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Communications to the Editor

Exploring the Boundary between Aromatic and Olefinic Character: Bad News for Second-Order Perturbation Theory and Density Functional Schemes

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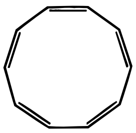
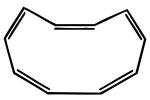
The question whether [10]annulene prefers olefinic structures with alternate single and double bonds or aromatic structures like all other small to medium sized uncharged $(4n + 2)\pi$ electron homologs (e.g. benzene, [14]annulene) has been controversial for more than 20 years. On the basis of their experimental observations (NMR data and UV spectra), Masamune and co-workers[1] concluded that, despite Hückel's $(4n + 2)\pi$ electron rule, the isolated all-*cis* and mono-*trans* conformations of [10]annulene have alternate single and double bonds.

Theoretical studies explored not only Masamune's suggested minima but also higher energy conformations, and in particular aromatic structures. As early as 1981 Farnell, Kao, Radom, and Schaefer[2] were able to show that among the all-*cis* structures the aromatic D_{10h} conformation (**1**) is much higher in energy than the corresponding, boat-shaped olefinic structure (**2**). A more recent reinvestigation of the [10]annulene potential energy surface at correlated levels confirmed the early HF results but showed that in general, at the MP2 level, the gap between the bond-alternate olefinic structures and the aromatic D_{10h} structure is much smaller.[3]

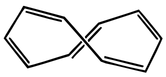


D_{10h}, **1**

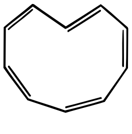


C_s, **2**, "boat"

For the structures which contain one *trans* double bond, the situation is yet unresolved. Masamune concluded that a twisted structure (C_2 symmetry) with alternate single and double bonds corresponded to the second experimentally observed compound (the "twist", **3**). This assignment was confirmed at the HF level of theory,[3] but it was superseded by a recent investigation by Sulzbach *et al*.[4] which employed second-order Møller−Plesset perturbation theory and density functional methods (Becke3LYP). Sulzbach *et al*. found that a nearly planar, aromatic structure, which has one hydrogen pointing toward the center of the ring and a plane of symmetry that bisects the molecule (the "heart", **4**), corresponds to an energy minimum and lies lower in energy (Table 1).[5]



C_2, **3**, "twist"



C_s, **4**, "heart"

The proposed heart-shaped aromatic structure agrees with the experimental UV spectrum. However, the low-temperature NMR spectrum has five peaks and fits the computed NMR shifts for the twist structure[6] but not that of the heart structure (six peaks, C_s).[1] We now report new results at the CCSD(T), UNO-CAS, and MP2-R12 levels of theory which show that both MP2 and density functional methods overestimate the stability of **4** (heart structure) with respect to **3** (twist structure).

The good performance of density functional methods, in particular of the gradient-corrected hybrid functionals (e.g. Becke3-Lee-Yang-Parr)[7] and their ability to reproduce MP2 or even CCSD results using modest computational resources, has led to their widespread application to many problems of chemical interest, including the [10]annulene potential energy surface. However, for [10]annulene the disagreement of the Becke3LYP and also the MP2 results with the experimental data raised the question whether the latter two methods are appropriate to determine the energy difference between aromatic and olefinic conformations. We have therefore evaluated energy single points for the MP2/DZd- and Becke3LYP/DZd-optimized geometries with the high-level CCSD(T) method using Gaussian94,[8] MOLPRO,[9] and ACES II.[10] In addition TX90[11] was employed to perform an unrestricted natural orbital-complete active space (UNO-CAS) calculation for the Becke3LYP/DZd-optimized geometries of **3** and **4**. All UHF natural orbitals with an occupation between 0.02 and 1.98 were included in the active space. For [10]annulene this definition of the active space yields a UNO-CAS wave function with 10 electrons distributed over 10 active orbitals, which corresponds to a full CI in the π/π^* space. The new results are summarized in Table 2 together with the HF energies.

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[5] For geometrical details, see ref 4.

[6] Sulzbach, H. M.; Xie, Y.; Schaefer, H. F. In *Proceedings of the Robert A. Welch Foundation*; Johnson, R. J. V., Ed.; Robert A. Welch Foundation: Houston, TX, 1995; pp 29−42.

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[9] MOLPRO is a suite of programs written by H.-J. Werner and P. J. Knowles, with contributions from J. Almlöf, R. D. Amos, S. T. Elbert, W. Meyer, E.-A. Reinsch, R. M. Pitzer, A. J. Stone, and P. R. Taylor.

[10] The Aces II Program System: Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; Bartlett, R. *Int. J. Quantum Chem*. **1992**, *S26*, 879.

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Table 1. Relative Energy (kcal/mol) of the Heart Structure with Respect to the Twist Structure Using the AM1 Method and the Hartree−Fock, MP2, Becke3LYP, and BLYP Levels of Theory

level of theory	NIMAG[c]	heart
AM1[a]	1	23.95
RHF/DZP[a]	1	11.47
MP2/DZ[a]	0	0.56
MP2/DZd[a]		−4.22
MP2/TZ2P//MP2/DZd[a]		−7.06
Becke3LYP/DZd[a]	0	−9.11
BLYP/DZd[b]	0	−12.76

[a] Reference 4. [b] This study. [c] Number of imaginary modes. A minimum corresponds to NIMAG = 0.

Table 2. Relative Energy (kcal/mol) of **4** with Respect to **3** of [10]Annulene at the HF, MP3, MP4, CCSD, and CCSD(T) Levels of Theory

level of theory	DZd, geom A[a]	cc-pVDZ, geom A[a]	cc-pVDZ, geom B[a]
HF	+10.44	+10.90	+8.30
MP3	+8.21	+4.93	+4.48
MP4	+1.35	−2.42	−2.13
CCSD	+10.75	+8.58	+8.05
CCSD(T)	+6.03	+3.52	+3.51
UNO-CAS(10 × 10)	+11.15		

[a] Geometry A denotes the Becke3LYP/DZd-optimized structure and geometry B the MP2/DZd-optimized structure.

Table 3. Relative Energy of **4** with Respect to **3** at the HF/TZ2P, MP2/TZ2P, and MP2-R12/TZ2P Levels of Theory for the Becke-3LYP/DZd-Optimized Geometry and the MP2(fc)/DZd-Optimized Geometry

level of theory	Becke3LYP/DZd geometry	MP2(fc)/DZd geometry
HF/TZ2P	+11.94	+9.20
MP2/TZ2P	−5.97	−5.28[a]
MP2-R12/TZ2P	+0.46	+2.10

[a] The TZ2P basis set as implemented in SORE (which is not identical to that in ref 4) was used.

The heart structure is only lower in energy at the MP2, MP4/cc-pVDZ, BLYP, and Becke3LYP levels (Tables 1 and 2), while all other correlated methods (Table 2) predict the olefinic twist structure to be the global minimum. Furthermore, the perturbation series is strongly oscillating, an indication that the MP results are unreliable, presumably because [10]annulene is not well described by a single (restricted) HF determinant. The fractional occupation numbers of the active orbitals of the heart (1.95, 1.93, 1.93, 1.80, 1.80, 0.20, 0.20, 0.06, 0.06, 0.04) and the twist (1.92, 1.92, 1.92, 1.89, 1.87, 0.13, 0.12, 0.09, 0.08, 0.07) that are obtained from the UNO-CAS calculation show that nondynamical electron correlation is very important. For the comparatively small DZd and cc-pVDZ basis sets, the CCSD(T) results demonstrate that the heart structure is higher in energy than the twist structure, reversing the MP2 and DFT results.

To approximate the basis set dependency and to extrapolate the effect that larger basis sets will have on the CCSD(T) energies, MP2-R12 studies were performed with the SORE program[12] for both sets of geometries (Table 3). The MP2-R12 method employs a first-order wave function which explicitly depends on the interelectronic coordinates and is generally able to reach the atomic orbital (AO) basis set limit for the system under study at much reduced cost.[13] Table 3 shows that near the basis set limit the MP2 energy of the twist structure is comparable to that of the aromatic heart structure. This suggests that for a very large basis set the CCSD(T) energy difference between the heart and twist structure increases and the olefinic structure becomes even lower in energy than indicated in Table 2.

Our new results suggest that only the high-order correlated methods will be able to correctly predict the [10]annulene potential energy surface. The UNO-CAS results and the strong oscillation of the MP series show that nondynamical electron correlation is important. Consequently, reliable results can only be expected at the highest correlated levels like the CCSD(T) method, which predicts the olefinic twist structure to be lower in energy by 3−7 kcal/mol. This prediction that the twist structure is lower in energy is supported by (a) the MP2-R12 method, which shows that large basis sets favor the olefinic structure relative to the aromatic, and (b) the fact that both structures are about equally affected by nondynamical electron correlation.

We conclude that [10]annulene is a system which cannot be described adequately by either second-order Møller−Plesset perturbation theory or density functional methods. The results that are obtained for similar systems with either method should therefore be treated with extreme caution and verified at higher levels of theory where possible.

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(12) SORE, a direct MP2-R12 code, written by W. Klopper.

(13) For a detailed description of the MP2-R12 method, see: Klopper, W. *J. Chem. Phys.* **1995**, *102*, 6168 and references therein.