

Conformations of [10]Annulene: More Bad News for Density Functional Theory and Second-Order Perturbation Theory

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Abstract: The molecular structures and relative energies of several of the lowest-energy conformations of [10]annulene (C₁₀H₁₀) have been investigated using the Hartree–Fock (HF) method, density functional theory (DFT), second-order Møller–Plesset perturbation theory (MP2), and (for the first time) coupled cluster singles and doubles with a perturbative inclusion of connected triple excitations [CCSD(T)]. For some years the HF method has been known to incorrectly favor bond-length-alternating structures for [10]annulene, and standard forms of DFT are now seen to incorrectly favor aromatic structures. For the naphthalene-like conformation, the B3LYP method is shown to require a large basis set before the geometry becomes properly bond-localized, i.e., similar to the predictions of CCSD(T) using even a modest basis set. With a basis set of 170 functions, B3LYP and BP86 predict that the aromatic heart-shaped conformation is 9.11 and 12.11 kcal mol⁻¹, respectively, lower than the bond-alternating twist form, while with the same basis set CCSD(T) places the heart-shaped conformation 6.29 kcal mol⁻¹ above the twist. Further large-scale CCSD(T) computations involving 340 basis functions predict that the twist conformation is lowest in energy, and the naphthalene-like and heart-shaped conformations lie higher than the twist by 1.40 and 4.24 kcal mol⁻¹, respectively. Implications of the computed structures and energetics for the interpretation of previous experiments are discussed.

I. Introduction

Despite Hückel's $(4n + 2)\pi$ -electron rule,¹ the [10]annulene molecule does not possess a stability comparable to that of benzene. Due to large angle strain in the all-*cis* D_{10h} conformation, the molecule is unable to adopt the geometry most conducive to aromatic stabilization. Aromatic and olefinic natures compete, and the resulting structures are quite unstable. Although [10]annulene had previously been cited as a reaction intermediate,² it was not until 1967, after the synthesis of both [18]annulene³ and [14]annulene,⁴ that van Tamelen and Burkoth⁵ reported the trapping of [10]annulene in a reaction mixture. Thereafter, Masamune and Seidner⁶ were able to observe NMR signals from two different conformations of [10]annulene. Crystalline samples of the two conformers were subsequently isolated by Masamune et al.⁷ via low-temperature photolysis of *cis*-9,10-dihydronaphthalene and chromatography on alumina.

Several geometrical structures have been suggested for [10]-annulene, including ones with D_{10h} and D_{5h} symmetry, as well

as a C₂ “twist”, a C₂ “naphthalene-like”, a C_s “heart”, a C₁ (or C₂) “azulene-like”, and a C_s “boat” form. The latter five structures are illustrated in Figures 1–5, respectively. For their observed conformer **1**, Masamune et al.⁷ reported a single peak for both ¹H and ¹³C NMR down to -160 °C. The authors assigned the boat geometry (Figure 5) to **1** in light of its apparent low-energy barrier for averaging of the magnetic environments of the nuclei, its thermal conversion to *cis*-9,10-dihydronaphthalene, its olefinic-type proton shift, and its UV spectrum. For their observed conformer **2**, Masamune et al.⁷ reported the separation of the one ¹³C NMR peak present at higher temperatures into five distinct peaks at -100 °C. The authors ruled out the possibility of the naphthalene-like structure (Figure 2), claiming it would lack a low-energy mechanism to interconvert the nuclei, and they assigned the twist structure (Figure 1) to **2**. Since their pioneering work, no other isolations of [10]-annulene have been reported in the literature.

Conversely, over the last few decades many scientists have employed computational quantum chemical methods in an attempt to confirm and/or elucidate the experimental findings. Many of these studies were dedicated to the investigation of the degree of aromaticity and bond-delocalization in D_{10h} or D_{5h} [10]annulene^{8–10} and to the improvement of general theories of aromaticity.^{11–13} Later studies attempted to determine the geometries and relative energies of different [10]annulene

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(1) Hückel, E. *Z. Phys.* **1931**, *70*, 204.

(2) Burkoth, T. L.; van Tamelen, E. E. In *Nonbenzenoid Aromatics*; Snyder, J. P., Ed.; Academic Press: New York, 1969; Vol. 1, Chapter 3, p 63.

(3) Sondheimer, F.; Wolovsky, R. *Tetrahedron Lett.* **1959**, *3*, 3.

(4) Sondheimer, F.; Calder, I. C.; Elix, J. A.; Gaoni, U.; Garrett, P. J.; Grohmann, K.; diMaio, G.; Mayer, J.; Sargent, M. V.; Wolovsky, R. *Chem. Soc., Spec. Publ.* **1967**, *21*, 75.

(5) van Tamelen, E. E.; Burkoth, T. L. *J. Am. Chem. Soc.* **1967**, *89*, 151.

(6) Masamune, S.; Seidner, R. T. *J. Chem. Soc., Chem. Commun.* **1969**, 542.

(7) Masamune, S.; Hojo, K.; Bigam, G.; Rabenstein, D. L. *J. Am. Chem. Soc.* **1971**, *93*, 4966.

(8) Kleier, D. A.; Dixon, D. A.; Lipscomb, W. N. *Theor. Chim. Acta* **1975**, *40*, 33.

(9) Haddon, R. C.; Raghavachari, K. *J. Am. Chem. Soc.* **1982**, *104*, 3516.

(10) Haddon, R. C.; Raghavachari, K. *J. Am. Chem. Soc.* **1985**, *107*, 289.

(11) Baird, N. C. *J. Am. Chem. Soc.* **1972**, *94*, 4941.

(12) Aihara, J. *J. Am. Chem. Soc.* **1976**, *98*, 2750.

(13) Haddon, R. C. *J. Am. Chem. Soc.* **1979**, *101*, 1722.

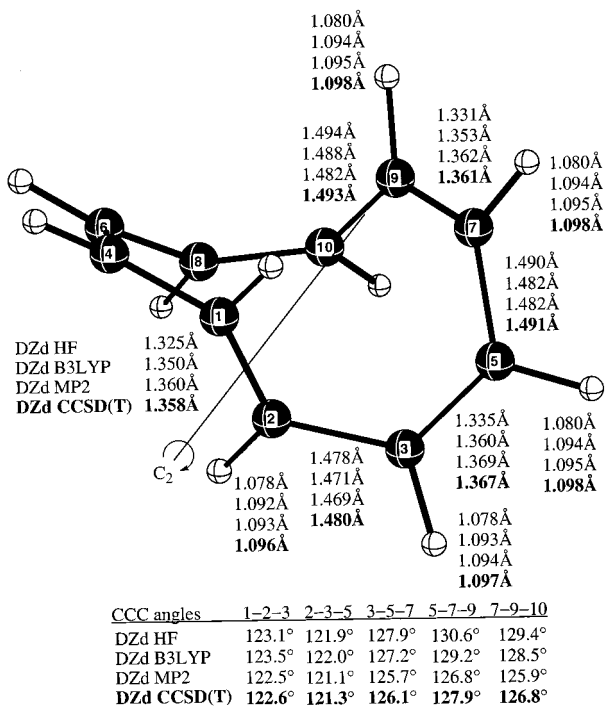


Figure 1. Fully optimized structures of the C_2 symmetry twist conformation of [10]annulene.

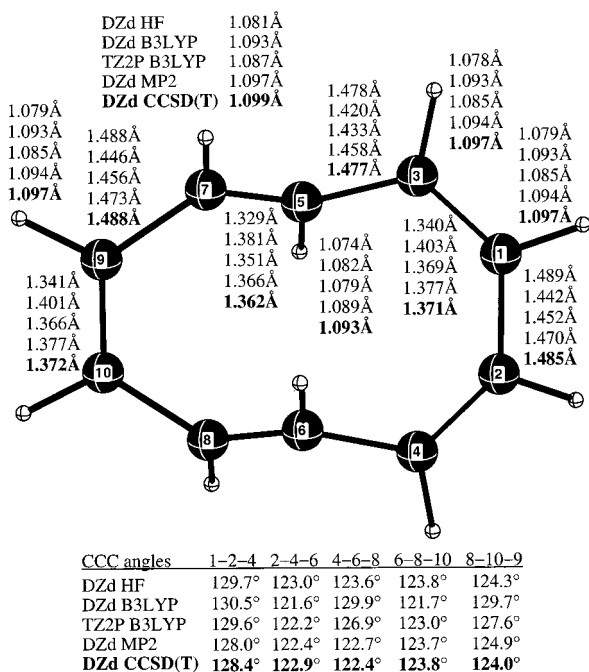


Figure 2. Fully optimized structures of the C_2 symmetry naphthalene-like conformation of [10]annulene.

conformations. For example, in 1978 Baumann¹⁴ reported the failure of MINDO methods as dramatic changes in the relative energies of localized versus delocalized naphthalene-like structures occurred when the treatment of electron correlation was improved. A summary of several such previous computational studies is provided in Table 1. In general, the methods used are clearly inadequate for the [10]annulene problem, and the results are erratic. Notwithstanding the stout obstacles overcome in the experimental isolation of [10]annulene, a computational description of its conformations and energetics has proven just as demanding.

(14) Baumann, H. *J. Am. Chem. Soc.* **1978**, *100*, 7196.

A recent computational contribution to the [10]annulene saga was that of Sulzbach et al.¹⁵ in 1995 when the C_s symmetry heart conformation (Figure 3) was advanced as an energetically competitive structure. The results of density functional theory (DFT)¹⁶ and second-order Möller–Plesset perturbation theory (MP2)¹⁷ computations indicated that the aromatic heart structure was a minimum, lying below the C_2 symmetry twist by approximately 7 kcal mol⁻¹. The heart was shown to be aromatic by its magnetic susceptibility exaltation and anisotropy.¹⁵ It was noted, though, that the computed NMR chemical shifts for the twist were in better accord with the experimental spectra of conformer 2 of Masamune et al.⁷ The persistence of Sulzbach et al.¹⁸ led to a subsequent publication in 1996 in which DFT and MP2 were found wanting in their ability to predict relative energies of [10]annulene accurately. Single-point energies at the MP2 and DFT geometries using more reliable computational methods led to the conclusion that the aromatic heart actually lies 3–7 kcal mol⁻¹ above the olefinic twist structure. The authors then recommended “extreme caution” in the use of DFT and MP2 results for similar systems. Of course, the fact that Sulzbach et al. did not reoptimize geometries with the coupled cluster method lessens the definitiveness of their conclusions.

DFT and MP2 have achieved tremendous popularity among computational chemists. Modern gradient-corrected DFT methods, in particular, have made predictions of molecular properties for diverse molecules that are surprisingly accurate,¹⁹ given their relative economy. Trust has increased to the extent that gradient-corrected DFT methods, such as B3LYP, are now commonly relied upon in the absence of confirmation from convergent quantum mechanical methods. This sacrifice is often necessary given the relatively friendly scaling of the DFT and MP2 methods. Nonetheless, the apparent failure of DFT and MP2 for [10]annulene calls for further investigation using the most reliable theoretical methods available.

The attractive choice for the treatment of electron correlation, when computationally feasible, is clearly the coupled cluster method including singles, doubles,²⁰ and perturbatively connected triple excitations [CCSD(T)].²¹ While expensive, this method is now more widely applicable than ever, and its accuracy is well-established for chemical problems that are not severely multi-reference in nature.^{22,23} In this work, CCSD(T) computations are employed in the pursuit of accurate structures and relative energies for the lowest-energy conformations of [10]annulene. This effort is inspired by (1) the demonstrated deficiency of MP2 and DFT; (2) the experimental isolation and NMR analysis of two distinct conformations; (3) the inherently interesting “boundary between aromatic and olefinic character”;¹⁸ and (4) the current lack of definitive computational results, as demonstrated in Table 1.

(15) Sulzbach, H. M.; Schleyer, P. R.; Jiao, H.; Xie, Y.; Schaefer, H. F. *J. Am. Chem. Soc.* **1995**, *117*, 1369.

(16) Kohn, W.; Sham, L. *J. Phys. Rev. A* **1965**, *140*, 1133.

(17) Möller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(18) Sulzbach, H. M.; Schaefer, H. F.; Klopper, W.; Luthi, H. P. *J. Am. Chem. Soc.* **1996**, *118*, 3519.

(19) Johnson, B. G.; Gill, P. M. W.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 5612.

(20) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.

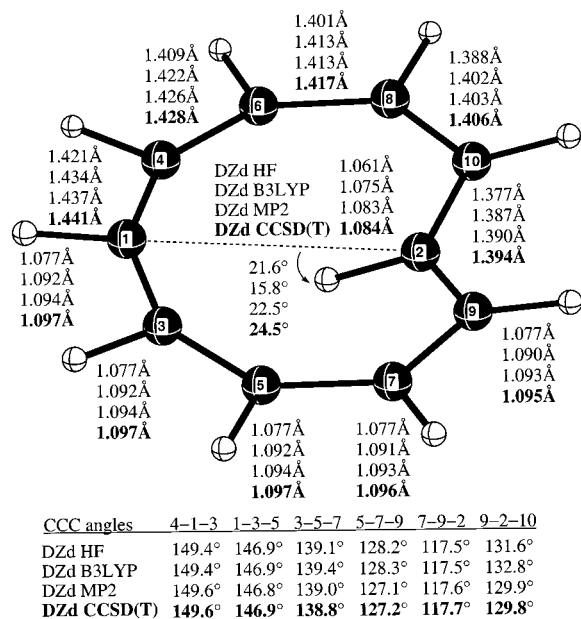
(21) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(22) Thomas, J. R.; DeLeeuw, B. J.; Vacek, G.; Crawford, T. D.; Yamaguchi, Y.; Schaefer, H. F. *J. Chem. Phys.* **1993**, *99*, 403.

(23) Lee, T. J.; Scuseria, G. E. In *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*; Langhoff, S. R., Ed.; Kluwer Academic Publishers: Dordrecht, 1995; pp 47–108.

Table 1. Previously Reported Relative Energies (in kcal mol⁻¹) for Conformations of [10]Annulene

	MINDO2 ⁴³	MINDO3 ⁴⁴	4-31G HF/ STO-2G HF ⁴⁵	MM3 ³⁴	AM1 ³⁴	DZP HF ³⁴	DZP MP2/ DZP HF ³⁴	TZP B3LYP ¹⁵	Dzd CCSD(T)/ Dzd B3LYP ¹⁸
<i>D</i> _{5h}		-65.0	32.7	67.0	40.8	31.2	20.7		
<i>D</i> _{10h}	8.7		30.7	69.2	41.4	31.9	13.8		
<i>C</i> _s boat (Figure 5)	-10.3	-36.1	2.1	15.5	2.4	1.9	6.2		
<i>C</i> ₂ azulene-like (Figure 4)			11.5	7.4		8.1	4.9		
<i>C</i> _s heart (Figure 3)	24.7							-7.0	6.0
<i>C</i> ₂ naphthalene-like (Figure 2)	9.4	-6.2	2.8	-3.6	-0.7	2.9	0.5		
<i>C</i> ₂ twist (Figure 1)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

**Figure 3.** Fully optimized structures of the *C_s* symmetry heart conformation of [10]annulene.

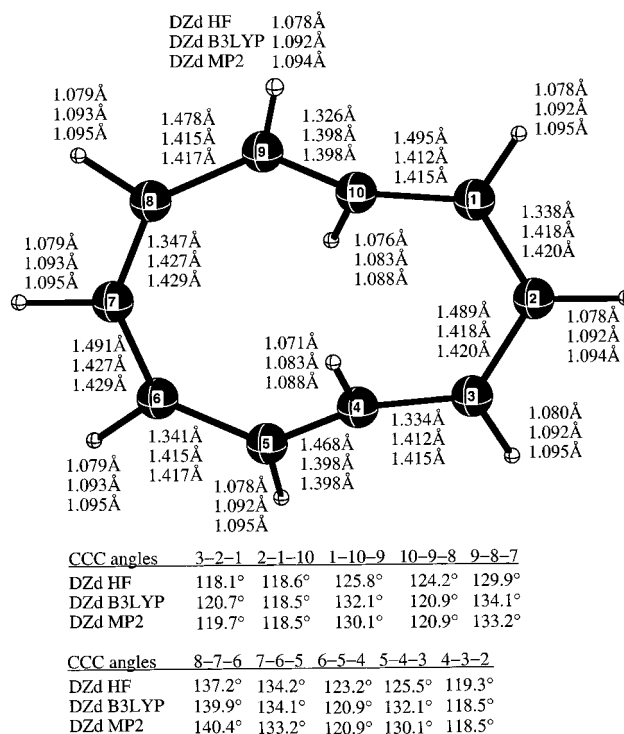
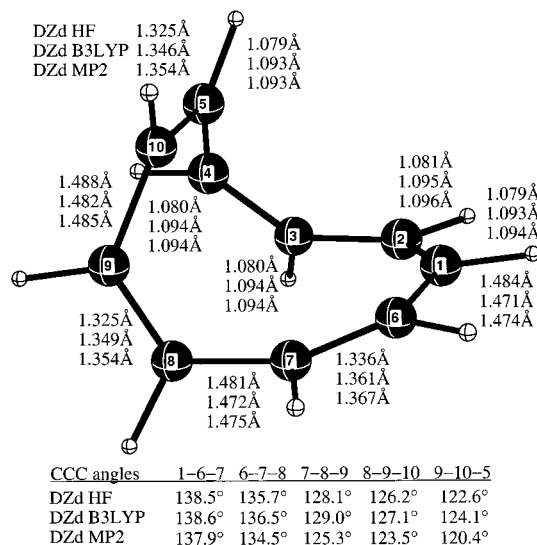
II. Theoretical Methods

Geometrical conformations of [10]annulene were fully optimized within the given symmetry constraints using a standard DZd basis set formed from the Huzinaga–Dunning^{24,25} double- ζ set of contracted Gaussian functions, augmented with a set of five d-type polarization functions on each C ($\alpha_d = 0.75$). At these geometries, single-point energies were then obtained using the larger DZP and TZ2P basis sets. The DZP basis set was formed from the DZd basis by the addition of a set of p-type polarization functions on each H ($\alpha_p = 0.75$). The TZ2P basis set was formed by augmenting the Huzinaga–Dunning^{24,26} triple- ζ set of contracted functions with two sets of five d-type functions on each C ($\alpha_d = 1.50, 0.375$) and two sets of p-type functions on each H ($\alpha_p = 1.50, 0.375$). The basis sets may be designated as follows for C: DZd 9s5p1d/4s2p1d, DZP 9s5p1d/4s2p1d, and TZ2P 10s6p2d/5s3p2d, and for H: DZd 4s/2s, DZP 4s2s1p/4s2s1p, and TZ2P 5s2p/3s2p.

The reported coupled cluster (CC) computations have been executed using a locally modified version of the ACESII²⁷ program package. Geometries were optimized at the DZd CCSD(T) level using analytic gradients^{28,29} with no core orbitals or virtual orbitals frozen. In the CCSD(T) single-point energy computations, no orbitals were frozen with the DZP basis set, while the ten lowest- and highest-energy

(24) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.(25) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.(26) Dunning, T. H. *J. Chem. Phys.* **1971**, *55*, 716.

(27) Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; Bartlett, R. J. ACES II. The package also contains modified versions of the MOLECULE Gaussian integral program of J. Almlöf and P. R. Taylor, the ABACUS integral derivative program written by T. U. Helgaker, H. J. Aa. Jensen, P. Jørgensen, and P. R. Taylor, and the PROPS property evaluation integral code of P. R. Taylor.

(28) Scheiner, A. C.; Scuseria, G. E.; Rice, J. E.; Lee, T. J.; Schaefer, H. F. *J. Chem. Phys.* **1987**, *87*, 5361.(29) Scuseria, G. E. *J. Chem. Phys.* **1991**, *94*, 442.**Figure 4.** Fully optimized structures of the *C₁* (HF) or *C₂* (B3LYP and MP2) symmetry azulene-like conformation of [10]annulene.**Figure 5.** Fully optimized structures of the *C_s* symmetry boat conformation of [10]annulene.

molecular orbitals were frozen with the TZ2P basis. The Gaussian 94³⁰ program system was used to obtain the spin-restricted Hartree–Fock (HF), the MP2, and the DFT results. The B3LYP method uses Becke's three-parameter exchange functional³¹ with the Lee, Yang, and Parr correlation functional.³² The BP86 method uses Becke's 1988 exchange

functional along with the correlation correction of Perdew.³³ The ten lowest- and highest-energy molecular orbitals were frozen for all of the MP2 computations.

III. Results and Discussion

In 1994 Xie et al.³⁴ examined the geometries and harmonic vibrational frequencies of many conformations of [10]annulene using HF, MP2, molecular mechanics, and semiempirical methods. The authors presented the twist, naphthalene-like, azulene-like, and boat forms as the lowest-energy structures found at the DZP MP2/DZP HF level, although all four were predicted to lie within 6.2 kcal mol⁻¹. These four isomers, in addition to the energetically competitive heart isomer reported by Sulzbach et al.,^{15,18} are examined in this work.

A. Structures. All five conformations studied here have been optimized at the HF, MP2, and B3LYP levels using a DZd basis set comprised of 170 functions. Due to the relative energetics described later, the twist, heart, and naphthalene-like structures were chosen for large-scale CCSD(T) optimizations as well. All bond distances and C–C–C angles are depicted in Figures 1–5. Complete optimized geometries are available as Supporting Information.

The first obvious conclusion from the computed geometries is that HF favors localized π -bonding structures and that, therefore, the effect of electron correlation is to reduce the amount of bond length alternation, as noted previously.^{10,14,34} Contrary to the observation obtained using the DZ HF and DZ MP2 methods by Xie et al.,³⁴ however, the addition of electron correlation does not increase *all* of the C–C bond lengths with a DZd basis set. For example, the DZd HF twist and naphthalene-like structures actually have their C–C single bonds reduced in length by MP2 and DFT, and hardly changed by CCSD(T), while the double bond lengths are significantly lengthened.

All correlated methods are in good agreement for the C_2 twist geometry (see Figure 1), which has also been previously optimized with MP2 and B3LYP.¹⁵ The amount of bond length alternation for the twist is reduced consistently by the correlated methods from 0.14–0.16 Å for HF to 0.11–0.13 Å for B3LYP and CCSD(T) and to 0.10–0.12 Å for MP2. The B3LYP method predicts bond lengths that are in every case 0.004–0.009 Å shorter than the corresponding CCSD(T) distances, and thus a very similar alternation. MP2, on the other hand, gives C–C double bonds which are virtually identical with those given by CCSD(T) while the single bonds are 0.01 Å too long, leading to a slightly larger alternation. Though the twist structure is olefinic, the DZd CCSD(T) single–double C–C bond alternations are quite a bit less pronounced than the 0.189 Å difference in the C–C bond lengths of ethane (1.537 Å) and ethylene (1.348 Å) at the same level of theory. In addition, electron correlation in the twist structure reduces the C–C–C bond angles so that all of them fall in the range of 121.3–127.9° with CCSD(T).

For the C_2 naphthalene-like conformation, the computed structures differ considerably from level to level (see Figure 2). As for the twist structure, the HF bond lengths alternate 0.14–0.16 Å, while the CCSD(T) bond-length alternation is 0.11–0.13 Å. The MP2 method again overestimates the correlation correction, predicting a smaller bond alternation of 0.08–0.11 Å and bond angles within 1° of those of CCSD(T). The B3LYP method, however, gives a much smaller range of 0.02–0.06 Å, as well as three large C–C–C bond angles of 130.5°, 129.9°, and 129.7°. The CCSD(T) structure, on the other hand, has only one ring angle greater than 124.0°. The incorrect bond delocalization present in the DZd B3LYP structure was ameliorated by extension of the basis set. The TZ2P B3LYP structure has a bond alternation of 0.06–0.10 Å and substantially improved bond angles.³⁵ The naphthalene-like conformation of [10]annulene is apparently a structure for which the B3LYP method converges the geometry more slowly with respect to basis set than the CCSD(T) method. Such a strong basis-dependence of DFT geometries is unexpected; indeed, one of the most desirable features of DFT methods is thought to be their insensitivity to basis set.

In the limit of delocalized bonding, the C_2 naphthalene-like structure may assume C_{2h} symmetry. This C_{2h} geometry was recently computed to be the lowest energy conformation of [10]-annulene using a newly calibrated MM3 method by Tai and Allinger.³⁶ The B3LYP C–C bond lengths of the C_2 structure in Figure 2 are in between the C–C bond lengths of the two minima predicted by MM3, one C_2 and one C_{2h} . At the DZd B3LYP level, we have optimized the C_{2h} structure and obtained its harmonic vibrational frequencies. Despite the strong preference of B3LYP demonstrated here for such delocalized bonding, the C_{2h} structure is found to lie higher in energy and to be a transition state.

Sulzbach et al.¹⁵ discovered the C_s heart isomer (see Figure 3) and performed DZd MP2 and B3LYP optimizations. The heart isomer is the only one of the five conformations investigated here for which the HF method predicts an aromatic structure. All methods predict that the C–C bond lengths are successively longer as one moves away from the inner H atom. This nearly planar structure favors π -bond delocalization at the expense of severe σ -bond strain; the two largest ring angles are 149.6° and 146.9° with DZd CCSD(T), which are far greater than any ring angles of the other four conformations.

The C_2 azulene-like structure (see Figure 4) was discovered by Xie et al.³⁴ using molecular mechanics and a stochastic searching algorithm. The authors optimized a C_1 symmetry DZP HF structure which is similar to our DZd HF structure. However, when this structure is optimized with MP2 and B3LYP, the C_1 stationary point disappears and the aromatic C_2 symmetry structure is formed. The HF prediction of a stationary point with localized bonding which disappears with MP2 or DFT is not surprising; HF also finds a D_{5h} stationary point on the potential energy hypersurface which does not exist with MP2.³⁴ The HF azulene-like structure is bond-alternating as usual (0.13–0.17 Å), but the very different MP2 and B3LYP structures are aromatic. MP2 and B3LYP both predict that all of the C–C bond lengths are within 0.03 Å of each other and do not alternate between longer and shorter.

(35) This competition between bond delocalization and strain-induced nonplanarity has been described by Haddon^{40–42} in terms of π -orbital axis vector (POAV) misalignment for many related conjugated organic molecules. The POAV analysis could be useful as a quantitative measure of this phenomenon in [10]annulene isomers as well.

(36) Tai, J. C.; Allinger, N. L. *J. Comp. Chem.* **1998**, *19*, 475.

(30) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94, Revision C.3*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(31) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(32) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B.* **1988**, *37*, 785.

(33) Perdew, J. P. *Phys. Rev. B.* **1986**, *33*, 8822.

(34) Xie, Y.; Schaefer, H. F.; Liang, G.; Bowen, J. P. *J. Am. Chem. Soc.* **1994**, *116*, 1442.

Table 2. Computed Relative Energies (in kcal mol⁻¹) for Conformations of [10]Annulene

	DZd HF	DZd B3LYP	DZd MP2
C _s boat (Figure 5)	+1.84	+2.47	+7.12
C ₂ azulene-like (Figure 4)	+8.13	-2.96	-1.14
C _s heart (Figure 3)	+11.77	-9.11	-4.22
C ₂ naphthalene-like (Figure 2)	+2.87	-2.89	+1.23
C ₂ twist (Figure 1)	0.00	0.00	0.00

	TZ2P HF/ DZd HF	TZ2P B3LYP/ DZd B3LYP	TZ2P MP2/ DZd MP2
C _s boat (Figure 5)	+1.61	+1.99	+6.81
C ₂ azulene-like (Figure 4)	+8.59	-1.17	-4.15
C _s heart (Figure 3)	+12.93	-6.92	-7.06
C ₂ naphthalene-like (Figure 2)	+3.29	-1.24	+0.53
C ₂ twist (Figure 1)	0.00	0.00	0.00

For the C_s boat structure (see Figure 5), the bond lengths predicted by DFT and MP2 are in quite good agreement (<0.008 Å difference). They each predict bond alternations which are slightly larger than those of the twist by about 0.01 Å. B3LYP is unable to equalize the bonds in the boat structure but again predicts bond angles which are 1–4° larger than MP2 values.

B. Energetics. The DZd HF, MP2, and B3LYP relative energies of the five conformations of interest are given in Table 2. The lowest-energy conformation is predicted to be the twist by HF, and the heart by B3LYP and MP2. The lack of consistency in Table 2 is problematic, and previous studies using less sophisticated computational methods have encountered even more severe divergence in the predictions of these relative energies (see Table 1). Single-point energies obtained with the TZ2P basis set (see Table 2) show relatively minor changes from the DZd energies. The TZ2P B3LYP/DZd B3LYP (-6.92 kcal mol⁻¹) and TZ2P MP2/DZd MP2 (-7.06 kcal mol⁻¹) energies for the heart conformation relative to the twist are nearly identical. However, it has already been demonstrated that both B3LYP and MP2 overestimate the stability of the heart structure relative to the twist.¹⁸ Like the heart, the azulene-like structure is aromatic and not favored by HF. Thus, the stability of the azulene-like structure may also be overestimated by MP2 and DFT. To obtain more reliable relative energies, single-point energies at the DZd CCSD(T)/DZd MP2 level of theory were performed (see Table 3). Based upon these relative energies, the twist, naphthalene-like, and heart conformations have been selected for further investigation with CCSD(T).

The DZd CCSD(T) relative energies of the optimized twist, naphthalene-like, and heart structures, along with single-point energies obtained from high-level CCSD(T) computations using the DZP (200 basis functions) and TZ2P (340 basis functions) basis sets, are reported in Table 3. The heart lies above the twist in energy by 6.29 kcal mol⁻¹ with DZd CCSD(T). The DZP basis reduces this difference to 4.10 kcal mol⁻¹, but the TZ2P basis set slightly increases the difference to 4.24 kcal mol⁻¹. The CCSD(T) energies reported here are consistent with the prediction of Sulzbach et al.¹⁸ that, in contrast with MP2 and B3LYP results, the twist is 3–7 kcal mol⁻¹ below the heart. The DFT error is apparently not caused by the choice of the specific exchange-correlation functional, B3LYP. If the BP86 form of DFT is used instead to optimize the twist and heart structures with the DZd basis, the heart is still predicted to be 12.11 kcal mol⁻¹ lower than the twist, a prediction that differs from CCSD(T) with the same basis set by an unsettling 18.4 kcal mol⁻¹. We are convinced by the results in Tables 2 and 3 that geometry optimizations using larger basis sets would not change the qualitative conclusion that the DFT conformational energetics for this system are significantly in error. However,

one referee has recommended caution in our criticism of DFT because of the absence of CCSD(T) geometry optimizations using a basis set that includes p-functions for H and f-functions for C.

Bettinger et al.³⁷ have recently investigated the heart versus twist competition for aza[10]annulene, where one of the carbon–hydrogen pairs is replaced by N, thereby reducing the transannular repulsion. Using DZd CCSD(T)/6-311+G** B3LYP, they concluded that the heart is closer to the twist than for [10]-annulene but still higher in energy by 2.1 kcal mol⁻¹. Also, behavior of the HF, MP2, and CCSD(T) relative energies similar to that reported here has been computed for conformations of C₁₀ by Watts and Bartlett.³⁸

The naphthalene-like structure is quite energetically competitive with the twist, and the DZd CCSD(T) energy difference of 1.74 kcal mol⁻¹ is not changed significantly by the DZP (1.27 kcal mol⁻¹) and TZ2P (1.40 kcal mol⁻¹) basis sets. The DZP HF harmonic vibrational frequencies computed by Xie et al.³⁴ suggest that zero-point vibrational energy will only slightly change (<0.2 kcal mol⁻¹) the relative energies of these [10]-annulene conformations.

IV. Conclusions

The assignment by Masamune et al.⁷ of their observed conformer **2** to the twist structure is consistent with the CCSD(T) energetics as well as the NMR chemical shifts computed previously by Sulzbach et al.¹⁵ The heart structure was originally proposed by Masamune et al.⁷ as a transition state between equivalent twist structures which average the magnetic environment of all nuclei at temperatures greater than -100 °C. Although MP2 and DFT predict that the heart structure is a minimum that lies *below* the twist,¹⁵ energetics obtained here from CCSD(T) computations are consistent with the original hypothesis. Masamune et al.⁷ assigned their conformer **1** to the boat structure and argued that a low-energy pseudorotation would result in the complete averaging of the magnetic environment of the nuclei, even at -160 °C, as experimentally observed. However, MP2 and B3LYP predict that the boat is the highest in energy of all of the five conformations investigated here, and CCSD(T) single-point energies place the boat at 5.66 kcal mol⁻¹ above the twist. Masamune et al.⁷ dismissed the naphthalene-like structure as lacking a low-energy process to make all of the nuclei equivalent. Given the extreme flatness and complexity of the potential energy hypersurface of [10]-annulene, such statements appear bold. The naphthalene-like structure has now been definitively shown to be quite energetically competitive with the twist, and Xie et al.³⁴ suggest some guidelines for the infrared differentiation of this conformation from the twist and boat. We hope that the recent *ab initio* studies of [10]annulene conformations will stimulate new experimental investigations.

The twist conformation of [10]annulene is predicted to be the lowest energy structure by TZ2P CCSD(T)/DZd CCSD(T) computations. The naphthalene-like and heart structures are predicted to be 1.40 and 4.24 kcal mol⁻¹, respectively, above the twist. When compared to these results, the predicted energies from both MP2 and B3LYP are seen to be quite poor. Both TZ2P B3LYP/DZd B3LYP and TZ2P MP2/DZd MP2 incorrectly predict that the heart is *lower* than the twist by 6.92 and 7.06 kcal mol⁻¹, respectively. TZ2P B3LYP/DZd B3LYP also predicts that the naphthalene-like structure is 1.24 kcal mol⁻¹

(37) Bettinger, H. F.; Sulzbach, H. M.; Schleyer, P. R.; Schaefer, H. F. *J. Chem. Phys.* **1999**, *110*, submitted for publication.

(38) Watts, J. D.; Bartlett, R. J. *Chem. Phys. Lett.* **1992**, *190*, 19.

Table 3. Computed CCSD(T) Relative Energies (in kcal mol⁻¹) for Conformations of [10]Annulene

	DZd CCSD(T)/DZd MP2	DZd CCSD(T)	DZP CCSD(T)/DZd CCSD(T)	TZ2P CCSD(T)/DZd CCSD(T)
C _s boat (Figure 5)	+5.66			
C ₂ azulene-like (Figure 4)	+8.61			
C _s heart (Figure 3)	+5.99	+6.29	+4.10	+4.24
C ₂ naphthalene-like (Figure 2)	+2.04	+1.74	+1.27	+1.40
C ₂ twist (Figure 1)	0.00	0.00	0.00	0.00

lower than the twist. The more reliable CCSD(T) energetics presented here should aid in the improvement of DFT and MM methods.³⁶ While HF has been known to underestimate the degree of bond delocalization in molecules such as [10]annulene for some time, the energetics and structures reported here strongly support the conclusion that MP2 and especially DFT *overestimate* this delocalization. An analogous tendency was recently noted by Choi and Kertesz³⁹ in a computational study of 1,6-methano[10]annulenes and their derivatives. The use of larger basis sets may ameliorate incorrect bond-alternation in the geometry, as in the case of the naphthalene-like con-

formation of [10]annulene, but not the errors in the relative energies of these and related species. The word of “extreme caution” given by Sulzbach et al.¹⁸ in the use of MP2 and B3LYP in the study of such systems is therefore confirmed by the use of full CCSD(T) geometry optimizations and larger basis sets.

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Supporting Information Available: Table of complete optimized geometries of [10]annulene (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(39) Choi, C. H.; Kertesz, M. *J. Phys. Chem. A* **1998**, *102*, 3429.

(40) Haddon, R. C. *J. Am. Chem. Soc.* **1986**, *108*, 2837.

(41) Haddon, R. C. *Acc. Chem. Res.* **1988**, *21*, 243.

(42) Haddon, R. C. *J. Am. Chem. Soc.* **1990**, *112*, 3385.

(43) Leška, J.; Loos, D. *J. Mol. Struct.* **1974**, *21*, 245.

(44) Loos, D.; Leška, J. *J. Collect. Czech. Chem. Commun.* **1980**, *45*, 187.

(45) Farnell, L.; Kao, J.; Radom, L.; Schaefer, H. F. *J. Am. Chem. Soc.* **1981**, *103*, 2147.