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Hydrogen bonding networks in *E*- or *Z*-2-(3'-pyridyl)-3-phenylpropenoic (α -pyridylcinnamic) acid assemblies – a molecular modeling study

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Abstract The aggregation properties of the stereoisomeric 2-(3'-pyridyl)-3-phenylpropenoic acids (PY3E, PY3Z, α -pyridylcinnamic acids) were studied by the PM3 semiempirical quantum chemical method. Calculations revealed that (aromatic)C–H...N hydrogen bonds made possible the attachment of dimer units. Thus, virtually infinite chains can be built out of PY3E and PY3Z. Three different energy minimized structures were identified: (i) zig-zag, (ii) ladder and (iii) helical configurations.

Keywords α -Pyridylcinnamic acids · Intermolecular hydrogen-bonded network · Molecular modeling · Semiempirical method

Introduction

A great deal of experimental (via infrared spectroscopic measurements [1, 2, 3]) and computational [4] information on the aggregation characteristics of stereoisomeric α -phenylcinnamic acids has been collected. It was found that hydrogen bonds between the carboxylic groups are responsible for short range organization (typically found in solution), while mainly (aromatic)C–H...O=C interactions govern the long-range arrangement of the molecules (typical for the crystalline state). When one or more carbon atoms in either of the two phenyl groups are replaced by heteroatoms capable of accepting hydrogen bonds, a larger variety of hydrogen-bonded networks may be envisaged than in the case of the α -phenylcinnamic acids. Indeed, when N was introduced in the α -position, i.e. pyridylcinnamic acids were obtained, first principle computations revealed the existence of intramolecular C–H...N hydrogen bonds. [5] Nitrogen may replace any of the carbon atoms in the α -phenyl ring, giving rise to various hydrogen bonding patterns. It was concluded from the optimization of three dimers at the

level of semiempirical quantum chemistry that virtually infinite chains might be built from the *E* as well as the *Z* stereoisomers, and ribbon- or ladder-like structures of limited length (two dimers or at maximum three dimers together) could be obtained from the *Z* isomer when the nitrogen is situated in the 4'-position. [6]

In further work we hoped to uncover other hydrogen bonding motifs beside those described previously and mentioned above by changing the position of the ring-nitrogen. [6] The results of this investigation are described in this contribution.

Method

The following two molecules (Fig. 1) were studied: *E*- and *Z*-2-(3'-pyridyl)-3-phenylpropenoic acids (α -pyridylcinnamic acids: PY3E and PY3Z). The figure contains the numbering scheme used in further considerations.

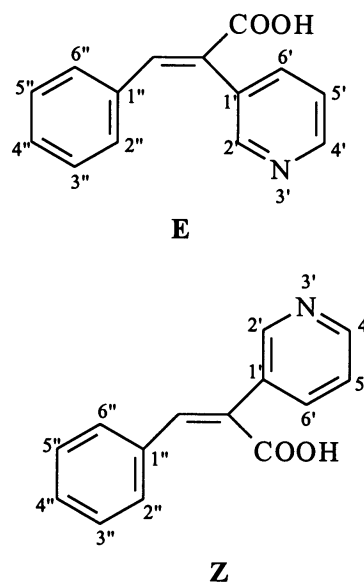


Fig. 1 The molecules studied with the numbering scheme used in the paper

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Fig. 2 The dimer of PY3E

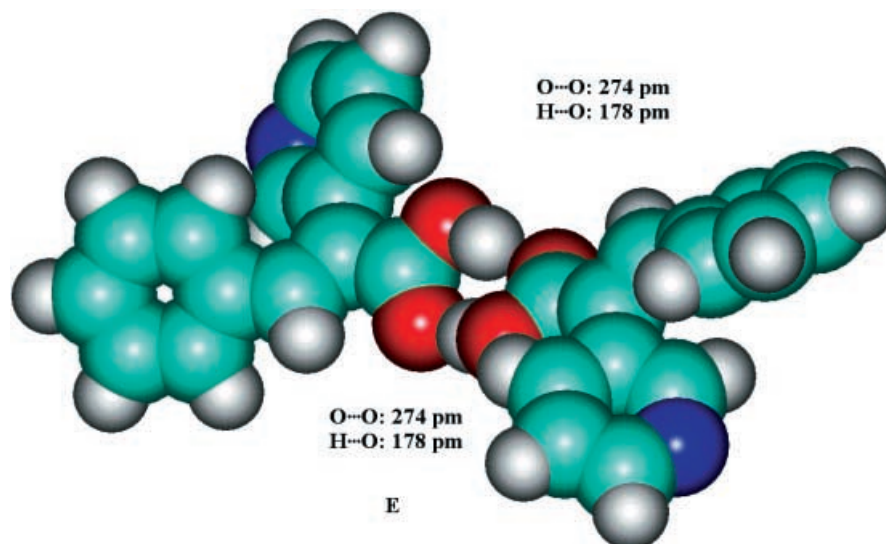
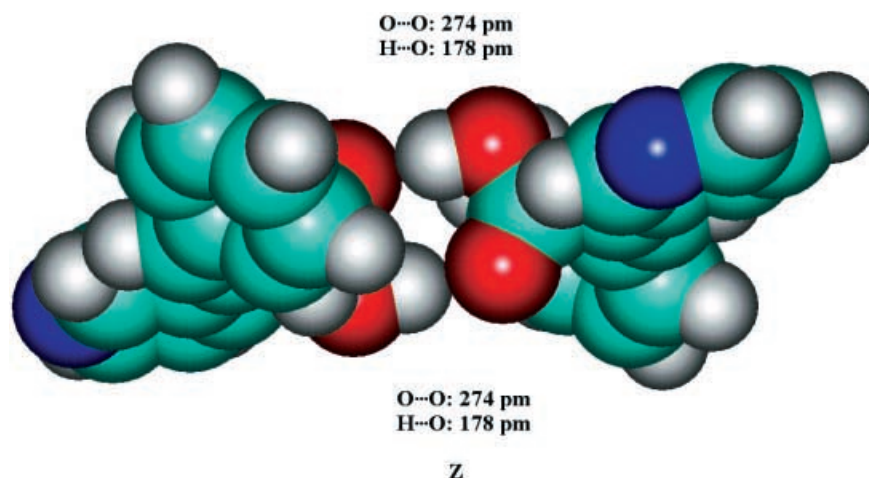


Fig. 3 The dimer of PY3Z



The dimers of the acids (hydrogen bonded via their carboxylic groups) were chosen as fundamental structural units and chains and ribbons were built enforcing the assumed close contacts. Then the assemblies were optimized using the PM3 [7] semiempirical quantum chemical method as implemented in the Hyperchem package. [8] The gradient norms were always less than 0.1 and the force matrices were found to be positive definite, verifying that minima were found. After convergence bond lengths were determined. Two criteria were chosen as a guide in considering whether they can be counted as hydrogen bonds. The distance between the heavy atoms should fall within the sum of their van der Waals radii compiled by Bondi [9] (O...O: 304 pm, C...N: 325 pm) and the angle defined by the two heavy atoms and hydrogen (donor atom-H-acceptor atom) should be larger than 90° . [10]

Results and discussion

The dimers bonded through the carboxylic groups could be constructed easily for both stereoisomers. They are

kept together by two hydrogen bonds of equal length. The dimers are depicted in Figs. 2 and 3 together with bond length data. Hydrogen bond angles are not shown in the figures; however, it is easy to see that here and in the other hydrogen bonds that they are larger than 90° .

When two dimers were optimized together (dimers of the dimers in the following) a number of possibilities emerges for both stereoisomers, since the expected "new" C-H...N hydrogen bond may be formed through the interaction of any hydrogen-carrying carbon atom of both aromatic rings and the nitrogen of the pyridyl ring of the other molecule. It was found that indeed the dimer of the dimers is kept together by C-H...N hydrogen bonding. Among the possibilities all except one combination gave a minimum on the potential energy surface as an aggregate. The exception was PY3E when C(3'')-H...N should have been the hydrogen bond. In this case the dimers remained closely attached (as if they were "alone"), but the two dimers found a minimum arrangement far away from each other, irrespective of the starting geometries. When the interaction of two pyridyl groups was considered, it was found that only the

Fig. 4 Optimum configuration of two dimers of PY3Z when in the initial geometry (aromatic) C(2'')-H...(pyridyl)N close contact was enforced

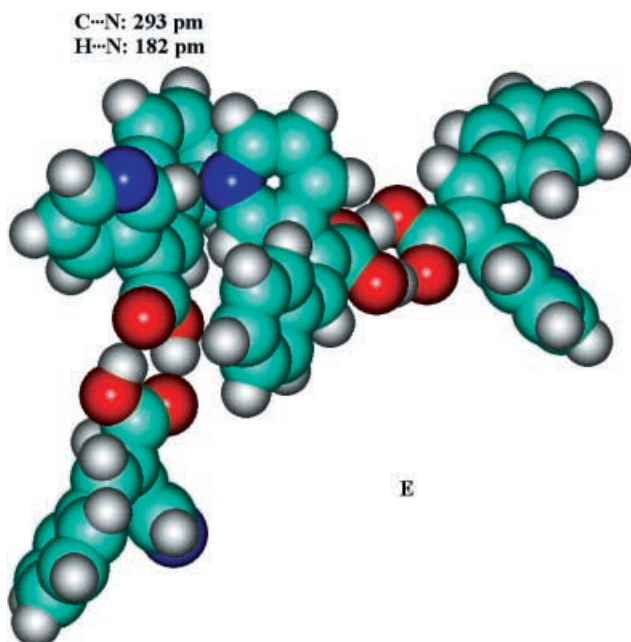
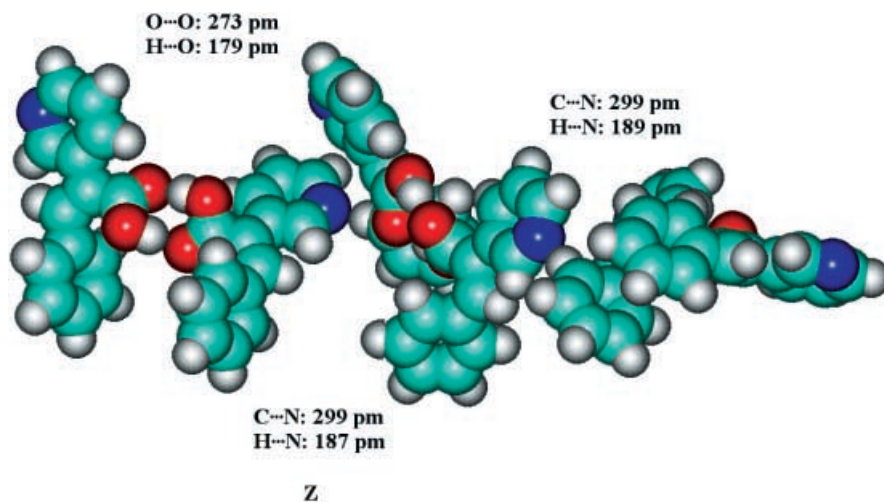


Fig. 5 Optimum configuration of two dimers of PY3E when in the initial geometry (pyridyl)C(2')...(pyridyl)N close contact was enforced

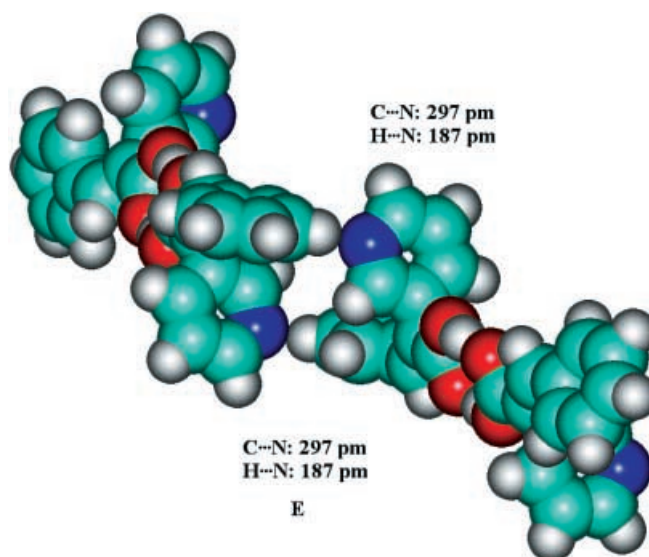


Fig. 6 The ladder-like structure of two dimers of PY3E after optimization, when in the initial geometry two (aromatic)C(3'')-H...N close contact was enforced

PY3E-tetramer structure with an enforced C(2')-H...N close contact converged as hydrogen-bonded dimers of the dimers. Two of the hydrogen-bonded dimers of dimers are shown in Figs. 4 and 5. One is for PY3Z and the other for PY3E is in Fig. 5, when in the former the phenyl and the pyridyl groups and in the latter the two pyridyl groups are in close contact via C-H...N hydrogen bonds.

Although enforcing one close contact did not give a hydrogen-bonded (C(3'')-H...N) dimer of dimers for PY3E, enforcing two close contacts gave a minimum structure kept together by two symmetric C(3'')-H...N hydrogen bonds after optimization (Fig. 6).

Moreover, this ladder-like structure could be built up to give the trimer of dimers, see Fig. 7.

We see no reason other than the limitation in computational resources why this ladder-like structure cannot be built further.

In the following, we show all three trimers of dimers with bond length data where C-H...N close contacts were retained after minimization (Fig. 8).

They all form zig-zag structures. The dimers in the chain are kept together by weak hydrogen bonds and we see no reason other than the limitation in computational resources why the chain cannot be built further or even branched. Let us note that the dimer of dimers shown in Fig. 5 could not be built up by an additional dimer unit keeping a fully hydrogen-bonded network. Two of the dimers remained closely tied, while the third dimer is farther from the other two dimers.

Fig. 7 The ladder-like structure of three dimers of PY3E after optimization, when in the initial geometry two (aromatic) C(3'')–H...N close contacts were enforced

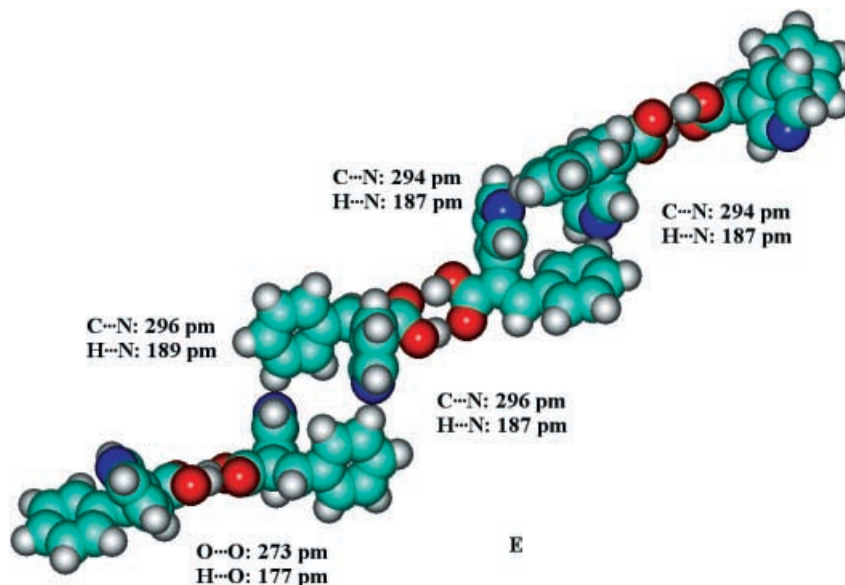


Fig. 8a–c The zig-zag structure of three dimers of α -pyridylcinnamic acids after optimization. **a** PY3E, when (aromatic)C(2')–H...N close contacts were enforced. **b** PY3Z, when (aromatic)C(2')–H...N close contacts were enforced. **c** PY3Z, when (aromatic)C(4')–H...N close contacts were enforced

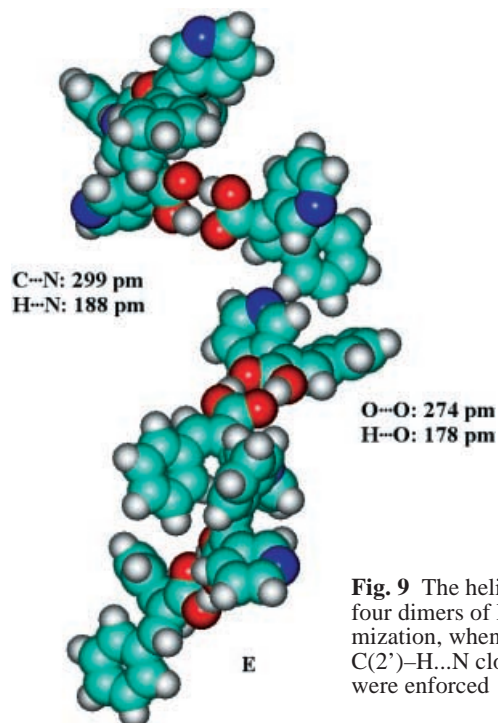
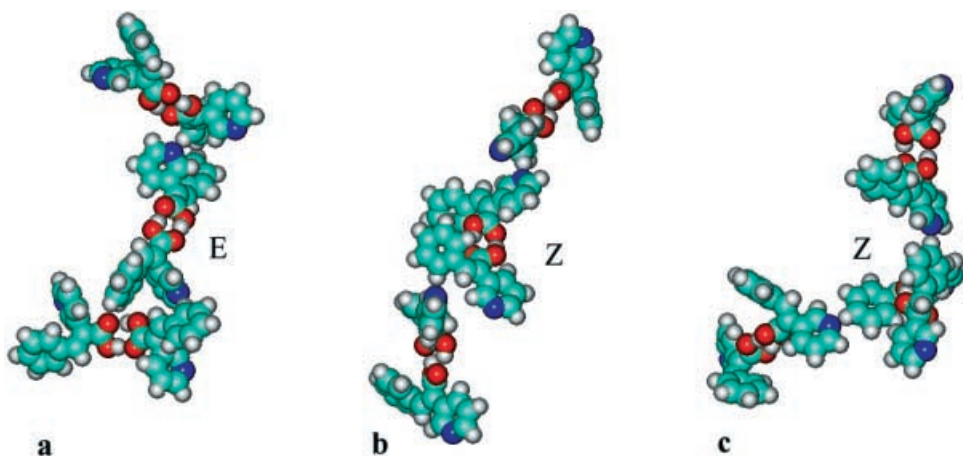


Fig. 9 The helical structure of four dimers of PY3E after optimization, when (aromatic)C(2')–H...N close contacts were enforced

Interestingly, when the trimer of dimers having C(2'')–H...N hydrogen bonds was extended by one dimer unit, a configuration not seen before appeared (Fig. 9).

After minimization of the hydrogen-bonded aggregate, the tetramer of dimers started to assume a helical structure.

Conclusions

Calculations revealed that (aromatic)C–H...N hydrogen bonds made possible the attachment of dimer units; thus, virtually infinite chains can be built out of both isomers of pyridylcinnamic acid. Besides the usual zig-zag configuration, among the higher order aggregates ladder-like and helical structures could also be identified.

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