The Preferred U-Conformation of *m*-Quinquephenyl. An X-Ray Crystal Structure Determination and Molecular Mechanics Study

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Surprisingly, the preferred geometry for *m*-quinquephenyl **1** has been shown to be U-shaped by both X-ray analysis and molecular mechanics calculations.

While the crystal and molecular structures of *p*-oligophenyls have been well investigated,[1] relatively few studies have appeared concerning the conformational preferences of *m*-oligophenyls.† The latter may potentially form helices since the heterocyclic analogues, quinque- and sexi-pyridine, have been found to form helical and double-helical complexes with transition metals.[3] However, in the absence of metals, the parent heterocyclic ligands adopt all-s-*trans* (zigzag) conformations as demonstrated in solution in the case of 2,2′-bipyridine[4a-c] and in the solid state for bipyridine,[4d] terpyridine[4e] and quaterpyridine.[4f]

It might be expected that the all-carbon analogue would also adopt a zigzag-type structure to minimize non-bonded interactions. Surprisingly, the room temperature X-ray analysis of *m*-quinquephenyl **1** shows a U-shaped conformation for both of the two independent molecules of the asymmetric unit, and

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† The structure of 1,3,5-triphenylbenzene (ref. 2) is still used as a model for *m*-polyphenyls.

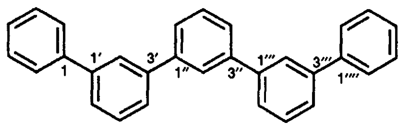

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Table 1 MM2/87 results for the conformers of *m*-quinquephenyl[a]

	t1	*t2*	*t3*	*t4*	Strain/ kcal mol^{-1}
U1	40.8	40.0	40.0	40.8	−22.86
U2	40.8	39.6	41.1	−40.8	−22.97
U3	40.4	39.9	−40.4	40.6	−23.15
U4	40.2	39.6	−39.6	−40.2	−23.03
U5	40.6	−41.9	41.9	−40.6	−23.30
U6	41.0	−40.0	−40.0	41.0	−23.09
Z1	40.9	140.5	140.5	40.9	−22.92
Z2	40.8	139.1	142.7	−41.1	−22.83
Z3	−41.0	140.8	140.8	−41.0	−22.76
Z4	40.8	139.2	−139.4	40.8	−22.97
Z5	40.9	139.3	−139.3	−40.9	−23.05
Z6	−40.8	138.5	−138.5	40.8	−22.91
M1	40.7	40.0	140.5	40.8	−22.99
M2	40.5	39.8	141.4	−40.8	−22.93
M3	−40.7	40.2	141.1	−41.2	−23.01
M4	−40.8	40.0	140.5	40.8	−23.09
M5	40.4	39.2	−139.4	40.2	−22.85
M6	40.7	40.1	−139.0	−41.1	−22.92
M7	−40.8	39.8	−139.2	−41.9	−23.01
M8	−40.8	39.6	−139.4	40.7	−22.93

[a] *t1*–*t4* in degrees; 1 cal = 4.184 J.

a high degree of twisting along the pivotal bonds with an average torsion angle of 34° (Fig. 1).‡ The nonplanarity of **1** is not unexpected since the *p*-oligophenyls, although planar in the crystal at room temperature, prefer nonplanar conformations either at low temperatures (phase transitions) or at room temperature when unsymmetrically substituted.[1] 1,3,5-Triphenylbenzene is also nonplanar in the solid state.[2] On the other hand, the U-shaped conformation of **1** is rather unexpected.

To investigate further the conformational preferences of **1**, we carried out molecular mechanics calculations for the isolated molecule using the MM2(87) program package.[6] This method seems to be the method of choice since it reproduces correctly the minimum energy geometries and barriers for rotation or inversion for biphenyl and its bridged derivatives.[7] The conformation of **1** is well described by four torsional angles, *t1*–*t4*. A plot of MM2 potential energy *vs.* rotation

t1: C(2)–C(1)–C(1′)–C(2′)
t2: C(2′)–C(3′)–C(1″)–C(2″)
t3: C(2″)–C3(″)–C(1‴)–C(2‴)
t4: C(2‴)–C(3‴)–C(1⁗)–C(2⁗)

about the pivotal bond in biphenyl exhibits two energy maxima at 0 and 90°, and two undistinguished minima at 37 and 143°.[7] Thus in **1**, *t1* and *t4* are expected to have values of *ca.* ±40°, whereas *t2* and *t3* may be ±40 or ±140°, giving the total number of nonplanar conformers as 64. However, some of these conformers are identical or enantiomeric, and this reduces the number of energetically distinct conformers to 20. Six of these represent U-shaped conformers (**U1**–**U6**; *t2* and *t3* = *ca.* ±40°), six are zigzag conformations (**Z1**–**Z6**; *t2* and *t3* = *ca.* ±140°), and the remaining eight conformers (**M1**–**M8**) are 'mixed' geometries. All the distinct conformers were fully optimized by MM2(87) and the results are presented in Table 1.§

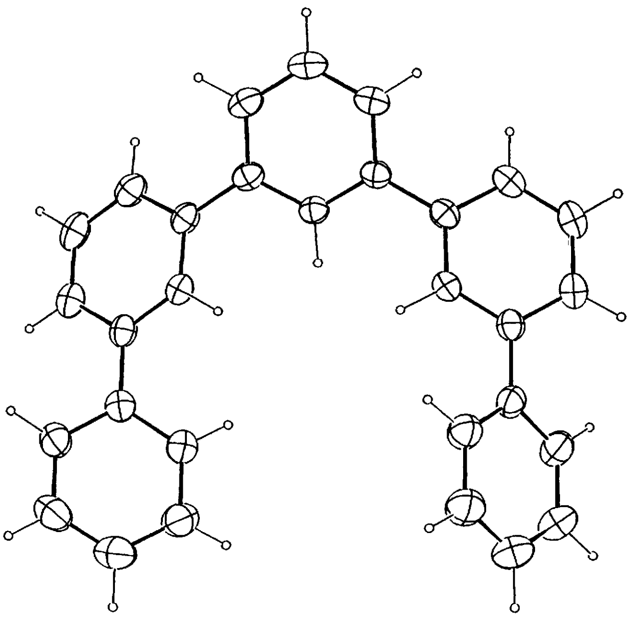

Fig. 1 X-Ray crystal structure of *m*-quinquephenyl **1** with 30% probability ellipsoids

Molecular mechanics calculations predict the differences in strain energies among these geometries to be relatively small. The most stable conformer, **U5**, is only 0.54 kcal mol^{-1} lower in energy than the least stable, **Z3**. Nonetheless, a preference for the U-shaped conformations over the zigzag ones is apparent. **U5** and **U3** are the most stable conformers, whereas **Z2** and **Z3** are predicted to be the least stable. Moreover, the averaged strain energy of all U-shaped conformations is lower than the analogous values for 'mixed' and zigzag geometries by 0.10 and 0.16 kcal mol^{-1}, respectively.

The conformer found in the crystal with *t1* = 35.6, *t2* = 30.5, *t3* = −33.0 and *t4* = 36.3° corresponds to **U3** in Table 1.¶ MM2 predicts **U3** to be the second most stable in the gas phase with **U5** as the most stable. Thus the predominance of **U3** in the crystal may be dictated by crystal packing forces given the small differences in the relative energies of the various conformers. Comparison of the calculated torsional angles for **U3** with those seen in the crystal show the latter to be lower. This is not surprising, however, since crystal packing forces may be expected to flatten the molecule as observed in the case of biphenyl.[9]

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‡ The crystal structure was determined using a colourless crystal of dimensions 0.12 × 0.13 × 0.70 mm, with intensity data collected on an Enraf-Nonius CAD4 diffractometer equipped with Cu-Kα radiation (λ = 1.54184 Å) and a graphite monochromator. *Crystal data*: $C_{30}H_{22}$, triclinic, space group $P\bar{1}$, a = 7.2620(6), b = 13.618(2), c = 21.623(5) Å, α = 80.58(2), β = 85.26(1), γ = 89.71(1)°, V = 2102.4(8) Å^3, Z = 4, D_c = 1.209 g cm^{-3}, T = 24 °C, R = 0.052, R_w = 0.052 for 6700 observed data having $2 < \theta < 75°$ and $I > 1\sigma(I)$. H atoms were located and refined. Refinement was carried out by full-matrix least squares with weights $w = \sigma^2(F_o)$ using the Enraf-Nonius MolEN programs.[5] Atomic coordinates, bond distances and angles and thermal parameters for independent molecules of the asymmetric unit have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ Reoptimization of selected conformers with semiempirical MO calculations (AM1 method[8]) produced geometries with differences in torsion angles smaller than 1° when compared to the MM2(87) geometries.

¶ Averaged values; there are two symmetry independent molecules in the unit cell. The values for *t1*–*t4* are 35.5, 30.7, −31.9 and 36.4° for molecule A and 35.7, 30.3, −34.0 and 36.2° for molecule B, respectively. Two other molecules (Z = 4) are related by inversion, and so they are enantiomers.

The conformation found in the crystal does not represent the ideal helical structure, nor is the helical geometry predicted by theory to be preferred in the gas phase. Actually, helical **U1** is calculated to be of highest energy of all U-shaped conformations (Table 1). However, since the U-shaped arrangement is preferred in **1**, it would be of interest to examine the conformational preferences for higher analogues of *m*-oligophenyls (*e.g. m*-septiphenyl) where possible π-stacking may lead to the helical arrangement. Although some stacking interactions are present in the crystal of **1**, they do not dominate the packing. The shortest intermolecular ring-centre to ring-centre distances are in the range of 4.1–4.4 Å, but only a few of these exist. The shortest C···C intermolecular distances are about 3.5 Å, but most are in the 4–5 Å range.

In conclusion, a U-shaped conformational preference of *m*-quinquephenyl was found both in the solid state and by molecular mechanics calculations. This preference suggests the possibility of spontaneous helix formation by higher analogues of *m*-oligophenyls.

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