

LETTERS TO THE EDITORS

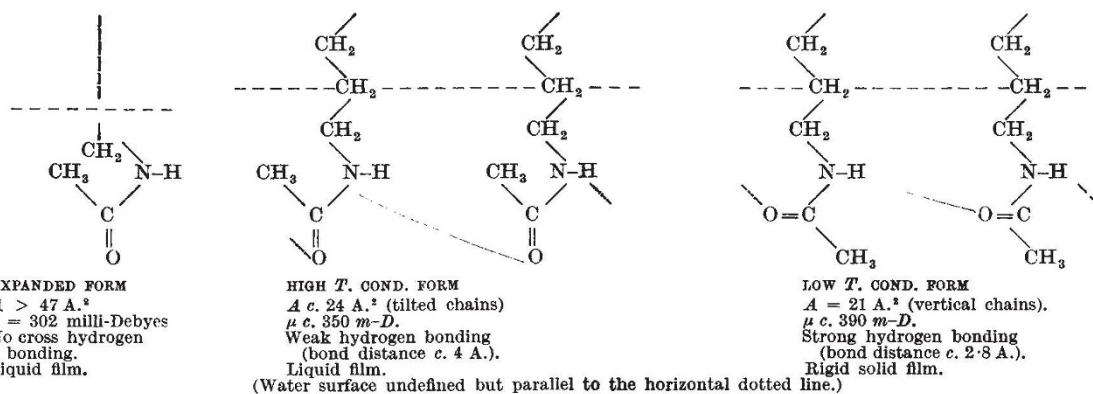
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A Possible New Approach to the Study of the Hydrogen Bond in Protein Structure

IN a recent review¹ Astbury has pointed out that the role of the hydrogen bond in protein structure, usually ascribed primarily to the keto-imino group, is largely unknown. Determination of the structure of such polar groups in the aqueous medium necessary for the normal functioning of the protein molecule is not easily achieved by means of the usual X-ray and infra-red methods. The monolayer technique has, however, proved of value in certain cases², and recent measurements upon simple compounds containing the $-\text{CO.NH}-$ link indicate that cross hydrogen bonding between such groups does occur in water provided that the molecular spacing is suitable.

Head-group	$T_{1/2}$	Nature of condensed film	Chain-length $\text{C}_{16}\text{H}_{33}$ in all cases.	$-\text{COCH}_3$	$-\text{COOCH}_3$	$-\text{COOH}$	$-\text{CHNOH}$	$-\text{CONH}_2$	$-\text{NHCONH}_2$
$-\text{O.CO.CH}_3$	20°	Liq.	Liq.	Liq.	Liq.	*'Plastic solid'	Not known	Solid	Solid
				33°	34°	37.5°	42°	44°	48°

The above principles are shown up most clearly by the acetamides which have now been studied in detail by both force-area and surface potential methods. The figure below shows the head-group configuration deduced for the expanded state and for the high- and low-temperature condensed forms.



Condensed monolayers of acetamides and ureas were shown by Adam³ to exist in two forms with a definite transition temperature, the latter being unusual in giving solid films even at an area of 26 \AA^2 . (Solid monolayers are usually only obtained with close-packed, vertical chains at $20\text{--}21 \text{ \AA}^2$.) These and other facts are readily explicable by assuming cross hydrogen bonding between the molecules in the monolayer. A comparison between substituted amides and the corresponding esters which cannot form cross hydrogen bonds, for example, octadecyl acetamide and acetate, methyl stearamide and stearate, shows that the former tend to give very stable solid, and the latter much less stable fluid, films. The half-expansion temperatures ($T_{1/2}$) given by Adam⁴ are also much higher for the compounds for which cross hydrogen bonding in the monolayer is now postulated (amides, ureas, aldoximes and acids), and the tendency towards solidification is also very apparent (see accompanying table).

Calculation of the hydrogen bond distances in the various cases gives results in quite good agreement with known values; for example, acetamides 2.8 \AA . at 21 \AA^2 , ureas 3.2 \AA . at 26 \AA^2 , acids 2.8 \AA . at 24 \AA^2 .

cross-linked (as in the low-temperature condensed form). The latter is found to be the more stable by about $800 \text{ cal./gm. mol.}$

The stabilizing action of the cross hydrogen bonds can be decreased, leading to liquefaction, by strongly acid substrates (for example, $5N.\text{H}_2\text{SO}_4$), as well as by increase of temperature. The effect of other reagents, such as urea, is being examined.

Similar considerations can be advanced to interpret the monolayer behaviour of the ureas, other amides, aldoximes, unsubstituted and α -amino acids, as well as mixed films, and will be given with further details in a forthcoming publication.

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¹ Astbury, *Trans. Far. Soc.*, **36**, 871 (1940).

² Alexander, *J. Chem. Soc.*, 177 (1939).

³ Adam, "Physics and Chemistry of Surfaces", p. 55 (Oxford Univ. Press, 1938).

⁴ Ref. (3), p. 64.

⁵ Alexander and Schulman, *Proc. Roy. Soc., A*, **161**, 115 (1937).