
Structural Motifs in α -Pyridyl- and α -Furylcinnamic Acid Assemblies— A Molecular Modeling Study

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ABSTRACT: The aggregation properties of stereoisomeric 2-(3'-furyl)-3-phenylpropenoic acids (FU3E, FU3Z, α -furylcinnamic acids) and 2-(4'-pyridyl)-3-phenylpropenoic acids (PY4E, PY4Z, α -pyridylcinnamic acids) were studied by the PM3 semiempirical quantum chemical method. Calculations revealed that (aromatic)C—H...N(O) hydrogen bonds made possible the attachment of dimer units; thus, virtually infinite chains can be built out of FU3Z, PY4E, and PY4Z. The energy-minimized structure had zig-zag configuration. PY4Z dimers allowed the formation of ribbonlike network; however, the number of structural units could not be increased infinitely. One of the furyl derivatives (FU3E) could not be stabilized either in the ribbon or the chain form; however, (aromatic)CH... π or (aromatic) π ...(aromatic) π interactions contribute to the packing pattern of the two dimers. © 2001 John Wiley & Sons, Inc. *Int J Quantum Chem* 84: 269–275, 2001

Key words: α -pyridyl- and α -furylcinnamic acids; intermolecular hydrogen-bonded network; molecular modeling; semiempirical methods

Introduction

A wealth of experimental (via infrared spectroscopic measurements [1–3]) and computational [4] information on the aggregation characteristics of stereoisomeric α -phenylcinnamic acids were collected previously. It was found that hy-

drogen bonds between the carboxylic groups were responsible for short-range organization (typically found in solution), while mainly (aromatic)C—H...O=C interactions governed the long-range arrangement of the molecules (typical for the crystalline state). As an extension of these investigations, first, the intramolecular hydrogen bonding characteristics of α -pyridyl- and α -furylcinnamic acids were described [5]. Now, in this contribution, the viable structural motifs in the assemblies of these acids are studied by computational tools. These molecules contain heteroatoms capa-

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ble of accepting hydrogen bonds; therefore, larger variety of hydrogen-bonded network may be envisaged than in the case of α -phenylcinnamic acids.

Methods of Evaluation

MOLECULES STUDIED

The following molecules (Fig. 1) were studied: E- and Z-2-(3'-furyl)-3-phenylpropenoic acids (α -furylcinnamic acids: FU3E and FU3Z), and E- and Z-2-(4'-pyridyl)-3-phenylpropenoic acids (α -pyridylcinnamic acids: PY4E and PY4Z).

METHOD OF CALCULATIONS

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 together by the PM3 [6] semiempirical quantum chemical method included in the Hyperchem package [7]. 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. As a guidance in considering whether they can be accounted as hydrogen bonds, two criteria were chosen. The distance between the heavy atoms should fall within the sum of their van der Waals radii compiled by Bondi [8] (O...O: 304 pm, C...O: 322 pm,

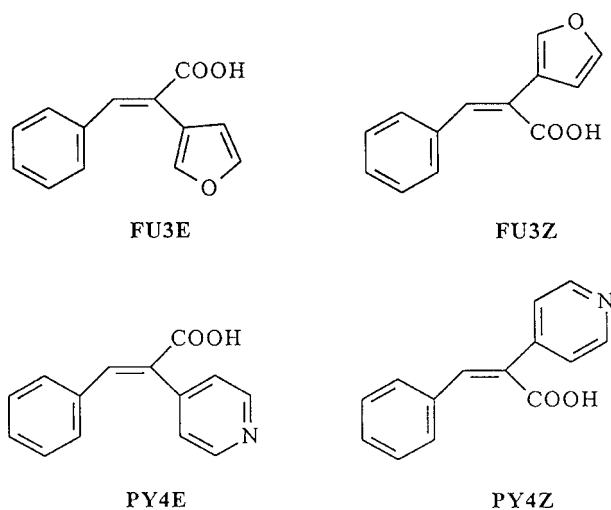


FIGURE 1. Molecules studied.

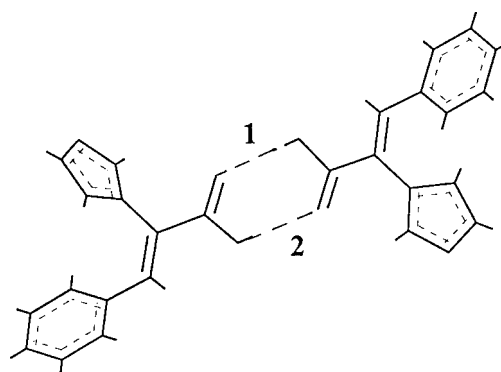


FIGURE 2. Dimer of FU3E.

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° [9]. However, if the distance between the two heavy atoms falls outside Bondi's limit but within 400 pm and the H...O(N) distance are within 300 pm, the H...O(N) contacts will be considered weak hydrogen bonds [10]. The angle criterion must still be strictly met, since the atoms in hydrogen bonding must face each other.

Results and Discussion

E- AND Z-2-(3'-FURYL)-3-PHENYLPROPENOIC ACIDS (FU3E AND FU3Z)

Dimers bonded through the carboxylic groups could be constructed easily. They are kept together by two hydrogen bonds of equal lengths. The dimers are depicted in Figures 2 and 3, while the

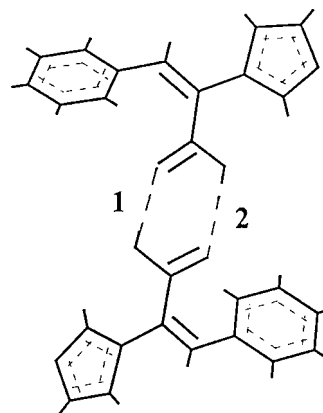


FIGURE 3. Dimer of FU3Z.

TABLE I
Hydrogen bonding parameters in α -furylcinnamic acid aggregates.

	1 ^a	2	3	4	5	6	11	12
Dimer								
O(C)...O (pm)	274 ^b	273						
	275 ^c	275						
H...O (pm)	178 ^b	178						
	178 ^c	178						
α C-H...O (deg)	170 ^b	177						
	169 ^c	177						
Di-dimer								
O(C)...O (pm)	275 ^c	275	274	274	—	—	387	
H...O (pm)	178 ^c	178	177	177	—	—	286	
α C-H...O (deg)	176 ^c	177	176	176	—	—	152	
Tri-dimer								
O(C)...O (pm)	276 ^c	275	275	275	274	274	375	376
H...O (pm)	179 ^c	178	179	178	177	178	290	272
α C-H...O (deg)	178 ^c	177	171	177	178	179	135	158

^a For the meaning of the numbers, please see Figures 2, 3, 6, and 7.

^b FU3E.

^c FU3Z.

geometric data of the hydrogen bonds are listed in Table I.

Problems arose, however, when two dimers of the E isomer were optimized together. The dimers remained closely attached (as if they were "alone"), but the two dimers found minimum arrangement far away from each other, irrespective of the starting geometries, i.e., whether (furyl)O - *meta* or *para* H-(aromatic)C contacts were enforced initially (these positions are understood relative to the attachment

of the cinnamic phenyl group to the olefinic carbon atom). [The (furyl)O - *ortho* H-(aromatic)C was not even considered since significant steric congestion were foreseen, which would work against aggregation.] The distance between the heavy atoms was very significantly outside 400 pm and the angle criterion was not met either. Even weak hydrogen bonds cannot be assumed. However, the minimum arrangements show certain patterns. In the case of (furyl)O - *meta* H-(aromatic)C initial geometry, the phenyl and the furyl rings are parallel, although

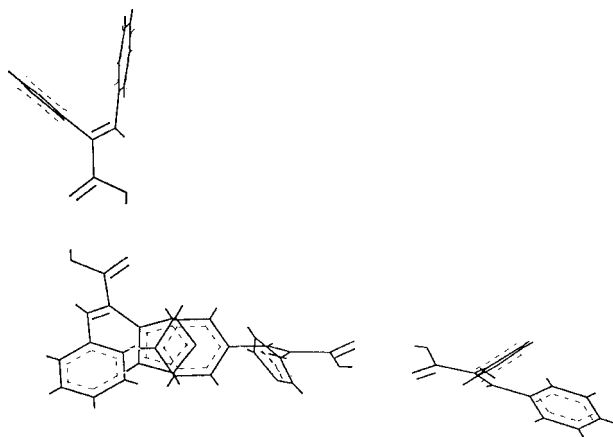


FIGURE 4. Optimum configuration of two dimers of FU3E when in the initial geometry (furyl)O - *meta* H-(aromatic)C close contact was enforced.

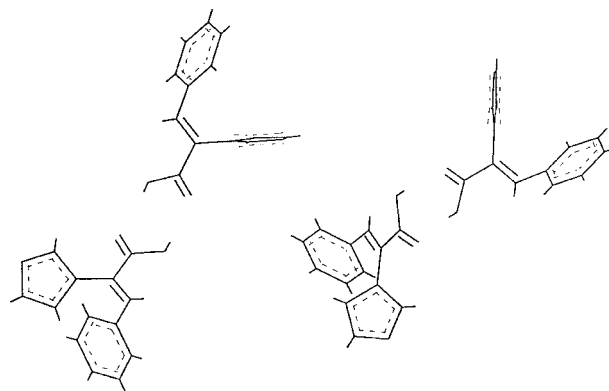


FIGURE 5. Optimum configuration of two dimers of FU3E when in the initial geometry (furyl)O - *para* H-(aromatic)C close contact was enforced.

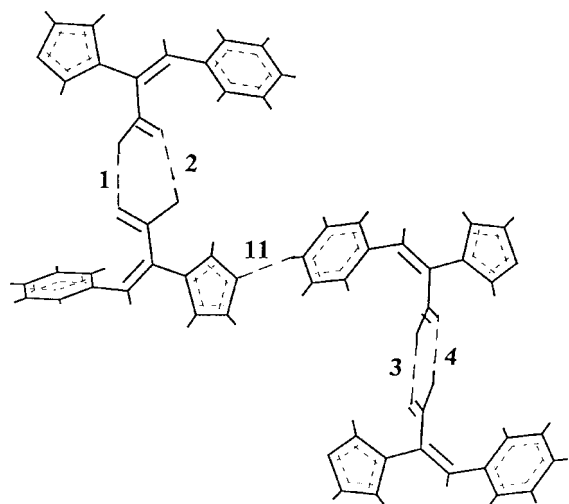


FIGURE 6. Zig-zag structure of two dimers of FU3Z.

somewhat displaced relative to each other (Fig. 4) in the minimum configuration. The distance between the planes of the aromatic rings are smaller than 410 pm. When the initial geometry was (furyl)O - *para* H-(aromatic)C, the minimum configuration re-

sulted in a perpendicular arrangement as concerns the planes of the two aromatic rings (Fig. 5).

These packing patterns may be the results of (aromatic) $\pi \dots$ (aromatic) π and (aromatic)C—H... π interactions, respectively.

The other stereoisomer dimers behaved closer to what was expected. Zig-zag-type chains could be created either with the participation of two or three dimers (Figs. 6 and 7). The dimers in the chain are kept together by weak hydrogen bonds (Table I) and we see no reason other than the limitation in computational resources why the chain cannot be built further or even branched.

E- AND Z-2-(4'-PYRIDYL)-3-PHENYLPROPENOIC ACIDS (PY4E AND PY4Z)

Steric effects can be tracked down when the lengths of the hydrogen bonds keeping together the dimers are compared. In the optimum arrangement the dimer built from the E isomer is kept together with significantly shorter, thus, stronger, hydrogen bonds between the carboxylic groups than those of the Z isomer or any of the furfurylcinnamic acids (FU3E, FU3Z) (Table II).

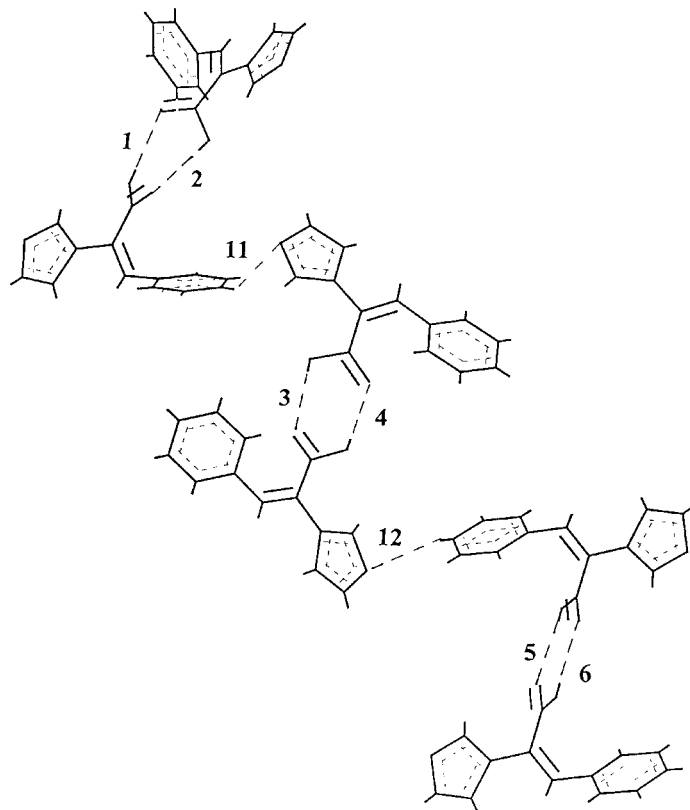


FIGURE 7. Zig-zag structure of three dimers of FU3Z.

TABLE II
Hydrogen bonding parameters in α -pyridylcinnamic acid aggregates.

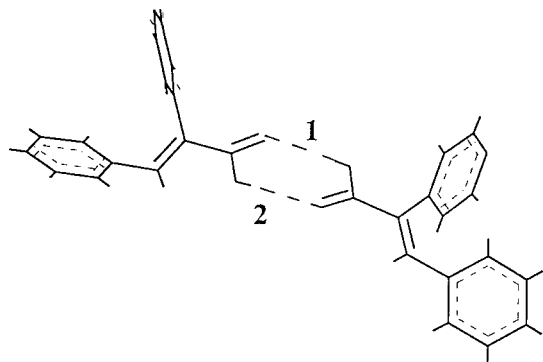
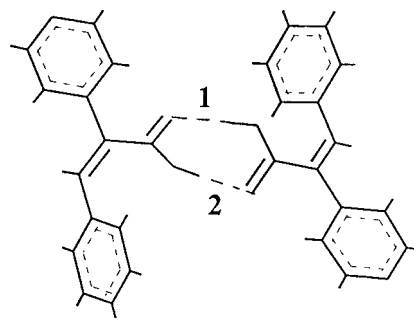
	1 ^a	2	3	4	5	6	11	12	13	14
Dimer										
O(C)...O (pm)	274 ^b	274								
	275 ^c	275								
H...O (pm)	176 ^b	178								
	97 ^c	97								
α C-H...O (deg)	170 ^b	177								
	173 ^c	174								
Di-dimer										
O(C)...O (pm)	275 ^b	272	274	274	—	—	298	—		
	275 ^c	275	275	275	—	—	300	300		
H...O (pm)	97 ^b	97	97	97	—	—	187	—		
	97 ^c	97	97	97	—	—	188	188		
α C-H...O (deg)	173 ^b	170	174	178	—	—	174	—		
	167 ^c	173	173	167	—	—	179	179		
Tri-dimer										
O(C)...O (pm)	272 ^b	274	275	275	274	272	297	298	—	—
	275 ^c	275	275	275	275	275	355	359	354	359
H...O (pm)	178 ^b	178	95	96	178	178	297	298	—	—
	97 ^b	97	97	97	97	97	278	289	292	286
α C-H...O (deg)	166 ^b	172	171	177	172	166	169	172	—	—
	169 ^b	169	169	169	169	169	163	164	164	164

^a For the meaning of the numbers, please see Figures 8–13.^b PY4Z.^c PY4E.

A difference between the stereoisomers may be expected since the E isomer is more linear than the Z; consequently, the dimer is less congested sterically. However, the difference in bond length between PY4E and FU3E is not so obvious since the optimum shape of these molecules are similar. For rationalization additional interactions are sought. It was found that the pyridyl ring of one

acid lies parallel with the phenyl ring of the other acid, though they are somewhat displaced from each other. Nevertheless, C—H... π and π ... π interactions may arise, and they are working together with hydrogen bonds. There are no similar possibilities in the optimum arrangement of FU3E dimers. The dimers are depicted in Figures 8 and 9.

When two dimers are optimized together [in the initial geometry one (pyridyl)N - *para* H-(aromatic)C close contact is enforced], one

**FIGURE 8.** Dimer of PY4E.**FIGURE 9.** Dimer of PY4Z.

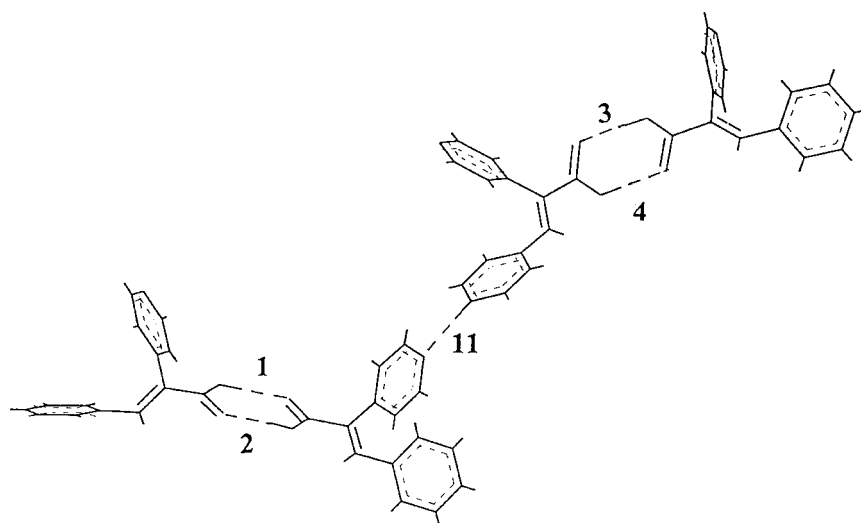


FIGURE 10. Zig-zag structure of two dimers of PY4E.

(pyridyl)N...H-(aromatic)C hydrogen bond, satisfying the criterion based on Bondi's van der Waals radii data too could be observed for both isomers in the optimum configuration. The obtained motif is zig-zag-like. Within the dimers the length of the H...O bonds remained the same as they were in the dimer, when it was optimized alone.

If for the Z isomer, two (pyridyl)N - *para* H-(aromatic)C close contacts are enforced, the optimized configuration showed two (pyridyl)N...H-(aromatic)C hydrogen bonds meeting the requirement based on Bondi's van der Waals radii data. The obtained motif is ribbonlike and it is perfectly symmetrical. It may be important to note that ribbonlike structure could not be built from the related furylcinnamic acid (FU3Z) molecule.

The structures are depicted in Figures 10 and 11 and the geometric parameters are listed in Table II.

When another dimer is added to the zig-zag motif, the hydrogen-bonded network could be contin-

ued (Fig. 12). Distances between the heavy atoms remained within the sum of their van der Waals radii. Interestingly, the H...O hydrogen bond lengths within the two terminating dimers became longer resembling that of the dimer built from the E isomer.

Here again, we see no reason other than the limitation in computational resources why the chain cannot be built further.

On building further the ribbonlike structure by one dimer (Fig. 13) lengthening of the H...N hydrogen bonds were experienced. They did not meet the strict criterion any longer, but they still may be considered as very weak hydrogen bonds. The structure is not symmetrical any longer, and it can be felt that the ribbon cannot be extended any further.

It should be noted that the zig-zag structure out of three dimers could also be built and the hydrogen bonds providing the network satisfy the criterion based on Bondi's van der Waals radii.

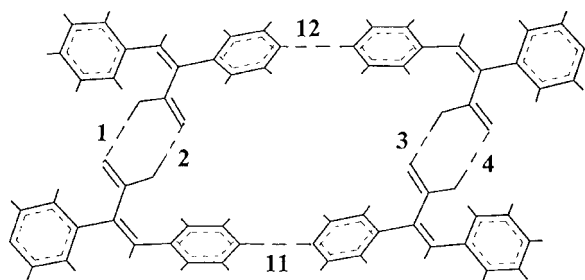


FIGURE 11. Ribbonlike structure of two dimers of PY4Z.

Conclusions

Calculations revealed that (aromatic)C—H...N(O) hydrogen bonds made possible the attachment of dimer units, thus, virtually infinite chains can be built out of the E isomer of the furylcinnamic acid and both isomers of the pyridylcinnamic acid. The energy minimized structure had zig-zag configuration. The Z-2-(4'-pyridyl)-3-phenylpropenoic acid dimers also allowed the

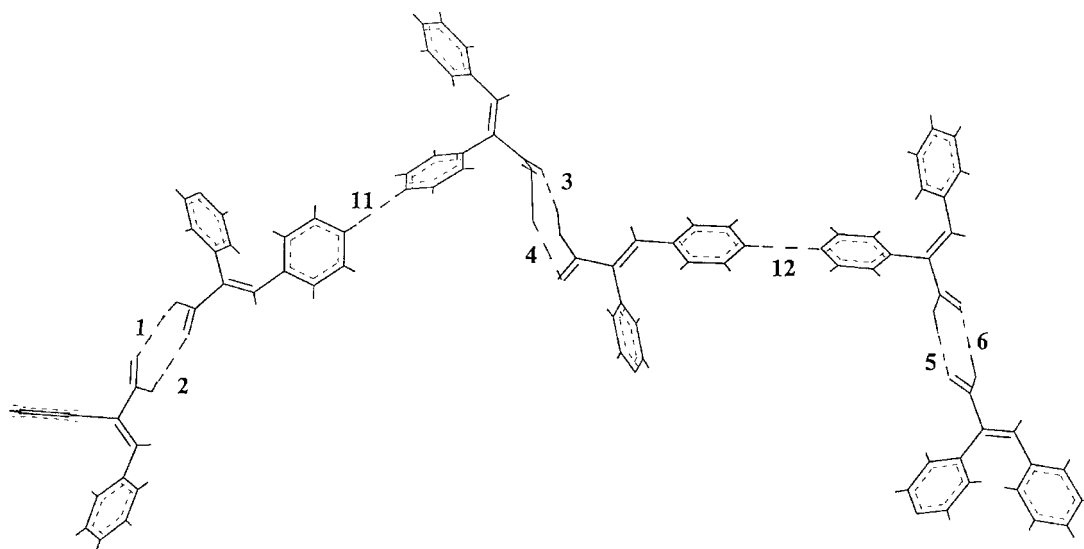


FIGURE 12. Zig-zag structure of three dimers of PY4E.

formation of ribbonlike network, however, the number of structural units could not be increased infinitely. The related furylcinnamic acid could not be stabilized in the ribbon form. The other isomer (FU3E) could not be stabilized either in the ribbon or the chain form, however, (aromatic)CH... π or (aromatic) π ...(aromatic) π interactions are thought to contribute to the packing pattern of the two dimers.

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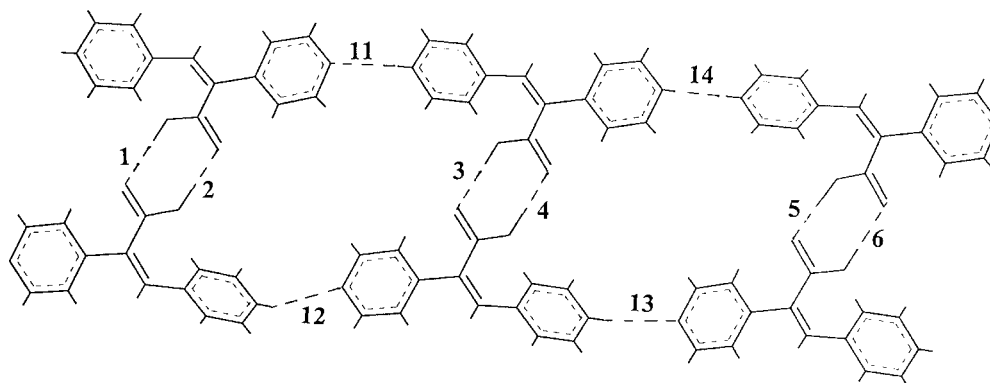


FIGURE 13. Ribbonlike structure of three dimers of PY4Z.