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Hydrogen bonding interactions in *E*- or *Z*-2-phenyl-3-(*X'*-pyridyl)propenoic acid (*X*=2, 3 or 4) assemblies—a molecular modeling study

Abstract The agglomeration properties of stereoisomeric 2-phenyl-3-(*X*'-pyridyl)propenoic acids (*X*=2, 3 or 4) were studied by the PM3 semiempirical quantum chemical method. Calculations revealed that dimers kept together by the intermolecular hydrogen bonding interactions of the carboxylic groups could be built from both stereoisomers irrespective of the position of the nitrogen heteroatom. The dimers of the *Z*-isomers could also be built through (aromatic)C–H...N hydrogen bonds between the dimer units. The longest agglomerate was the pentamer of the dimers when the nitrogen was in the 2' position. Longer hydrogen-bonded agglomerates than dimers could only be constructed from the *E*-isomer with the nitrogen in position 4'. Here, the trimer of the dimers proved to be the longest hydrogen-bonded entity and similarly to the *Z*-isomers, the dimer units are kept together by (aromatic)C–H...N intermolecular hydrogen bonds.

Keywords 2-Phenyl-3-(*X*'-pyridyl)propenoic acids (*X*=2, 3 or 4) · Intermolecular hydrogen bonded network · Semiempirical method

Introduction

A great deal of experimental (via infrared and NMR spectroscopic measurements [1, 2, 3]) and computational [4] information on the aggregation characteristics of stereoisomeric α-phenylcinnamic acids has been collected previously. 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 CH groups in any of the two phenyl groups are replaced by heteroatoms capable of accepting hydrogen bonds, a larger variety of hydrogen-bonding patterns may be envisaged than in the case of α-phenylcinnamic acids. Indeed, when a furyl or pyridyl group was introduced in position 2, ab initio [HF/3-21G//3-21G and HF/6-31G(d,p)//HF6-31G(d,p)] computations revealed the existence of intramolecular C–H...(O)N hydrogen bonds [5]. When the positions of the oxygen or the nitrogen atom within the heteroaromatic ring was altered, a large variety of networks (chain-, ladder-, ribbon-like or helical) could be obtained, kept together by (aromatic)C–H...O(N) intermolecular hydrogen bonds [6, 7].

To further our work concerning the 2,3-disubstituted propenoic acid stereoisomers, it was decided to study extended hydrogen-bonding networks of 2-phenyl-3-(*X*'-pyridyl)propenoic acid (*X*=2, 3 or 4) stereoisomers. The exploration of possible hydrogen-bonding patterns as well as finding the maximum length of aggregation were aimed at. The results obtained are communicated in the following.

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Method

Six molecules were studied (Fig. 1). They are the *E*- and *Z*-stereoisomers of 2-phenyl-3-(*X*'-pyridyl)propenoic acids (where *X*=2, 3 or 4). The figure contains the numbering scheme used in further considerations.

The dimers of the acids (hydrogen bonded via their carboxylic groups) were chosen as fundamental structural units and chains were built enforcing the assumed close contacts. Then, the assemblies were optimized using the PM3 [8] semiempirical quantum chemical method as implemented in the HyperChem package [9]. The gradient norm was always less than 0.1 and all force constants were positive, verifying that minima were found. After convergence, bond lengths were determined. As guidance in considering whether they can be accounted as hydrogen bonds two criteria were chosen. First, the distance between the heavy atoms should fall within the sum of their van der Waals radii compiled by Bondi [10] (O...O: 304 pm, C...N: 325 pm), second, the angle defined by the two heavy atoms and hydrogen (donor atom–H–acceptor atom) should be larger than 90° [11].
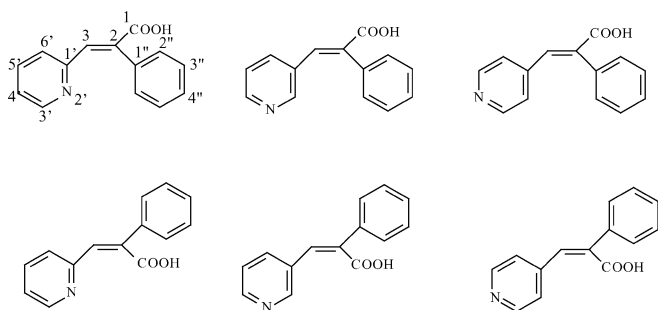
Fig. 1 The molecules studied with the numbering scheme used in the paper
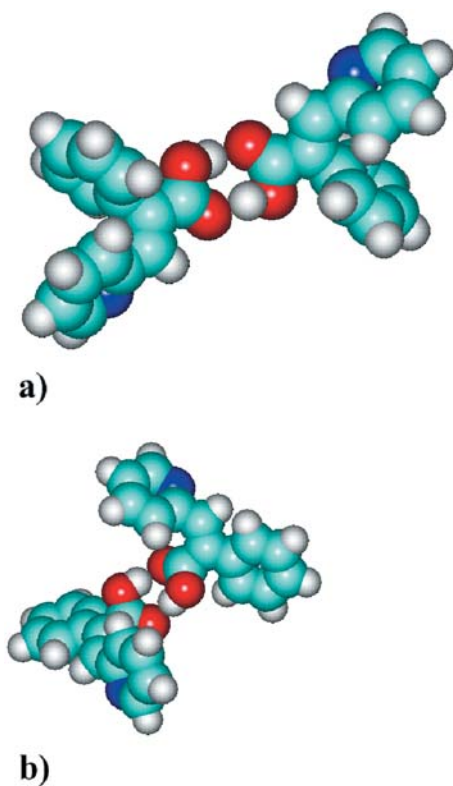

Fig. 2 The dimers of 2-phenyl-3-(2'-pyridyl)propenoic acid stereoisomers: **a** the *E*-isomer; **b** the *Z*-isomer
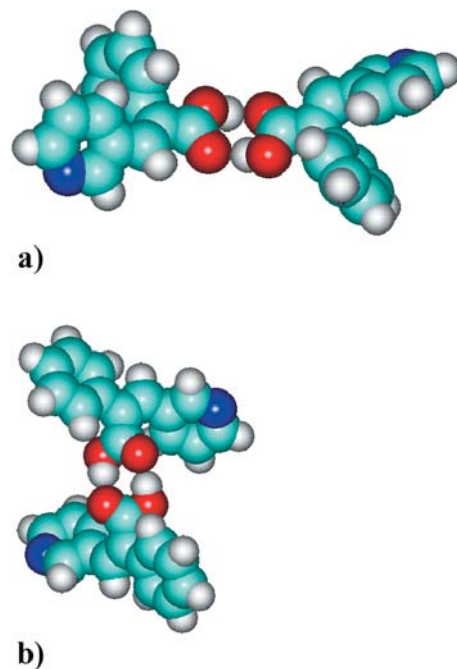

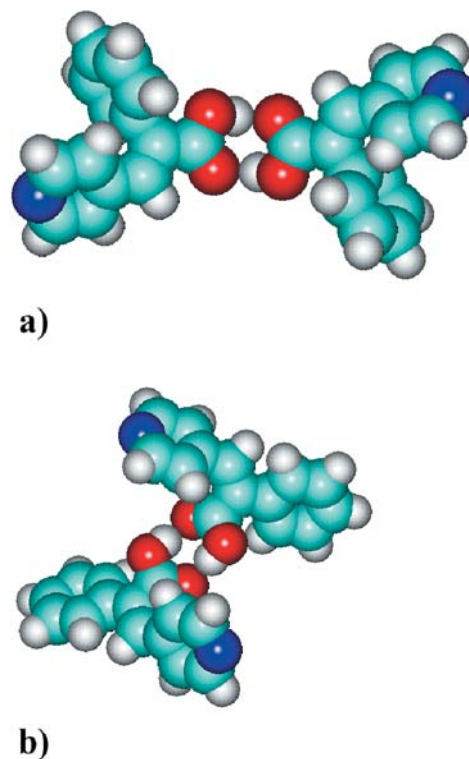Fig. 3 The dimers of 2-phenyl-3-(3'-pyridyl)propenoic acid stereoisomers: **a** the *E*-isomer; **b** the *Z*-isomer

Fig. 4 The dimers of 2-phenyl-3-(4'-pyridyl)propenoic acid stereoisomers; **a** the *E*-isomer; **b** the *Z*-isomer

Results and discussion

Dimers bonded through the carboxylic groups could be constructed easily for both stereoisomers of each molecule. They are kept together by two hydrogen bonds of equal length. The dimers are depicted in Figs. 2a, 3a and 4a for the *E*-isomers and in Figs. 2b, 3b and 4b for the *Z*-isomers. The O...O distances and the O...H hydrogen bond lengths are 275 pm and 179 pm, respectively and the hydrogen bond angles are definitely 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

a)

b)

c)

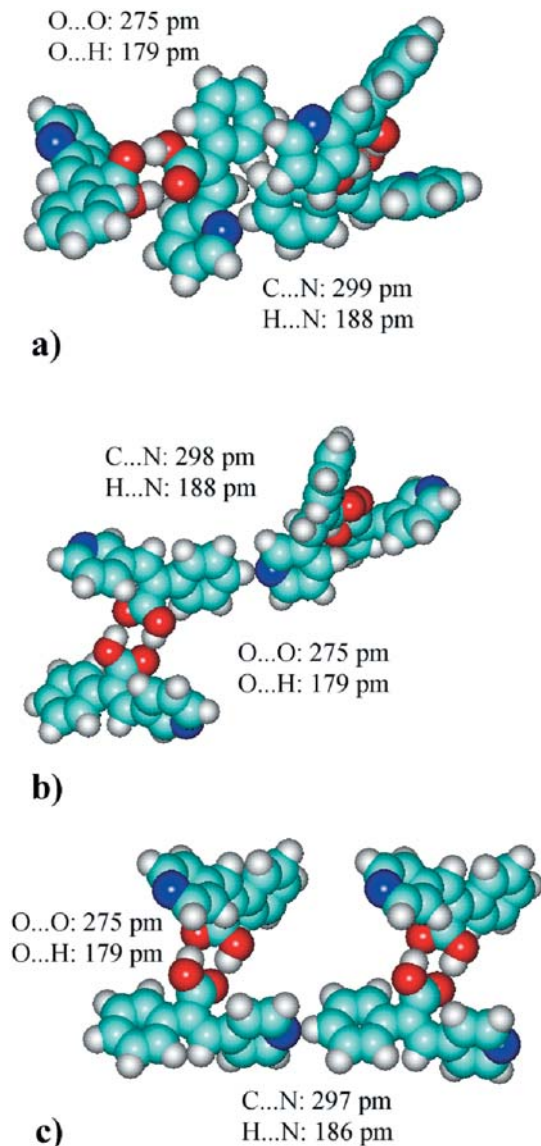**Fig. 5** Optimum configurations of the dimers of the dimers for the Z-2-phenyl-3-(X'-pyridyl)propenoic acid molecules **a** X=2, **b** X=3 and **c** X=4, when in the initial geometry (aromatic)C(4")–H...N close contact was enforced

Fig. 6 Optimum configuration of the dimer of the dimers for the E-2-phenyl-3-(4'-pyridyl)propenoic acid molecule, when in the initial geometry (aromatic)C(4")–H...N close contact was enforced

While the dimers of the dimers of each Z-isomer are indeed kept together with C–H...N hydrogen bonds (Fig. 5a–c), interestingly, such dimers could only be built from the E-isomer of 2-phenyl-3-(4'-pyridyl)propenoic acid (Fig. 6).

Among the aggregates where the dimers of the dimers were kept together by (aromatic)C–H...N intermolecular hydrogen bonds, trimers of the dimers could also be constructed successfully (Fig. 7a–c) for the Z-isomers and (Fig. 7d) for the E-isomer when the N atom is in position 4'.

Longer aggregates, however, could not be built except for Z-2-phenyl-3-(4'-pyridyl)propenoic acid, where the longest hydrogen-bonded oligomer was the pentamer of the dimers (Fig. 8). The oligomer was of a helical structure.

When the decamer of the dimers for this molecule was constructed, it fell into two hydrogen-bonded pentamers on optimization (Fig. 9). The two pentamers remained in the vicinity of each other in an ordered manner. The terminal phenyl group of one pentamer unit is nearly perpendicular to the terminal pyridyl ring of the other. The arrangement is marked with an arrow in Fig. 9.

Conclusions

Calculations revealed that via (aromatic)C–H...N hydrogen bonds dimer units could be attached to each other, but not infinitely. The maximum length was obtained with Z-2-phenyl-3-(2'-pyridyl)propenoic acid. The hydrogen-bonded aggregate was of helical structure and contained five dimer units. The E-isomers did not participate in hydrogen-bonded oligomer formation except E-2-phenyl-3-(4'-pyridyl)propenoic acid, where hydrogen-bonded trimer of the dimers could be constructed.

interaction of any hydrogen-carrying carbon atom of the phenyl group of one molecule and the nitrogen of the pyridyl ring of the other. Since one of our targets was to find the longest possible aggregates, it was decided to pick only the phenyl carbon at position 4", because it may be sensible to assume that this is the sterically least hindered position.
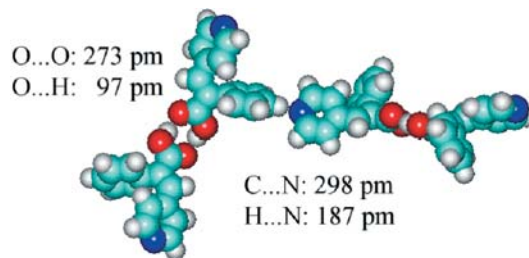
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Fig. 7 Optimum configurations of the trimers of the dimers for the Z-2-phenyl-3-(X'-pyridyl)-propenoic acid molecules **a** X=2, **b** X=3, **c** X=4 and **d** the E-2-phenyl-3-(4'-pyridyl)pro-penoic acid molecule, when in the initial geometry (aromatic)C(4")–H...N close contact was enforced

O...O: 275 pm
H...O: 178 pm

C...N: 299 pm
H...N: 187 pm

a)

O...O: 275 pm
O...H: 179 pm

C...N: 298 pm
H...N: 188 pm

b)

O...O: 275 pm
O...H: 179 pm

C...N: 297 pm
H...N: 186 pm

c)

C...N: 296 pm
H...N: 186 pm

O...O: 273 pm
O...H: 178 pm

C...N: 298 pm
H...N: 186 pm

d)

C...N: 299 pm
H...N: 187 pm

O...O: 275 pm
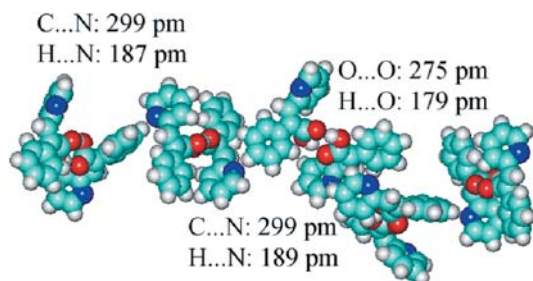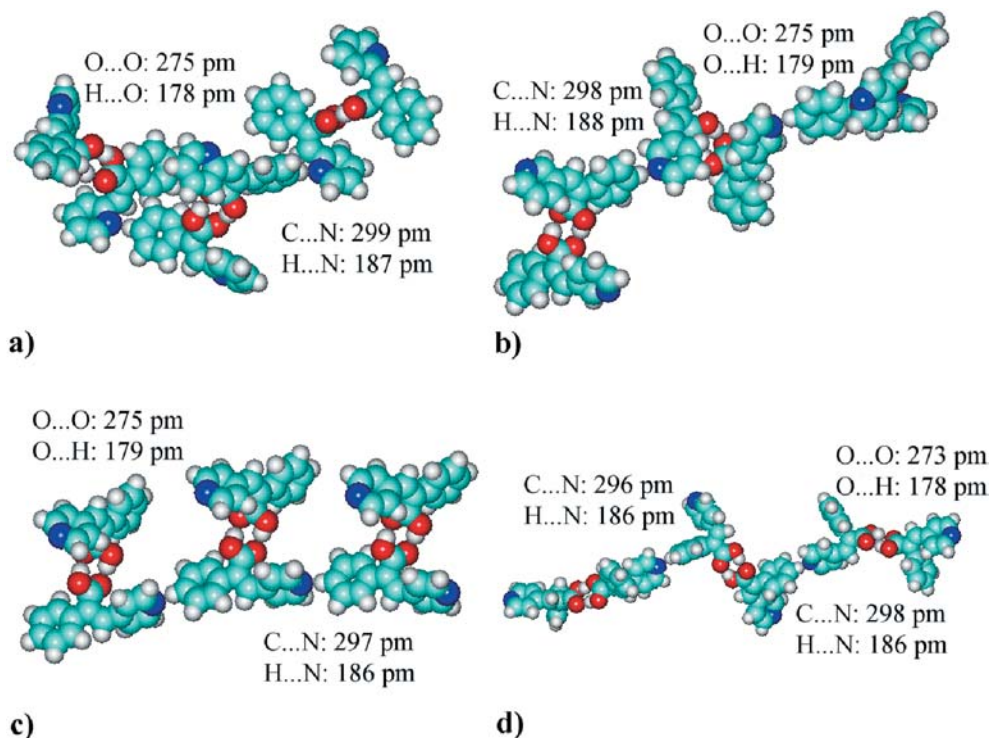H...O: 179 pm

C...N: 299 pm
H...N: 189 pm

Fig. 8 The helical structure of the pentamer of dimers for the Z-2-phenyl-3-(2'-pyridyl)propenoic acid molecule, when in the initial geometry (aromatic)C(4")–H...N close contact was enforced

O...O: 275 pm
H...O: 178 pm

C...N: 300 pm
H...N: 188 pm
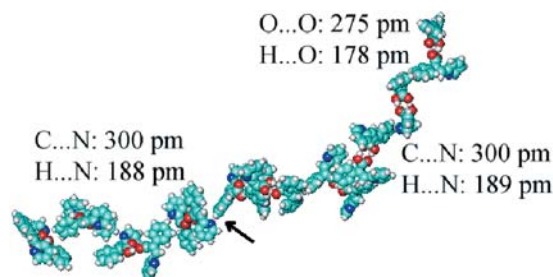
C...N: 300 pm
H...N: 189 pm

Fig. 9 The optimum structure of the decamer of dimers for the Z-2-phenyl-3-(2'-pyridyl)propenoic acid molecule, when in the initial geometry (aromatic)C(4")–H...N close contact was enforced

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