

## LETTERS TO THE EDITORS

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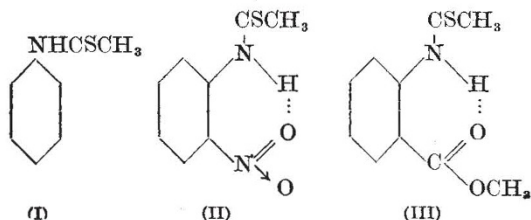
## Hydrogen Bonds Involving the Sulphur Atom

THE view is very generally expressed<sup>1</sup> that sulphur does not take part in hydrogen-bond formation. This conclusion is based mainly on the normal physical properties of hydrogen sulphide, as compared with water, and on the absence of molecular association in thioalcohols and thiophenols. Such evidence is obviously only valid against the S-H-S bond.

On the contrary, there are various indications that the sulphur atom can form hydrogen bonds of the type S-H-O and S-H-N possessing considerable stability. For example, quinhydrone-like complexes between quinones and thiophenols or mercaptans have long been known; their existence is probably due to S-H-O bonds. Again, the tautomerism of the thio-acids,  $R.COSH \rightleftharpoons R.CSOH$ , is probably attributable to their associated (hydrogen bond) structure. Contemporary American workers have recently attributed the anomalous behaviour of mercaptans in certain donor solvents in regard to heats of mixing<sup>2</sup>, and infra-red absorption<sup>3</sup>, to the formation of weak S-H-N and S-H-O bonds.

Recent work<sup>4</sup> from this laboratory has indicated that a factor which contributes more than any other to hydrogen-bond stability is the condition that the hydrogen atom constituting the bond should be tautomeric. We have, therefore, sought evidence of hydrogen-bond formation in the thioamides and the thioanilides, the tautomeric behaviour of which is formally represented by the equilibrium  $R.CSNHR' \rightleftharpoons R.C(SH) : NR'$ . Cryoscopic measurement of molecular weight of a large number of thioamides in naphthalene solution has shown that those which possess an unsubstituted imino-hydrogen atom (as in  $R.CSNH_2$  and  $R.CSNHR'$ ) exhibit marked molecular association, whereas those in which both imino-hydrogen atoms have been replaced (for example,  $R.CSNRR'$ ) are invariably unimolecular. It would appear, then, that the association of the former type is due to intermolecular S-H-N bonds.

Further evidence of the hydrogen-bond structure of the thioamides is provided by the behaviour of nuclear-substituted derivatives of thioacetanilide (I). We find that the considerable molecular association shown by this compound<sup>5</sup> is completely checked by the substitution of suitable *o*-substituents capable of chelating with the anilido-hydrogen atom. Evidently, the hydrogen atom thus engaged is incapable of further union with the sulphur atom of a second molecule. Thus, *o*-nitro- (II) and *o*-carbomethoxy-thioacetanilide (III) are substantially unimolecular.



A parallel investigation of the molecular condition of the thioacids has confirmed that they also are associated (originally observed in the single case of thioacetic acid by Auwers<sup>5</sup>), whereas their esters ( $R.COSR'$ ) are not. Evidently the association of the thioacids is due to intermolecular S-H-O bonds.

A more complete account of this work will be published elsewhere.

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<sup>1</sup> See, *inter alia*, Sidgwick, "The Covalent Link" (Cornell, 1933), p. 164. Lassetre, *Chem. Rev.*, **20**, 267 (1937); Pauling, "The Nature of the Chemical Bond" (Cornell, 1940), p. 290.

<sup>2</sup> Copley, Marvel, and Ginsberg, *J. Amer. Chem. Soc.*, **61**, 3161 (1939).

<sup>3</sup> Gordy and Stanford, *J. Amer. Chem. Soc.*, **62**, 497 (1940).

<sup>4</sup> Hunter *et al.*, "The Associating Effect of the Hydrogen Atom, Parts I-IX", *J. Chem. Soc.* (1937-1941).

<sup>5</sup> Auwers, *Z. phys. Chem.*, **30**, 529 (1899).

## Quantum Efficiency of Photosynthesis

It is generally accepted that about four energy quanta of red light ( $\lambda = 660 \mu\mu$ ) are needed to promote the assimilation of one molecule of carbon dioxide. This conclusion is based in the main on the measurements of Warburg and Negelein<sup>1</sup>, who determined the ratio  $W/E$ , that is, the volume of carbon dioxide assimilated by *Chlorella* during the absorption of one calorie of light energy. They designated this ratio by  $\phi$  and, since it is well known that  $\phi$  increases with decrease in light intensity, the value  $\phi_0$  found with the minimum intensity was adopted.

As the mean of nine measurements it was found that 116.8 c.c.m. of carbon dioxide were assimilated during the absorption of one calorie of red light energy. It follows from this that 191,781 calories would be absorbed during the assimilation of one gram mole of carbon dioxide and, since the value of  $Nh\nu$  at  $\lambda = 660 \mu\mu$  is 43,112 calories, that 4.45 energy quanta were absorbed for each molecule of carbon dioxide assimilated. In a similar series of measurements with blue light ( $\lambda = 436 \mu\mu$ ) it was found 5.1 energy quanta were absorbed for each molecule of carbon dioxide assimilated.

Now these and any similar determinations of the quantum efficiency of photosynthesis are based on the assumption that the whole of the light energy absorbed is utilized in promoting the assimilation of carbon dioxide. Expressed in other words, this assumption means that the absorption of light energy by *Chlorella* is entirely caused by the photo-assimilation which takes place. If this were correct, a suspension of *Chlorella* in which photo-assimilation has been inhibited by hydrogen cyanide would not absorb red or blue light and hence would be almost colourless.

Furthermore, Warburg<sup>2</sup> proved that, when the light intensity and temperature are maintained constant, the number of molecules of carbon dioxide assimilated in unit time by *Chlorella* increases at first very rapidly and then more slowly as the external concentration of carbon dioxide is increased from  $1 \times 10^{-8}$  to  $90 \times 10^{-6}$  gram mole per litre. On the assumption made by Warburg and Negelein, this indicates that the number of energy quanta needed