me
22, *p*-C_6H_4Me·NH·CS_2Me
23, *m*-C_6H_4Me·NH·CS_2Et
24, Ph·NH·CS_2Et
25, *p*-C_6H_4Me·NMe·CS_2Et
26, Ph·NEt·CS_2Me
27, *p*-C_6H_4Me·NMe·CS_2Me
28, Ph·NMe·CS_2Et
29, Ph·NMe·CS_2Me

FIG. 3.

30, *p*-MeO·C_6H_4·NH·CS·OMe
31, Ph·NH·CS·OEt
32, *m*-C_6H_4Me·NH·CO·SEt
33, *p*-MeO·C_6H_4·NH·CS·OEt
34, Ph·NH·CO·SEt
35, *m*-C_6H_4Me·NH·CS·OEt
36, *o*-C_6H_4Me·NH·CO·SEt
37, *o*-C_6H_4Me·NH·CS·OEt
38, *o*-MeO·C_6H_4·NH·CS·OEt
39, *o*-MeO·C_6H_4·NBz·CS·OEt
40, *p*-MeO·C_6H_4·NBz·CS·OEt

FIG. 4.

41, {*p*-MeO·C_6H_4·NH·CS_2Me / *p*-EtO·C_6H_4·NH·CS_2Me
42, *p*-MeO·C_6H_4·NH·CS_2Et
43, *p*-EtO·C_6H_4·NH·CS_2Et
44, *o*-MeO·C_6H_4·NH·CS_2Me
45, *o*-EtO·C_6H_4·NH·CS_2Et
46, *o*-EtO·C_6H_4·NH·CS_2Me

FIG. 5.

47, *p*-C_6H_4Br·NH·CS_2Et
48, *p*-C_6H_4Br·NH·CS_2Me (in C_6H_6)
49, ,, (in $C_{10}H_8$)
50, *m*-C_6H_4Br·NH·CS_2Me (in $C_{10}H_8$)
51, *o*-C_6H_4Br·NH·CS_2Me

FIG. 6.

52, *m*-CO_2Et·C_6H_4·NH·CS_2Me
53, *m*-CO_2Et·C_6H_4·NH·CS_2Et
54, Ph·NH·CS·OMe (for comparison)
55, C_6H_{11}·NH·CS·OMe
56, CH_2Ph·NH·CS·OMe
57, CH_2Ph·NH·CS_2Me
58, CH_2Ph·NH·CS_2Et
59, CH_2Ph·NPh·CS_2Et

Thiolcarbamic ester, R·NH·CO·SR′.

R′	R	Formula	M. p.	Found, % C	H	N	S	Required, % C	H	N	S
Et	*m*-Tolyl	$C_{10}H_{13}ONS$	59	—	—	—	16·7	—	—	—	16·4

N-*Benzoylthioncarbamic esters*, R·NBz·CS·OR′.

Me	Ph	$C_{15}H_{13}O_2NS$	95	67·2	4·9	5·2	12·0	66·4	4·8	5·2	11·8
Et	Ph	$C_{16}H_{15}O_2NS$	84	67·8	5·2	4·8	11·1	67·3	5·3	4·9	11·2
Me	*o*-Tolyl	$C_{16}H_{15}O_2NS$	92	67·9	4·8	4·9	11·0	67·3	5·3	4·9	11·2
Et	*m*-Tolyl	$C_{17}H_{17}O_2NS$	96	67·0	5·8	4·6	10·0	68·2	5·7	4·7	10·7
Et	*p*-Tolyl	$C_{17}H_{17}O_2NS$	115	68·7	6·0	4·7	10·3	68·2	5·7	4·7	10·7
Et	*o*-MeO·C_6H_4	$C_{17}H_{17}O_3NS$	104	65·2	5·5	4·3	9·6	64·7	5·4	4·4	10·2
Et	*p*-MeO·C_6H_4	$C_{17}H_{17}O_3NS$	89	64·8	5·3	4·2	10·0	64·7	5·4	4·4	10·2

Dithiocarbamic esters, R·NH·CS_2R′.

Et	*m*-Tolyl	$C_{10}H_{13}NS_2$	63°	—	—	—	30·4	—	—	—	30·3
Me	*o*-C_6H_4Et	$C_{10}H_{13}NS_2$	75	—	—	—	30·8	—	—	—	30·3
Me	*p*-MeO·C_6H_4	$C_9H_{11}ONS_2$	101	—	—	—	29·5	—	—	—	30·1
Et	*p*-MeO·C_6H_4	$C_{10}H_{13}ONS_2$	77	—	—	—	28·6	—	—	—	28·2
Me	*o*-EtO·C_6H_4	$C_{10}H_{13}ONS_2$	52	—	—	—	28·2	—	—	—	28·2
Et	*o*-EtO·C_6H_4	$C_{11}H_{15}ONS_2$	79	—	—	—	27·1	—	—	—	26·6
Me	*p*-EtO·C_6H_4	$C_{10}H_{13}ONS_2$	104	—	—	—	28·1	—	—	—	28·2
Et	*p*-EtO·C_6H_4	$C_{11}H_{15}ONS_2$	93	—	—	—	26·7	—	—	—	26·6
Me	*m*-CO_2Et·C_6H_4	$C_{11}H_{13}O_2NS_2$	73	—	—	—	25·0	—	—	—	25·1
Et	*m*-CO_2Et·C_6H_4	$C_{12}H_{15}O_2NS_2$	67	—	—	—	23·2	—	—	—	23·8
Me	2 : 4 : 1-$C_6H_3Me_2$	$C_{10}H_{13}NS_2$	103	—	—	—	30·3	—	—	—	30·3
Et	2 : 4 : 1-$C_6H_3Me_2$	$C_{11}H_{15}NS_2$	65	—	—	—	28·4	—	—	—	28·4
Me	CH_2Ph	$C_9H_{11}NS_2$	57	—	—	—	32·9	—	—	—	32·5
Et	CH_2Ph	$C_{10}H_{13}NS_2$	52	—	—	—	29·8	—	—	—	30·3

				Br	S	Br	S
Me	*o*-C_6H_4Br	$C_8H_8NBrS_2$	100	31·0	24·4	30·5	24·5
Me	*m*-C_6H_4Br	$C_8H_8NBrS_2$	111	31·2	25·0	30·5	24·5
Me	*p*-C_6H_4Br	$C_8H_8NBrS_2$	120	31·1	24·3	30·5	24·5

Dithiocarbamic esters, RR′N·CS_2R″.

R″	R′	R	Formula	M. p.	Found, % C	H	N	S	Required, % C	H	N	S
Me	Me	*p*-Tolyl	$C_{10}H_{13}NS_2$	82°	—	—	—	29·6	—	—	—	30·3
Et	Me	*p*-Tolyl	$C_{11}H_{15}NS_2$	84	—	—	—	28·4	—	—	—	28·4
Et	CH_2Ph	Ph	$C_{16}H_{17}NS_2$	76	—	—	—	22·3	—	—	—	22·3

Revised m. p.s are recorded for the following: methyl phenylthioncarbamate, m. p. 98° (lit., 95—96, 97°), methyl *o*-tolyldithiocarbamate, m. p. 137° (lit., 132°), methyl *m*-tolyldithiocarbamate, m. p. 94° (lit., 89°), ethyl *N*-methyl-*N*-phenyldithiocarbamate, m. p. 99° (lit., 94·5—95·5°).

Molecular-weight Data.—Molecular weights were measured cryoscopically in benzene, with the two exceptions noted in Fig. 5, and were deduced according to ideal-solution laws. In the Figures concentrations are expressed as g.-mols. $\times 10^{-2}$/100 g. of solution, and the association factor (α) is calculated as the ratio of the apparent molecular weight to the formula weight.

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