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Computational Study of [10]Annulene NMR Spectra

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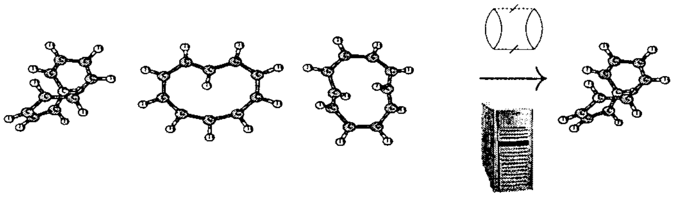
ABSTRACT



High-level theoretical methods are applied to calculate the ^{13}C NMR chemical shifts of three isomers of [10]annulene. Comparison with experiment clearly shows that the carrier of NMR signals of the so-called B form is the "twist" isomer. The results of this study strongly support predictions of relative energies of mono-trans [10]annulene isomers at the CCSD(T) level, which in turn are in qualitative disagreement with DFT and MP2 calculations.

One of the cornerstones of organic chemistry is the concept of aromaticity, a property predicted for cyclic hydrocarbons with $4n + 2\pi$ electrons and epitomized by benzene. On this basis, one might expect a stable cyclic geometry with D_{10h} symmetry for the monocyclic $C_{10}H_{10}$ molecule, [10]annulene. While the resonance energy associated with this structure is indeed high,[1] it has been shown to be outweighed by the unfavorable strain energy associated with the 144° CCC bond angle of this high-symmetry structure. Consequently, the molecule distorts to one or more lower-symmetry forms, the identity of which remain a subject of debate.[1−11]

In 1967, van Tamelen and Burkoth[2] were the first to prepare [10]annulene. Four years later, Masamune et al.[3,4] prepared crystalline forms (**A** and **B**) of this species resulting from low-temperature photolysis of *cis*-9,10-dihydronaphthalene. The NMR spectrum of **A** exhibits only single proton and ^{13}C signals down to −160 °C, whereas that of **B** resolves into five peaks at low temperature. The products of ring closure led Masamume and co-workers to speculate that **A** and **B** are all-cis and mono-trans [10]annulenes, respectively. The former was assigned to a nonplanar boat structure, although this remains an open question.[11] Meanwhile, the identity of the mono-trans form has stimulated considerable interest in the computational chemistry community.

Since the early 1980s, several theoretical studies on [10]-annulene have appeared, using methods ranging from molecular mechanics[8] to CCSD(T).[10,11] A number of potential candidates for the structure of this molecule were identified by molecular mechanics, three of which are consistently found to be most stable by various quantum chemical methods. These are the "twist" (**1**), the "heart" (**2**), and the "naphthalene-like" (the name usually applied, even though

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

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

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

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

(5) Masamune, S.; Darby, N. *Acc. Chem. Res.* **1972**, *5*, 272.

(6) Mislow, K. *J. Chem. Phys.* **1952**, 20, 1489.

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

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

(9) 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; p 29.

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

(11) King, R.; Crawford. T. D.; Stanton, J. F.; Schaefer, H. F. *J. Am. Chem. Soc.* **1999**, *121*, 10788.

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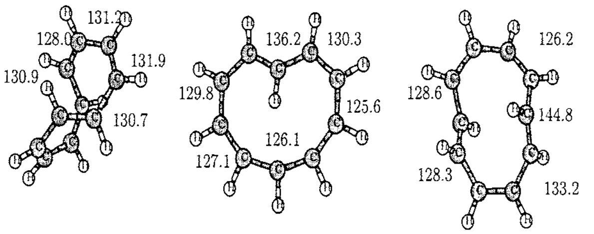
the structure is monocyclic rather than bicyclic) form (**3**), all of which are shown in Figure 1. This system has proven to be particularly interesting because the two most widely used quantum chemical approaches that incorporate electron correlation effects—density functional theory (albeit indirectly), DFT; and second-order many-body perturbation theory, MP2—appear to fail in predicting the relative energetic ordering of these isomers. Calculations carried out in 1995 with the B3LYP density functional method predicted **2** to be the most stable form, with **1** and **3** at 6.9 and 5.7 kcal/mol higher energies, respectively. MP2 theory gave corresponding isomerization energies of 7.1 and 7.6 kcal/mol.[1] Hence, the energetic ordering of isomers given by these approaches is **2** < **3** < **1** (DFT) and **2** < **1** < **3** (MP2). These methods consistently predict the heart form to be the most stable mono-trans isomer of the type likely responsible for the NMR signals of **B**. However, in the same work, Sulzbach et al. also calculated NMR shifts for the isomers at the GIAO-SCF level (which neglects electron correlation effects) but found that the twist (**1**) rather than the heart (**2**) form gave the best agreement with experimental spectrum of **B**.



"twist" **1**

"heart" **2**

"naphthalene-like" **3**

Figure 1. Structures of [10]annulene isomers investigated in this study. Values of "best estimate" ^{13}C NMR chemical shifts shown near all unique carbon atoms.

Subsequent energetic studies using the CCSD(T) coupled-cluster method gave qualitatively different results from those presented by Sulzbach et al. Using relatively low-level geometries and a small basis set, CCSD(T) calculations found **1** and **3** to be 6.0 and 4.0 kcal/mol *lower* than **2** in energy,[10] thereby predicting the heart form to be *least* stable energetically. The most recent CCSD(T) calculations, which employed a better basis set and geometry, predict the relative energies 0 (**1**), 4.2 (**2**), and 1.4 (**3**) kcal/mol.[11]

While the CCSD(T) energy calculations and the GIAO-SCF calculations of Sulzbach et al. suggest that **1** is the favored mono-trans form of [10]annulene, it is hard to draw a firm conclusion on the basis of these calculations. One could argue that even the CCSD(T) approach could be in error when energy differences of less than 5 kcal/mol are at stake. Furthermore, the apparently confirmatory nature of the GIAO-SCF calculations must be regarded with some caution because NMR shift calculations at this level of theory neglect the electron correlation effects that play such an important role in the energetic ordering of the isomers. To this end, we have explored both correlation and basis set effects on the computed NMR chemical shifts of isomers **1**−**3** and have applied the most sophisticated level of theory routinely available [GIAO-CCSD(T)][13] to this important, intriguing, and persistent chemical problem.

Chemical shift calculations based on gauge-including atomic orbitals (GIAOs) were carried out at the equilibrium geometries of **1**−**3** presented by King et al.[11] using two different basis sets. The first is the standard Dunning-Hay double-ζ[14] set augmented by a set of polarization functions on all atoms (DZP),[15] and the second is the tzp basis from the Karlsruhe group[16] that has proven reliable in previous studies of NMR chemical shifts.[17] Calculations were performed at the SCF, MP2, and CCSD(T) levels of theory using the DZP basis set, and SCF and MP2 were applied with the larger basis. Relative shifts were obtained by subtracting the absolute shieldings from those calculated for tetramethylsilane with the same basis sets. The geometry of TMS used in the calculations was optimized at the same level of theory used by King et al.[11] to obtain the [10]annulene structures. Final "best estimate" values for the relative chemical shifts were determined by assuming additivity of higher-order correlation and basis set effects:

$$\sigma = \sigma^{\mathrm{tzp}}_{\mathrm{MP2}} + \sigma^{\mathrm{DZP}}_{\mathrm{CCSD(T)}} - \sigma^{\mathrm{DZP}}_{\mathrm{MP2}}$$

and are displayed in Table 1 as well as graphically in Scheme 1.

Table 1. Calculated ^{13}C NMR Chemical Shifts (ppm, relative to TMS) for Isomers **1**, **2**, and **3** of [10]Annulene and Experimental Values

isomer	^{13}C chemical shifts					
"twist" (**1**)	128.0	130.7	130.9	131.2	131.9	
"heart" (**2**)	125.6	126.1	127.1	129.8	130.3	136.2
"naphthalene-like" (**3**)	126.1	128.3	128.6	133.2	144.8	
experimental[a]	128.4	131.4	131.6	132.3	132.5	

[a] From ref. 3.

The results leave little question that the isomer observed experimentally and designated as **B** is the twist form **1**. Four of the five best estimate chemical shifts are within 0.7 ppm of experiment; the remaining one is only 1.1 ppm in error. The naphthalene-like isomer, which is calculated to be the next most stable form at the CCSD(T) level, can easily be ruled out, because the most shielded peak (calculated at 144.8 ppm) is 12.3 ppm away from the closest peak in the

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(12) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251.

(13) Gauss, J.; Stanton, J. F. *J. Chem. Phys.* **1996**, 104, 2574.

(14) Dunning, T. H. *J. Chem. Phys.* **1970**, 58, 2823.

(15) Redmon, L. T.; Purvis, G. D.; Bartlett, R. J. *J. Am. Chem. Soc.* **1978**, *101*, 2856.

(16) Schäfer; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, 97, 2571.

(17) For a review, see: Gauss, J.; Stanton, J. F. *Adv. Chem. Phys.*, in press.

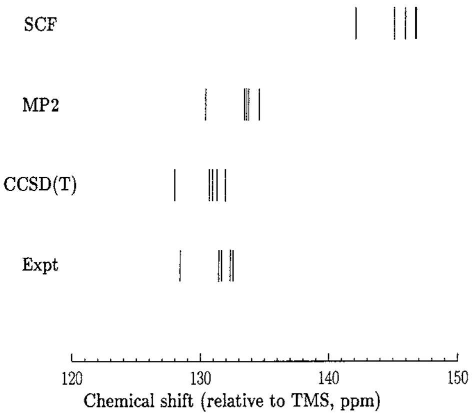

Figure 2. Calculated NMR spectrum of the “twist” isomer (**1**) at the SCF, MP2, and “best estimate” CCSD(T) levels using the tzp basis set.

experimental spectrum. Moreover, the experimental spectrum exhibits two sets of closely spaced resonances for the most shielded centers (spacings of 0.2 ppm in both cases), while the corresponding calculated gaps for **3** are 0.3 ppm (acceptable) and 11.6 ppm (clearly unacceptable). Finally, the heart isomer (favored energetically by both DFT and MP2 calculations) can be ruled out because (1) there are six, rather than five, unique carbons; (2) closely spaced resonances are not predicted by theory (which serves to close a potential loophole in an argument based on (1) alone), and (3) the calculated shifts span a range of roughly 11 ppm, about three times that found experimentally. Hence, we conclude that form **B** of Masamune[3,4] is the twist form of [10]annulene. The identity of **A** remains a mystery, but computational studies focused on this question are underway in our laboratory.

Figure 2 shows a graphical representation of the best estimate chemical shifts for the twist isomer, along with the SCF and MP2 values calculated with the tzp basis and the experimental values. It is clear from the above that a high-level treatment of electron correlation is essential for removing all ambiguity and uncertainties associated with interpretation of the NMR spectrum.

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