

An AM1 semiempirical study of longitudinal twisting in PAH and CPAH

L. Kraig Steffen*, Ching Kong, Mike Papagikos

Department of Chemistry, Fairfield University, Fairfield, CT 06430, USA

Received 1 November 1996; accepted 18 March 1997

Abstract

The twisting along the major axis of a series of linear polycyclic aromatic hydrocarbons has been studied by using AM1 semiempirical calculations. Polycyclic aromatic hydrocarbons (PAH) containing only six-membered rings are shown to be easier to twist along their long axis compared with similar PAH containing embedded cyclopentene rings (CPAH). The difference in the energies is evident even at very low twist angles and becomes more pronounced as the twist angle approaches 90°. The calculations were done by defining sets of parallel dihedrals along the long axis of the PAH and CPAH and driving the dihedrals symmetrically while allowing for a full geometry optimization of the rest of the molecule. © 1997 Elsevier Science B.V.

Keywords: PAH; CPAH; Torsion; Energy; AM1

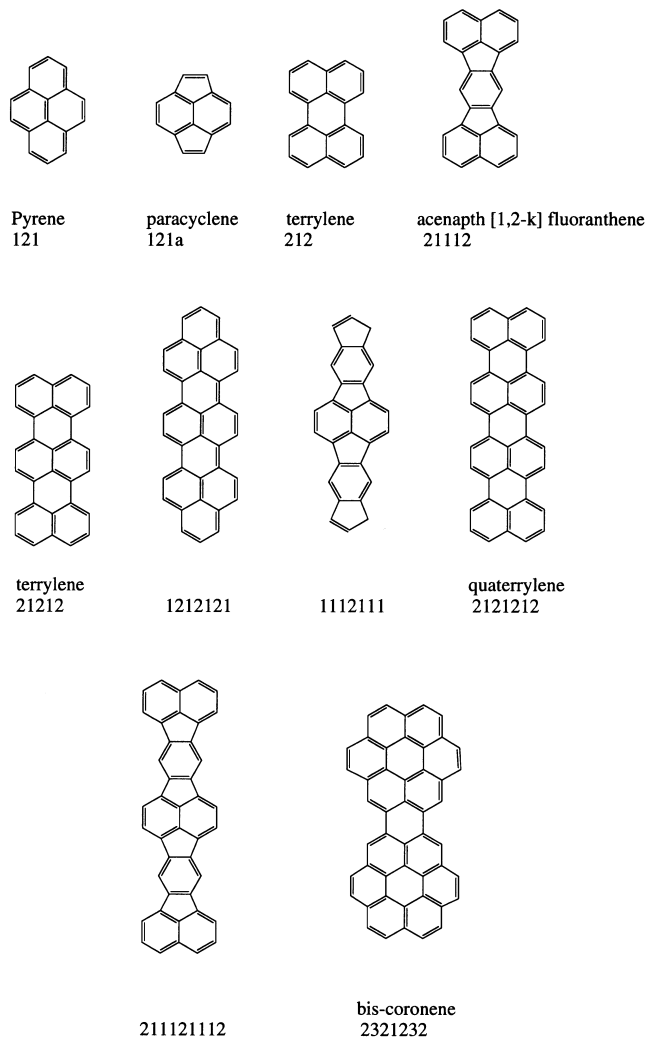
1. Introduction

Interest in the physical and chemical properties of polycyclic aromatic hydrocarbons (PAH) has increased owing to, among other things, questions regarding their carcinogenicity [1]. PAH and CPAH are common pollutants [2] and are formed in almost all incomplete hydrocarbon combustion reactions including the burning of coal, fuel oil, diesel fuel, wood fires and tobacco smoke [3]. PAH containing embedded cyclopentene rings (CPAH) are intriguing because the introduction of the cyclopentene rings increases angle strain [4]. Also, if the cyclopentene ring is surrounded by other rings, it will cause the CPAH to distort from planar geometry as exemplified by the bowl-shaped molecule corannulene. The

discovery and intense investigation [5] of the fullerenes, which are CPAH, has increased interest in the smaller CPAH. These CPAH may also serve as rational synthetic intermediates along the path to fullerenes as illustrated by the work of Scott et al. and Biederman et al. [6]. Some examples of well-known small CPAH include fluoranthene, corannulene and acenaphthylene. In previous work involving the principal author, the physical properties of CPAH were investigated by means of computational and spectroscopic techniques [7]. Conformational distortions of PAH and CPAH are of interest because the increased energy of strained systems may make them more potent carcinogens [8] and they are useful as models for the limits of aromaticity as investigated extensively by Herndon and others [9]. In this paper we investigate the twisting motions of a series of PAH and closely related CPAH, and compare their

* Corresponding author.

Table 1
PAH and CPAH



energies. Our hypothesis is that the increased angle strain in CPAH arising from the inclusion of five-membered rings will result in a concomitant increase in the energy needed for torsional distortion of the CPAH. The exact geometric distortions that occur as the PAH and CPAH are twisted are hard to quantify, but the overall energy and minimized structures should reflect clearly the underlying trade-offs between angle, bond length and torsional distortions. If correct, consistently higher torsional energies

for closely related CPAH versus PAH will be observed.

Table 1 assigns a number, gives a structural diagram, and a name (if known) for each of the compounds studied. The numbers represent a simple graphical method for describing the number of rings in each layer and are arbitrary. The series of compounds was chosen as a progression from small, difficult-to-twist compounds, up to large, relatively easy-to-twist compounds with successive sets being

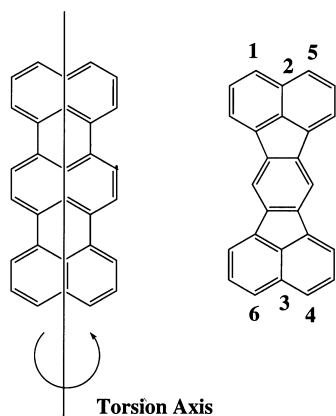


Fig. 1. Illustration of the longitudinal axis and dihedrals defined. Two dihedrals (1–2–3–4 and 5–2–3–6) were defined for each molecule and their angles set so that the overall twist or torsion was the total value for the torsion desired.

similar PAH and CPAH. An example is shown in Fig. 1. On the left is a CPAH and on the right a closely related PAH. Dihedral angles were defined along the major axis of each molecule as shown. The two dihedrals used for the PAH are highlighted. It was necessary to define two dihedrals because, as an artefact of how the dihedrals were defined, the molecules would sometimes roll up into a ‘‘U’’ shape. Paracyclene (**121a**) is unusual for two reasons. First, it was necessary to twist along a diagonal axis and second, it is a paratropic molecule.

2. Experimental

The compounds investigated were chosen primarily on the basis of molecular similarity. Some have not been made, and some (such as compound **1112111** and paracyclene) are known or are likely to be quite unstable. The heats of formation values plotted in the graphs were determined by using the AM1 [10] semi-empirical force field as implemented by the CAChe [11] molecular modeling system on a Centris 650. Except for constraining the dihedrals, as explained in Section 1, the molecules were geometry optimized. In a few cases, AM1 calculations were performed with MacSpartan (PowerPC 8500) or Spartan (IBM RS6000) [12] and the results were within 0.05%, as would be expected since the underlying AM1 code is essentially identical.

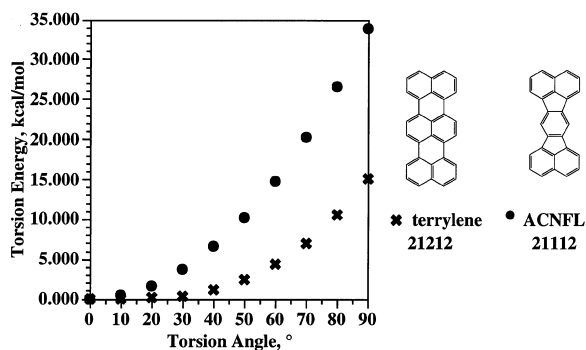


Fig. 2. Change in the torsion energy in kcal mol⁻¹ for representative PAH and CPAH. The energies plotted are the difference between the conformer at a given twist angle and the lowest energy conformer. ACNFL stands for acenaph[1,2-k]fluoranthene.

3. Results and discussion

Refer to Table 1 for compound structures and reference numbers. Table 2 is a compilation of the heat of formation data calculated for each molecule as it was twisted. The *.pdb text files for all of the calculations performed may be obtained from the principal author. The angle referred to is the overall twist along the length of a molecule. Zero is flat and 90° represents a total twist of 90° for the whole molecule. The lowest-energy conformers for the CPAH were always flat. The flat conformers for the PAH contained slight *ortho* hydrogen interactions that distorted them minimally from planarity so that they were frequently slightly higher in energy than the close-by minimally twisted conformers.

Fig. 2 shows a plot of dihedral angle versus the relative heat of formation for the CPAH **21112** (acenaph[1,2-k]fluoranthene) and **21212** (terrylene). Note that the energy differences have been normalized for each compound (i.e., the difference between the energy of each successive higher-energy conformer and the lowest-energy conformer has been plotted instead of the actual heat of formation). As expected, the energy rises smoothly as the compounds are distorted from planarity. It is clear that the energy needed to twist the CPAH increases more rapidly with respect to the twisting energy than for the closely related PAH. Figs. 3 and 4 give the twist angle versus *H_f* energy for the PAH and CPAH, respectively. The same trend is observed for the entire set of

Table 2
Longitudinal twisting energies (heats of formation, H_f in kcal mol⁻¹)

Twist angle (°)	Compound/ID number				
	Pyrene 121	Paracyclene 121a	Perylene 212	Terrylene 21212	ACNFL 21112
90	152.133		126.391	152.994	187.550
85	141.628				
80	131.986		116.637	148.537	180.310
75	123.165				
70	115.132	188.887	108.565	144.981	174.003
65	107.853				
60	101.292	174.568	102.120	142.267	168.58
55	95.416				
50	90.189	162.518	97.162	140.320	164.030
45	85.583				
40	81.560	152.72	93.572	139.048	160.337
35	78.095				
30	75.155	145.158	91.213	138.338	157.480
25	72.716				
20	70.754	139.638	89.901	138.047	155.454
15	69.250				
10	68.189	136.638	89.390	137.998	154.232
5	67.555				
0	67.346	135.586	89.316	138.010	153.826
	1212121	1112111	21121112	quaterrylene 2121212	bis-coronene 2321232
90	185.066	298.636	298.188	193.488	220.985
85	182.470	296.445	296.054		
80	180.089	293.660	294.045	191.185	215.840
75	177.918	291.411	292.163		
70	175.950	289.329	290.406	189.429	211.625
65	174.182	287.367	288.772		
60	172.604	285.574	287.233	188.164	208.266
55	171.213	283.930	285.872		
50	169.999	282.427	284.608	187.325	205.690
45	168.956	281.073	283.464		
40	168.071	279.870	282.444	186.838	203.830
35	167.339	278.803	281.550		
30	166.746	277.884	280.763	186.614	202.611
25	166.283	277.105	281.431		
20	165.938	276.469	279.565	186.558	201.962
15	165.693	275.976	280.066		
10	165.531	275.623	278.848	186.566	201.769
5	165.443	275.410	278.669		
0	165.416	275.343	278.607	186.575	201.802

compounds: the CPAH are consistently more difficult to distort along the longitudinal axis than similar PAH. A close-up view of the twisting data for the first eight compounds between zero and 40° is shown in Fig. 5. Compound **21121112** appears to have somewhat anomalous energies for twisting but, in reality, it is just that a considerably shorter PAH,

212 (perylene), has comparable but slightly flatter twist energies. When compared with quaterrylene, this CPAH is not unusual.

Visualization of the twisting observed for compound **21121112**, the largest CPAH compound studied, clearly shows that the twisting distortion is spread fairly evenly across the entire compound.

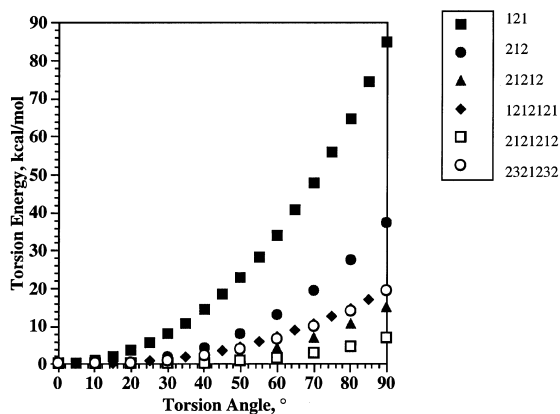


Fig. 3. Relative torsion energies for the PAH. The energies plotted are the difference between the conformer at a given twist angle and the lowest-energy conformer. See Table 1 for the structures.

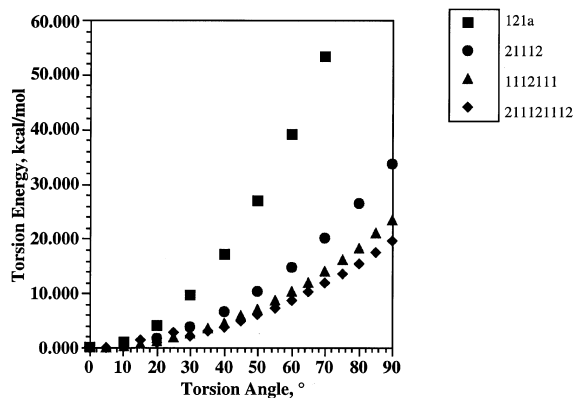


Fig. 4. Relative torsion energies for the CPAH. The energies plotted are the difference between the conformer at a given twist angle and the lowest-energy conformer. See Table 1 for the structures.

However, close inspection of many of the compounds studied indicates a slight preference for less twisting in “naphthylene” units and more twisting in the connecting five- or six-membered rings. Fig. 6 shows an

edge-on view of **211121112** that illustrates the point. Adjacent “naphthalene” hydrogens are twisted less than those that are close, but separated by a bridging ring. At low twist angles, this may be due simply to

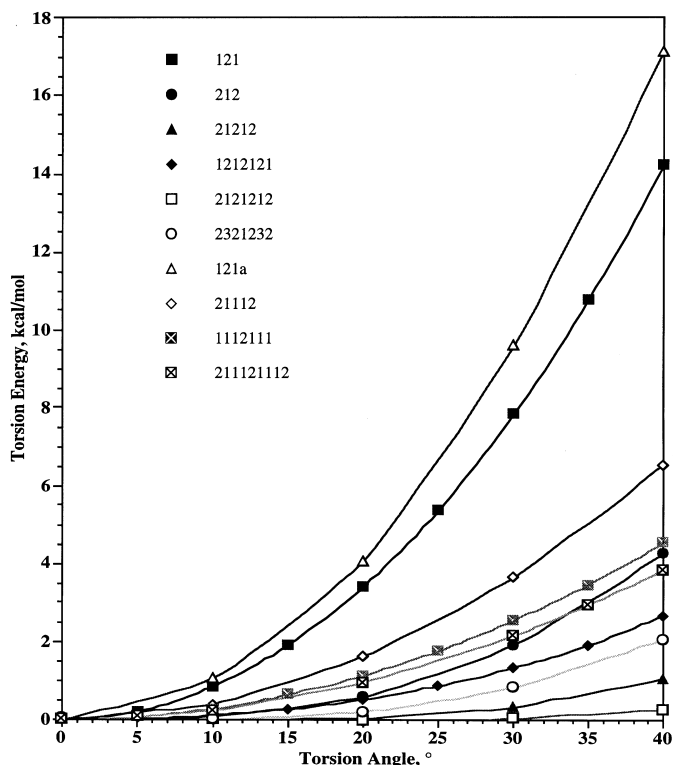


Fig. 5. Relative torsion energies for the CPAH and PAH at low twist angles. The energies plotted are the difference between the conformer at a given twist angle and the lowest-energy conformer. See Table 1 for the structures.

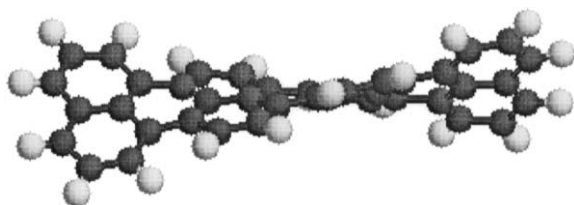


Fig. 6. Edge-on view of quatterrylene, showing the apparent greater twist in the connecting six-membered rings as against that in the “naphthalene” units.

“ortho” interactions. One way to investigate this further was to tie the naphthalene units together. This was done for the quatterrylene structure, giving bis-corannulene. It is indeed more difficult to twist the bis-corannulene when compared with the closely related quatterrylene. A 40° twist of bis-corannulene raises its energy $2.06 \text{ kcal mol}^{-1}$ above the lowest-energy conformer whereas at 40° the quatterrylene conformer is only $0.27 \text{ kcal mol}^{-1}$ higher. An AM1 frequency calculation was done on a subset of the compounds studied and the lowest or second lowest energy vibration observed corresponds closely to the longitudinal twisting modeled in this paper.

4. Conclusions

AM1 calculations can clearly distinguish between the energies for twisting of the various PAH and CPAH. Similar CPAH always required more energy for twisting than the PAH. For the larger PAH and CPAH significant twisting distortions can occur with very low energies. For example, compound **21112** can distort 50° along its major axis with a concomitant rise in energy of only $10.2 \text{ kcal mol}^{-1}$. Likewise, the closely related PAH, **21212**, takes a mere $2.31 \text{ kcal mol}^{-1}$ for the same 50° twist and can twist 80° for 10 kcal mol^{-1} . Quatterrylene needs only 7 kcal mol^{-1} to twist 90° !

One problem that is not resolved from this work is that the PAH and CPAH are similar, not identical. The differences observed may be due not to the presence of the cyclopentene rings but instead to the fact that the CPAH are, on average, slightly shorter than the corresponding PAH and contain fewer atoms and bonds to distribute the torsional energy amongst. For example, the distance from C1 to C6 (as defined in

Fig. 1) in **21112** is 11.115 \AA and the distance from C1 to C6 in **21212** is 11.668 \AA . However, this is unlikely since the clearly shorter perylene is easier to twist than the considerable longer acenaphth[1,2-k]fluoranthene. Further work is in progress to correlate the results obtained with fluorescence data for PAH and to evaluate fully the orbital perturbations which occur upon torsional distortion.

Acknowledgements

L.K.S. would like to thank the Dreyfus Foundation for funds used to purchase the CAChe system and Ben Plummer for stimulating his interest in hydrocarbons.

References

- [1] R.G. Harvey, *Polycyclic Aromatic Hydrocarbons: Chemistry and Carcinogenesis*, Cambridge University Press, Cambridge, 1991; J. Jacob, *Pure Appl. Chem.*, 68 (1996) 301–308; P.M.V.B. Barone, A. Camilo Jr., D.S. Galvao, *Phys. Rev. Lett.*, 77(6) (1996) 1186–1189; G. Grimmer, *J. Nat. Cancer Inst.*, 78 (1987) 935–942.
- [2] J. Hilborn, M. Still, *A State of the Environment Report: Canadian Perspectives on Air Pollution*. SOE Report No. 90-1, Environment Canada, Ottawa, 1990.
- [3] For example: I. Alfheim, T. Ramdahl, *Environmental Mutagenesis*, 6 (1984) 121–130; *Environmental Tobacco Smoke in the Workplace — Lung Cancer and Other Health Effects*, NIOSH report #91-108, June 1991.
- [4] Y.-D. Gao, W.C. Herndon, *Mol. Phys.*, 77 (1992) 585–599; F. Diederich, R. Ettl, Y. Rubin, R.L. Whetten, R.B. Marcos, S. Anz, D. Sensharma, F. Wudl, K.C. Khemani, A. Koch, *Science*, 252 (1991) 548–551; B.F. Plummer, L.K. Steffen, W.B. Herndon, *Struc. Chem.*, 4 (1993) 279–285.
- [5] R.F. Curl, R.E. Smalley, *Science*, 242, (1988) 1017–1022; M.S. Dresselhaus, G. Dresselhaus, P. Eklund, *Science of Fullerenes and Carbon Nanotubes*, Academic Press, 1996.
- [6] C. Crowley, H.W. Kroto, R. Taylor, D.R.M. Walton, M.S. Bratcher, P.-C. Cheng, L.T. Scott, *Tetrahedron Lett.* 36 (1995) 9215–9218; L.T. Scott, M.S. Bratcher, S. Hagen, *J. Am. Chem. Soc.*, in press; P. Biedermann, P. Ulrich, L.T. Yau, W.T.C. David, C.H. Kuo, J.J. Stezowski, I. Agranat, *Polycyclic Aromat. Compd.* 8(2–3) (1996) 167–175.
- [7] B.F. Plummer, L.K. Steffen, T.L. Braley, W.G. Reese, K. Zych, G. VanDyke, B. Tulley, *J. Am. Chem. Soc.* 115 (1993) 11542–11551.
- [8] C.J. Carrell, H.L. Carrell, J.P. Glusker, E. Abu-Shaqara, C. Cortez, R.G. Harvey, *Carcinogenesis*, 15(12) (1994) 2931–2936; C.E. Afshar, C.J. Carrell, H.L. Carrell, R.G. Harvey, A.S. Kiselyov, S. Amin, J.P. Glusker, *Carcinogenesis* 17(11) (1996) 2507–2511.

- [9] R. Goddard, M.W. Haenel, W.C. Herndon, C. Kruger, M. Zander, *J. Am. Chem. Soc.* 117 (1995) 30–41 and Refs. 1 and 2 therein. See also: W.C. Herndon, P.C. Nowak, *Adv. Theor. Interesting Mol.* 2 (1992) 113–141.
- [10] J.J.P. Stewart, M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, *J. Am. Chem. Soc.* 107 (1985) 3902–3909.
- [11] CAChe Scientific, Version 3.6, Beaverton, OR.
- [12] MacSpartan 1.01, Spartan 4.1.2, Wavefunction Inc., Irvine, CA.