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Relationes

Additivity of the Hydrogen Bridges in Several Polymers of Formamide

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The purpose of the study was to examine the energy additivity of the hydrogen bridges in formamide polymers. Consideration was given to both the linear polymers observed in polypeptides, and to the cyclic polymers observed in the crystal structure. Additivity was found in several geometries. The linear polymers were considered as far as the tetramer, and the cyclic as far as the heptamer.

Key word: Hydrogen bridges in formamide polymers

1. Introduction

The physical chemistry approach to several biopolymers, particularly nucleic acids and proteins, requires ample knowledge of the hydrogen bridges behaviour. Additivity is an important quality in the collective treatment; this and other characteristics have been analysed in specific systems and have been found to conform to a general pattern [1, 2].

The dependence of the additivity, both on the system and on the method of calculation, have led us to do an extensive study in formamide polymers. The linear and cyclic dimers have already been treated and non-additivity found in the linear trimer.

The presented analysis, done with the semiempirical method PCILO [3][1] suitable for conformation analysis, attempts to obtain qualitative rather than quantitative information of the hydrogen bridges behaviour.

2. Results

The geometrical parameters [4, 5] of Fig. 1 were utilized. The energies per hydrogen bridge (HB) in several linear polymers were calculated, all of them

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[1] PCILO (Perturbative Configuration Interaction Using Localised Orbitals) is a semiempirical method with the same approximations as CNDO/2, but without iteration. The Slater determinant is constructed from the localized orbitals, following the chemical formula, the excited states from antibonding orbitals. A Rayleigh-Schrödinger expansion, in terms of mono and biexcited states, is done for the Epstein-Nesbet Hamiltonian.

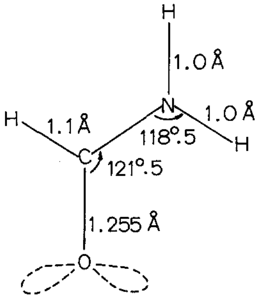

Fig. 1. Formamide monomer, experimental geometry

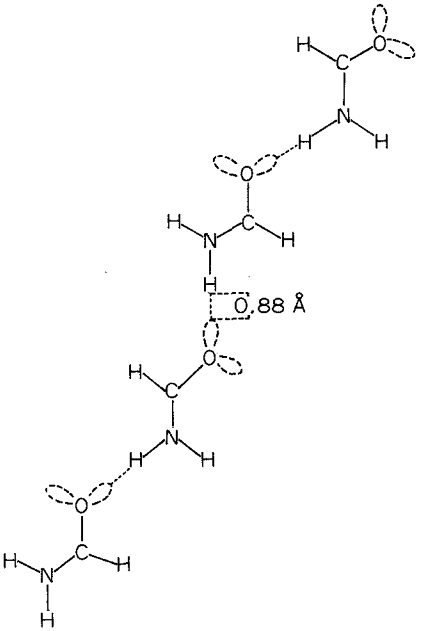

Fig. 2. Linear tetramer. Monomer geometry Fig. 1

linear non-parallel configurations with a distance r(O–N) of 2.88 Å, Fig. 2. The observed energies (Table 1) show additivity of the HB.

Previous calculations in several systems [1] predict a nonadditivity associated with the reduction of the intermolecular distances. That is the inclusion of another monomer would permit the polymer contraction. In order to analyse this effect the distances r(O–N) of the above polymers were optimized. In spite of the fact that the method could underestimate the distances, the qualitative behaviour can be treated in a suitable manner. A common optimum distance was found for the three polymers (2.72 Å). The energies per HB are: 6.12 kcal/mol in the dimer, 6.09 kcal/mol in the trimer, and 6.09 kcal/mol in the tetramer. The calculation predicts a complete additivity for these systems.

Table 1. Total energies and HB energies for the considered polymers, Total energy given to third perturbation order [3]

	Geometries Fig. 1 r(O–HN) = 2.88 Å		Geometries Fig. 1 r(N–H) = 1.1 in the HB	
	Energy	Energy per HB	Energy	Energy per HB
Monomer	− 24701.04		− 24705.92	
Linear Dimer	− 49407.71	5.64	− 49414.12	6.16
Cyclic Dimer	− 49409.97	3.95	− 49422.67	5.43
Linear Trimer	− 74114.27	5.58	− 74127.24	7.18
Cyclic Trimer	− 74115.97	4.29	− 74134.84	5.69
Linear Tetramer	− 98820.77	5.54	− 98840.17	7.13
Cyclic Tetramer	− 98824.95	4.16	− 98856.54	5.73
Cyclic Pentamer	−123530.57	4.22	−123567.41	5.60
Cyclic Hexamer	−148238.31	4.01	−148288.43	5.56
Cyclic Heptamer	−172949.31	4.21	−173012.21	5.81

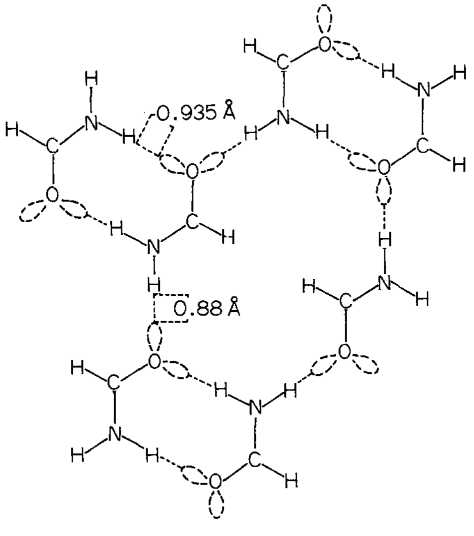

Fig. 3. Cyclic heptamer, planar geometry. Monomer geometry Fig. 1

The linear polymers exist both in the structure of polypeptides and in the crystal geometry, but the crystal shows a different way of polymerization; cyclic dimers, with two HB of $r = 2.935$ Å, are attached to themselves by a HB of $r = 2.88$ Å, Fig. 4. For the sake of simplicity all the polymers which involve one of these cyclic dimers, will be called cyclic.

The calculated energies of the cyclic polymers show: 1) additivity of the hydrogen bridge with slight variations of the trimer and the tetramer due to the linear union of one monomer; 2) greater energy per HB in linear polymers, due to the minor nuclear repulsion; 3) the cyclic polymers are more stable, a normal result. However, we must remember that the method, under ZDO approximation, favours these configurations.

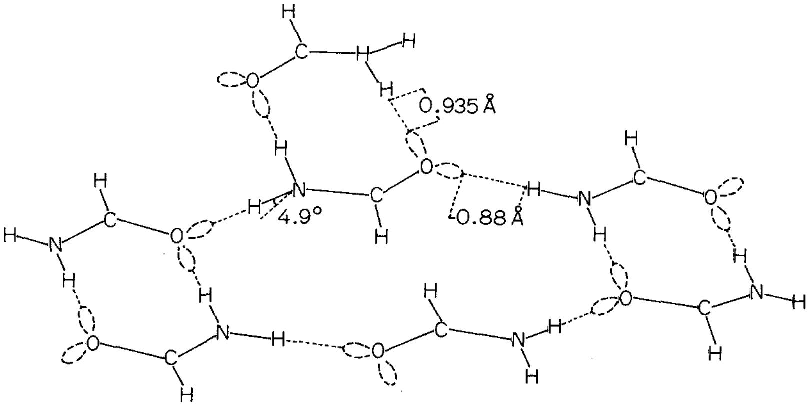

Fig. 4. Cyclic heptamer, non-planar geometry

The optimization of the intermolecular distance in the linear polymers, reduces the energy by 1 kcal/mol. It is expected that a larger energy variation would be produced by modification of the monomer geometry. The reported experimental geometries are in good general agreement but they do show slight discrepancies e.g. the N–H bonds have a value of 1.0 Å for Dreyfus *et al.* [4, 6] and 1.1 Å for Ladell and Post [5]. Using the N–H bond of 1.1 Å (Table 1) a general decrease in the energies is observed but the additivity is conserved. The optimization of the monomer, with respect to the N–H bonds, predicts a geometry similar to the experimental. But in spite of this the energies for the two geometries are rather different.

3. Non-Planar Polymers

The formamide monomer is considered planar [4, 6, 7] and the cyclic dimers in the crystal geometry are almost planar, but larger polymers are not [5]. In non-planar polymers the charge distribution is affected, hence qualitative modifications in the HB behaviour could be expected. Several polymers, constructed with planar monomers, were twisted around the axis NH–O. A minor stability and additivity were again obtained.

The hexamer and the heptamer were calculated using the geometry represented in Fig. 4. The obtained energies are slightly lower; the reason was the decrease of the monomer energy itself. Additivity was again observed.

4. Discussion

The optimized HB and N–H bond distances reported in this work seem reasonable. Christensen and Kartzeborn [8] in an extended *ab initio* calculation obtained a slight non-planar geometry as the most stable monomer. The method used here seems to be suitable for the HB treatment [9], but because all the geometrical parameters have not been separately varied, one has to be careful about the authenticity of the results.

However, although the absolute values may have very little accuracy the important result is that there does not seem to be any large scatter or variation in the HB energies. Indeed, it would be very surprising that we should compute an almost constant energy if, in fact, experimentally they varied considerably from one molecule to another.

There are several calculations on dimers of formamide, Pullman and Dreyfus [4] in an *ab initio* calculation of the linear dimer obtained ~8 kcal/mol for the HB energy, Johansson and Kollman [10] in another *ab initio* ~9 kcal/mol. Dreyfus *et al.* [6] obtained ~7 kcal/mol for the cyclic dimer using the same basis set than [4] and ~9 kcal/mol with one smaller.

In this work additivity was found in a large range of polymers. Murthy *et al.* [7] obtained an increase in the HB energy with a decrease in the HB distance, when the third monomer is attached in the linear trimer, the effect was not observed in the present work. However, both this effect and the non-additivity defined as the difference between cyclic and linear union, could have been produced by the tendency to favour the compact geometries [1].

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