

The implications of the calculation for the process of linkage (2) are explored in the accompanying letter by my colleague, F. C. Frank.

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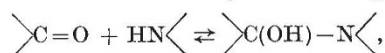
¹ D. M. Wrinch, NATURE, 137, 411 (1936).

² See, for example, J. W. Baker, "Tautomerism" (1934), p. 38.

³ The figures of Pauling and Sherman given in *J. Chem. Phys.*, 1, 606 (1933), calculated on the basis of the value of 208 kilogram calories for the heat of dissociation of N₂, have been modified to take account of the revised value of 169 kilogram calories (see Mulliken, *Phys. Rev.*, 46, 144 (1934); Herzberg and Sponer, *Z. phys. Chem.*, B, 26, 1, though this modification is without effect on these calculations.

⁴ *J. Biol. Chem.*, 109, 325, 329 (1935).

WRINCH¹ recently proposed that in monolayers or globular molecules of proteins, polypeptide chains are knitted into a fabric by the bonding process



which Frank² had shown to be required in keratin to make permissible the structure Astbury deduced for it by X-ray crystallography. It is desirable to estimate the energy balance of this process, which is chemically analogous to lactam-lactim tautomerism, or to the ring closure in sugars associated with mutarotation.

Taking link values of heat of rupture from Pauling and Sherman³, we find the process of linkage represented above is endothermic by about 7.3 kcal., while a lactam-lactim transformation is 10.7 kcal. endothermic, without allowance for resonance energies in either case. Resonance in the lactam form increases both these figures by some 20 kcal., if taken as the same as in acetamide: there must be a similar but presumably smaller resonance energy in the lactim, but the 'cyclol' molecule in itself offers no chance of constructing a resonant system.

Though these are not free energies, and in any event not very accurate, they appear certainly too large to allow the equilibrium to rest close to the right hand of the equation, as the theory requires, so that we must either abandon the theory or find some compensating source of energy. This is provided in the keratins by strain in the side-chain cross-linkages, which Astbury² and Speakman⁴ have shown to provide the main driving force of contraction from the β -form. In the proposed 'cyclol' monolayers, we have a similar source of energy which we may call a heat of crystallization, for the cyclization into a compact strainless form is evidently at the same time a process of two-dimensional crystallization; but this by itself cannot be sufficient.

An additional source is provided by hydration (or association through hydroxyl bonds generally), which is well known to stabilize lactims, non-chelate enols, and hydroxylic tautomeric forms in general⁵, a fact directly related to their superior solubility in water and other hydroxylic solvents. Not only the hydroxyls but also the nitrogens, which are more aliphatic in nature in the cyclized form, are available for hydration: protein hydroxyls can also associate with each other. Each hydroxyl bond formed may be supposed to provide energy of the order of half the internal latent heat of vaporization of ice, thus about 5 kcal., so that the whole may be a sufficient compensating source of energy, about 20 kcal.

Thus it appears that if the protein molecules are fabricated with the aid of this linkage, they can only be stable when hydrated. Any conditions tending to

dehydration will render the protein excessively liable to opening into chain forms, unless restrained by side chains or deprived of catalysts necessary for transformation. Mildly dehydrating conditions should be most effective because water is a catalyst for transformation as well as a stabilizer of one form. So long as the rings only occasionally open they can re-form in the same configuration, but as soon as the opening becomes too frequent this will cease to be the case and they will then re-form in altered structures, derived more directly from open chains. This conforms with all observations on the processes of degeneration and denaturation, including Astbury's X-ray studies of these processes^{6,7}. Thus what seems at first to be a destructive obstacle to the theory may be capable not only of reconciliation with it, but even of enhancing its effectiveness.

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¹ D. M. Wrinch, NATURE, 137, 411 (1936).

² See W. T. Astbury, *Proc. Textile Inst.* (1936), in the press.

³ L. Pauling and J. Sherman, *J. Chem. Phys.*, 1, 606 (1933).

⁴ J. B. Speakman, *Proc. Textile Inst.* (1936), in the press.

⁵ See, for example, J. W. Baker, "Tautomerism" (1934), p. 38.

⁶ W. T. Astbury and R. Lomax, *J. Chem. Soc.*, 846 (1935).

⁷ W. T. Astbury, S. Dickinson and K. Bailey, *Biochem. J.*, 29, 3351 (1935).

Insect Coloration

IN the article on the Oxford Congress of the South Eastern Union of Scientific Societies in NATURE of July 11, p. 88, reference is made to the address of the president, of which the main topic was the coloration of insects by natural selection. Prof. Hale Carpenter is reported as saying:

"Sometimes it pays an insect to change its appearance according to whether it appears in a dry or in a wet season. Poulton pointed out that a dry season is one of scarcity of food, and certain butterflies then remain inconspicuous and of skulking habits, whereas in a wet season they are conspicuously coloured, and they can afford to allow some of the species to be eaten by reason of their number."

Prof. Hale Carpenter referred to an African *Charaxes*, which is conspicuous in the wet season but in the dry assumes a dead-leaf-brown and deliberately hides itself among clusters of dead leaves. To assert that an insect *deliberately* hides, is going far. When bug hunting in Australia and Sumatra, it seemed to me that the butterflies all made for shade behind leaves, when not madly careering in the sun. May not the food in the two seasons vary, not merely in quantity but in quality? It certainly will. The temperature also. As we know nothing about the relation of coloration to quality of food, the subject is beyond discussion, at present. Darwinian discussion is largely on 'Alice' lines. No chemist can believe in change by any process of direct mimicry—nor even a MacBride. Nature is held under strict enzymic control, though inspection of any good collection shows the actual variations are very wide. Discussions too are often wide of the mark: if they were all scientific, our shelves would have an easy burden. Are the morals of the insect world on so high a plane that it can be asserted that there has never been a cross of mimetics? Mistakes, we know, are made even in the best regulated families.

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