

A [10]Annulene Isomer May Be Aromatic, After All!

Horst M. Sulzbach,^{1a,b} Paul von Ragué Schleyer,^{*1a,b} Haijun Jiao,^{1b}
Yaoming Xie,^{1a} and Henry F. Schaefer III^{*1a}

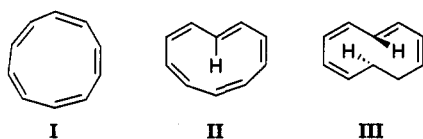
Contribution from the Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602, and the Computer Chemistry Center, Institut für Organische Chemie, Universität Erlangen–Nürnberg, Henkestrasse 42, D-91054 Erlangen, Germany

Received September 2, 1994[Ⓢ]

Abstract: Despite its adherence to Hückel's rule, [10]annulene is thought to prefer nonaromatic, nonplanar structures. This seemingly reasonable conclusion is based on experimental studies carried out a quarter century ago, but the detailed nature of the [10]annulene isomers has not been fully elucidated. A new, nearly planar aromatic *mono-trans* [10]annulene configuration has now been characterized at the second-order perturbation (MP2) and density functional (B3LYP) levels of theory. The structure, with a symmetry plane that bisects the molecule, is not a stationary point at uncorrelated levels, but it is the most stable [10]annulene isomer at MP2(fc)/DZd and at higher levels. The inner hydrogen is only bent out of the approximate carbon plane by about 20°. The estimated aromatic stabilization energy (17.7 kcal/mol, after correction for strain), the diamagnetic susceptibility exaltation ($\Lambda = -66.9$ ppm cgs, $\Lambda_{\text{Naphthalene}} = -28.2$), and the upfield NMR chemical shift of the inner hydrogen ($\delta = -6.1$ ppm) confirm the aromaticity of this new C_s [10]annulene conformation.

Introduction

According to Hückel's $4n + 2\pi$ electron rule, [10]annulene is expected to be the next higher uncharged homologue of benzene.² But the problem with strain is apparent: the CCC bond angles are 144° in the idealized all-*cis* planar D_{10h} conformation, **I**. If the CCC angle in propene is artificially widened to 144°, the energy increases by 7.6 kcal mol⁻¹ (MP2-(fc)/DZd, Table 1). As the strain energy in **I**, about 76 kcal mol⁻¹ on this basis, exceeds the expected aromatic stabilization³ considerably, nonplanar nonaromatic conformations³ are favored (at least for the all-*cis* configuration). The *mono-trans* (**II**) and *di-trans* (**III**) configurations have less angle strain than **I**, but they suffer from the transannular hydrogen repulsions implied in the schematic representations below.



Indeed, rather than exhibiting benzenoid behavior, the [10]annulenes are known to be highly reactive.^{4,5} Even so, remarkably few experimental studies have been reported. While van Tamelen and co-workers apparently were the first to prepare

[Ⓢ] Abstract published in *Advance ACS Abstracts*, January 1, 1995.

(1) (a) University of Georgia. (b) Universität Erlangen–Nürnberg.

(2) (a) Recent overview: Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Ya. *Aromaticity and Antiaromaticity. Electronic and Structural Aspects*; Wiley-Interscience: New York, 1994. (b) Garratt, P. J. *Aromaticity*; Wiley-Interscience: New York, 1986.

(3) The Hückel energy for [10]annulene (**I**, D_{10h}) is 1.618 times that of benzene. If the aromatic stabilization energy (ASE) of benzene is taken as 21.7 kcal mol⁻¹, the ASE of **I** is about 35 kcal mol⁻¹. Other estimates are lower (see ref 2).

(4) (a) van Tamelen, E. E.; Burkoth, T. L. *J. Am. Chem. Soc.* **1967**, *89*, 151. (b) Burkoth, T. L.; van Tamelen, E. E. In *Nonbenzenoid Aromaticity*; Snyder, J. P., Ed.; Academic Press: New York, 1969; Vol. 1, Chapter 3. (c) van Tamelen, E. E.; Greeley, R. H. *J. Chem. Soc., Chem. Commun.* **1971**, 601. (d) van Tamelen, E. E. *Acc. Chem. Res.* **1975**, *5*, 187.

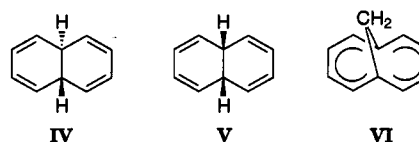
(5) (a) Masamune, S.; Seidner, T. *J. Chem. Soc., Chem. Commun.* **1969**, 542. (b) Masamune, S.; Hojo, K.; Hojo, K.; Bigam, G.; Rabenstein, D. L. *J. Am. Chem. Soc.* **1971**, *93*, 4966. (c) Masamune, S.; Darby, N. *Acc. Chem. Res.* **1972**, *5*, 272.

Table 1. Strain Energy for Compounds **I** and **IIb** Evaluated at the MP2(fc)/DZd Level

compd	angle, deg	no. of angles in the molecule	strain, (kcal/mol) hartree
I	144.0	10	0.012 134 (7.61)
sum ^a			0.121 339 (76.14)
IIb	129.9	1	0.000 988 (0.62)
	117.6	2	0.002 131 (1.34)
	127.1	2	0.000 248 (0.16)
	139.0	2	0.006 896 (4.33)
	146.9	2	0.015 725 (9.87)
	149.6	1	0.019 393 (12.17)
sum ^a			0.070 380 (44.16)

^a Sum = \sum strain(angle) \times (number of angles in the molecule).

[10]annulene,⁴ Masamune *et al.* isolated two distinct crystalline isomers, **A** and **B**, by low-temperature photolysis of *cis*-9,10-dihydronaphthalene (**V**) followed by chromatography on alumina at -80 °C.⁵ Cyclization occurred readily: **B** gave *trans* **IV** thermally ($\Delta H^\ddagger = 20$ kcal mol⁻¹), whereas **A** formed *cis* **V** ($\Delta H^\ddagger = 17$ kcal mol⁻¹).



Because of the strain, only a few of the possible configurations of the five *cis* or *trans* double bonds in [10]annulene (e.g., **I**, **II**, and **III**) are feasible structurally, but each of these may possess more than one conformation. Indeed, both **A** and **B** gave single-line decoupled ¹³C and ¹H DNMR spectra; for **A** there was no change even down to -160 °C. Since **A** gave

Table 2. Experimental ^{13}C NMR Chemical Shifts of Masamune's Compound **B** and Computed NMR Chemical Shifts (GIAO-SCF/TZP//MP2/DZd) for **IIa** and **IIb** in ppm^a

exper B	IIa	IIb
128.4 (2)	128.9 (2)	123.5 (2)
131.5 (2)	132.9 (2)	125.2 (1)
131.5 (2)	133.9 (2)	126.8 (2)
132.3 (2)	134.0 (2)	128.1 (2)
132.5 (2)	134.1 (2)	130.7 (2)
		136.6 (1)

^a The numbers in parentheses refer to the symmetry-equivalent atoms that contribute to the signal.

cis-9,10-dihydronaphthalene **V** on warming and had only weak UV absorptions, Masamune *et al.*⁵ assigned an all-*cis* configuration (**I**, but with nonplanar conformations). Based mainly on Dreiding models, isomer **III**, which has two *trans* double bonds, was deemed not to be a likely alternative.

On cooling below $-100\text{ }^\circ\text{C}$, the conformational changes of **B** were frozen out, and a five-line ^{13}C NMR spectrum resulted (Table 2).^{5b} As *trans*-9,10-dihydronaphthalene (**IV**) was produced thermally, configuration **II** with one *trans* C=C double bond was assigned to **B**. Figure 1 shows the conformational transformation suggested by Masamune⁵ for **II** which exchanges the position of all carbon atoms rapidly. They assumed the twisted conformer **IIa** (C_2 symmetry, five ^{13}C signals) to be the minimum and "nearly coplanar" conformer **IIb** (C_s symmetry, six ^{13}C signals) to be the low-energy transition state between **IIa** and **IIa'**. Unlike **A**, the UV spectrum of **B** showed an intense absorption and was very similar to that of Vogel's bridged 1,6-methano[10]annulene (**VI**).^{6,7} However, rather than being attributed to **IIb**, the electronic spectrum of **B** was interpreted as being due to the "coplanarity of two or three double bonds".^{5b}

The recent computational study of [10]annulene by Xie, Schaefer, Liang, and Bowen⁸ refined a number of [10]annulene structures which had been examined earlier by Farnell, Kao, Radom, and Schaefer.⁹ Additional structures were identified by random search procedures employing the MM3 force field. Instead of nonplanar **I** (which Masamune had assigned to isomer **A**), *trans,trans* **III** (which also might give *cis*-9,10-dihydronaphthalene thermally by conrotatory cyclization) was indicated to be the second most stable minimum. Masamune's **IIa** had the lowest energy at both the self-consistent field (SCF) and the second order perturbation theory (MP2/DZ) levels.⁸ Despite its aromaticity, planar **I** was not a minimum, and it was higher in energy than **IIa**, **III**, and several other structures.

In this study we present theoretical results for Masamune's "transition structure" **IIb** (Figure 1) for the first time. Not only is **IIb** a minimum at correlated levels, but the computed geometry, NMR chemical shifts, magnetic susceptibility exaltation, and magnetic anisotropy also all show straightforward aromatic character.

Methods and Computational Details

All *ab initio* and density functional geometry optimizations and

(6) (a) Vogel, E.; Roth, H. D. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 228. (b) Vogel, E. In *Current Trends in Organic Synthesis*; Nozaki, H., Ed.; Pergamon Press: Oxford, 1983.

(7) The UV spectra reported for **B** (ref 5b) [257–263 nm ($\epsilon = 29000\text{--}19000$), sh ca. 300 nm (ϵ ca. 4000)] and for **VI** (ref 6a) [256 nm ($\epsilon = 68000$), 259 nm ($\epsilon = 63000$), 298 nm ($\epsilon = 6200$)] are nearly identical. The basis for the statement (ref 5b) that the UV spectrum of **B** is "dramatically different" from that "expected for ten- π aromatic systems" (ref 6a cited) is not clear to us.

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

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

analytic second derivative computations employed the Gaussian 92/DFT package.¹⁰ The DZ basis employed was the double- ζ C(9s5p/4s2p), H(4s/2s) set of Huzinaga¹¹ in Dunning's contraction.¹² The DZd basis added a set of five d polarization functions on carbon (orbital exponent $\alpha_d = 0.75$). The DZP basis was obtained from the DZd basis by the addition of a set of p polarization functions on hydrogen (orbital exponent $\alpha_p = 0.75$). The TZP basis was the triplet- ζ C(10s6p1d/5s3p1d), H(5s1p/3s1p) Huzinaga¹¹–Dunning¹³ set appended with pure angular momentum polarization functions with $\alpha_d = 0.75$ and $\alpha_p = 0.75$. The NMR chemical shifts were computed with Texas90¹⁴ and employed the TZP basis set. The magnetic anisotropies and the magnetic susceptibility exaltations were obtained with IGLO.¹⁵ The latter computations employed a Huzinaga (7s,3p) DZ basis for carbon and a (3s) DZ basis for hydrogen in an IGLO-specific contraction scheme.¹⁵

Results and Discussion

Our new theoretical results for **IIb** (which has not been examined theoretically before)^{8,9} contradict the prevailing opinion, e.g., as stated by Masamune, that "[10]annulene by no means belongs to the category of aromatic compounds". Despite being a transition state at lower levels of theory, **IIb** is the global [10]annulene minimum with more sophisticated e.g. MP2(fc) (frozen core) and density functional (Becke3LYP) treatments (Table 3). Dynamic electron correlation is important for aromatic systems.¹⁶ Hence, the MM3 based search procedures that were previously employed to find new conformations of [10]annulene⁸ could not locate **IIb**, because it is not a minimum at any but correlated levels.

Structure **IIb** has no imaginary vibrational modes at e.g. MP2(fc)/DZ and Becke3LYP/DZd and it is lower in energy than **IIa** at correlated levels, if at least one set of carbon polarization functions is employed (Table 3). Extension of the basis set favors **IIb** even more. At semiempirical (AM1¹⁷) and HF levels, **IIb** is not a minimum and it is higher in energy than **IIa** (Table 3).

Masamune was right in that structure **IIb** is "nearly coplanar". The point group is C_s , rather than C_{2v} , but the inward-pointing hydrogen is only bent out of the approximate carbon plane by about 20° . Also to reduce steric strain, the inner C–H bond distance is shortened by about 0.01 Å. The carbon–carbon bond lengths (Figure 2) are all close to the benzene value (1.395

(10) Gaussian 92/DFT, Revision F.2: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Wong, M. W.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A.; Gaussian, Inc.: Pittsburgh, PA, 1993. For DFT see: Labanowski, J. W.; Andzelm, J. *Density Functional Methods in Chemistry*; Springer: New York, 1991. Parr, R. G.; Yang, W. *Density Functional Theory in Atoms and Molecules*; Oxford University Press: New York, 1989. Gaussian 92/DFT, *New Methods and Features in Gaussian 92/DFT*; Gaussian Inc.: Pittsburgh, 1993.

(11) Huzinaga, S. *J. Chem. Phys.* **1965**, *45*, 1293.

(12) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.

(13) Dunning, T. H. *J. Chem. Phys.* **1971**, *55*, 716.

(14) (a) Pulay, P.; Wolinski, K.; Hinton, J. F. *J. Am. Chem. Soc.* **1990**, *112*, 8251. (b) The benzene NMR chemical shifts computed at the same level (GIAO-SCF/TZP//MP2/DZd) showed a deviation of -0.49 ppm for the ^1H signal and -10.09 ppm for the ^{13}C signal between the theoretical and the experimental values. Since the [10]annulene structures and benzene are more similar to benzene than to TMS, the NMR chemical shifts we reported have been corrected accordingly.

(15) The sign convention for χ (not always observed in the literature) is such that $\chi < 0$ implies diamagnetism and $\chi > 0$ paramagnetism. For the magnetic susceptibility treatment using the IGLO (Individual Gauge for Localized Orbitals) method, see: (a) Kutzelnigg, W.; Fleischer, U.; Schindler, M. *NMR, Basic Principle and Progress*; Springer-Verlag: Berlin, 1990; Vol. 23, p 165. (b) Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193. (c) Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1919.

(16) For example, compare the relative energies of the all-*cis* aromatic (D_{10h}) structure of [10]annulene in ref 8 at the HF and MP2 levels.

(17) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

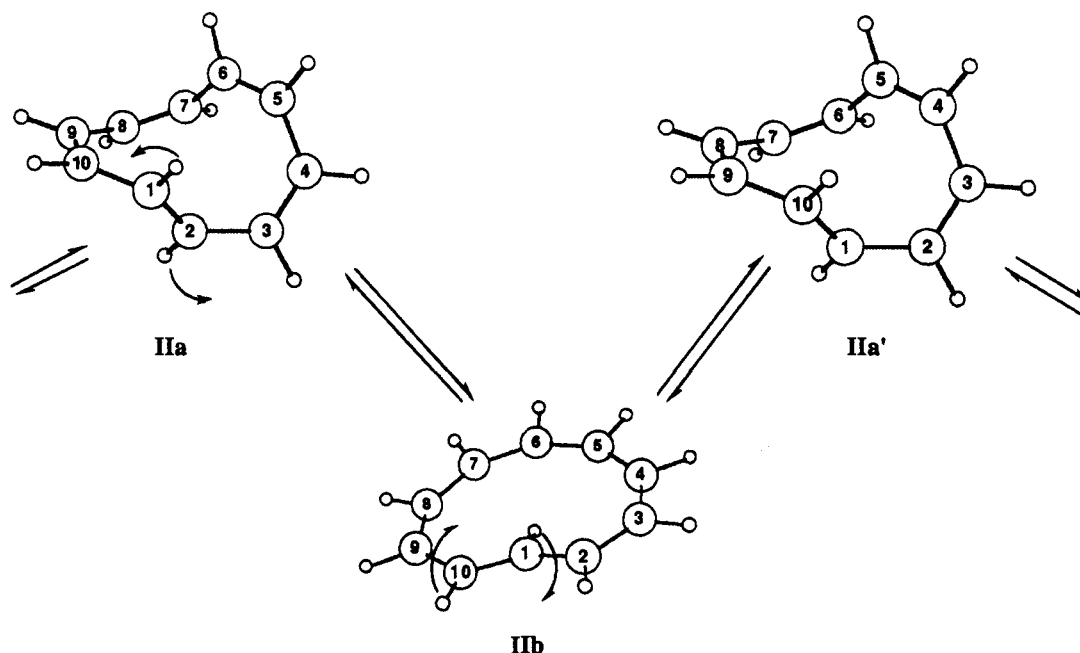


Figure 1. Masamune's suggested rearrangement for the single-*trans* conformers (**II**) of [10]annulene. Eventually, all the CH groups become equivalent by repetition of this process.

Table 3. Number of Imaginary Vibrational Modes (NIMAG), Absolute Energies, and Relative Energy of **IIb** Compared to **IIa** at Various Levels of Theory

level of theory	NIMAG for IIb	rel energy, kcal/mol (absolute energy, hartree) of IIb
AM1	1	+23.95
RHF/DZ	1	+8.05
		(-384.258 198)
RHF/DZP	1	+11.47
		(-384.426 631)
MP2/DZ ^a	0	+0.56
		(-385.120 153)
MP2/DZd ^b		-4.22
		(-385.665 191)
MP2/DZP//MP2/DZd ^c		-6.46
		(-385.755 911)
MP2/TZP//MP2/DZd ^c		-4.18
		(-385.880 864)
MP2/TZ2P//MP2/DZd ^c		-7.06
		(-385.967 839)
B3LYP/DZd	0	-9.10
		(-387.000 381)
B3LYP/TZP		-6.99
		(-387.101 991)

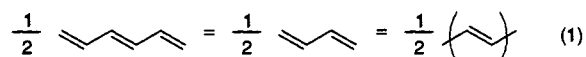
^a In addition to freezing the ten core molecular orbitals, the ten highest virtual orbitals were deleted. ^b The ten core molecular orbitals were frozen. ^c The ten core molecular orbitals were frozen for the geometry optimization and the single point calculation.

Å).^{18a-d} Planar **II**, computed by imposing C_{2v} symmetry, has a nearly identical energy to **IIb** (B3LYP/6-31G* + zero-point vibrational energy) and serves as the TS for inversion of the hydrogen through the plane. The bond lengths and the bond angles in **II** (C_{2v}) and **IIb** are practically the same.

Not only the geometrical but also the energetic criteria of

(18) (a) Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1763. (b) Jiao, H.; Schleyer, P. v. R. *J. Chem. Soc., Perkin Trans. 2* **1994**, 407. (c) Jiao, H.; Schleyer, P. v. R. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1559. (d) Herges, R.; Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1376. (e) Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.*, 1995, in press. (f) Schleyer, P. v. R.; Jiao, H.; Glukhovtsev, M. N.; Chandrasekhar, J.; Kraka, E. *J. Am. Chem. Soc.* **1994**, *116*, 10129. (g) Bühl, M.; Thiel, W.; Jiao, H.; Schleyer, P. v. R.; Saunders, M.; Anet, F. A. L. *J. Am. Chem. Soc.* **1994**, *116*, 6005. Fleischer, U.; Kutzelnigg, W.; Lazzeretti, P.; Mühlkamp, V. *J. Am. Chem. Soc.* **1994**, *116*, 5298.

aromaticity are met. For unstrained aromatics (e.g. benzene) the aromatic stabilization energy (ASE) corresponds to the energy lowering of the molecule of interest with respect to the sum of =CH- increments in conjugated polyenes derived from eq 1.²



Note that such =CH- increments include some resonance stabilization, but not that due to aromaticity. If the aromatic system is strained, these increments are inappropriate. A correction for the strain energy is needed, which leads to eq 2.¹⁹

$$\text{ASE} = -(E_{\text{COMPOUND}} - E_{\text{INCREMENTS}}) + E_{\text{STRAIN}} \quad (2)$$

For example, when corrected for the angle strain, ca. 76 kcal/mol (see above), we compute an aromatic stabilization energy (ASE) of 26 kcal/mol for **I** at the idealized D_{10h} symmetry (Table 4). This is somewhat smaller than the crude Hückel estimate^{2,3} and may be compared with the 36 kcal/mol ASE for the 10 π electron naphthalene.²⁰

As only five of the CCC bond angles in **IIb** are widened significantly, the strain should only be roughly half that in **I** (D_{10h}). We estimated the angle strain in **IIb** quantitatively by computing the deformation energies of propene constrained to the various CCC angles (MP2/DZd, Figure 2). A total strain energy of **IIb**, 44 kcal/mol (Table 1), is deduced in this manner, as well as an ASE of 18 kcal/mol (Table 4). Other possible $C_{10}H_{10}$ forms are less strained, but they do not benefit from aromatic stabilization. For **IIb**, the ASE outweighs the increase in strain and a nearly planar geometry results.

The aromaticity of **IIb** also is revealed by the magnetic properties, evaluated with the IGLO¹⁵ and GIAO¹⁴ programs.

(19) A positive ASE corresponds to aromatic stabilization.

(20) The ASE was evaluated from experimental heats of formation. We employed the following equation: naphthalene (36.06 kcal/mol) + ethane (-20.24 kcal/mol) + 4 ethylene (12.45 kcal/mol) \rightarrow 4 *trans*-1,4-butadiene (26.11 kcal/mol) + 2,3-dimethyl-*trans*-butadiene (10.78 kcal/mol).

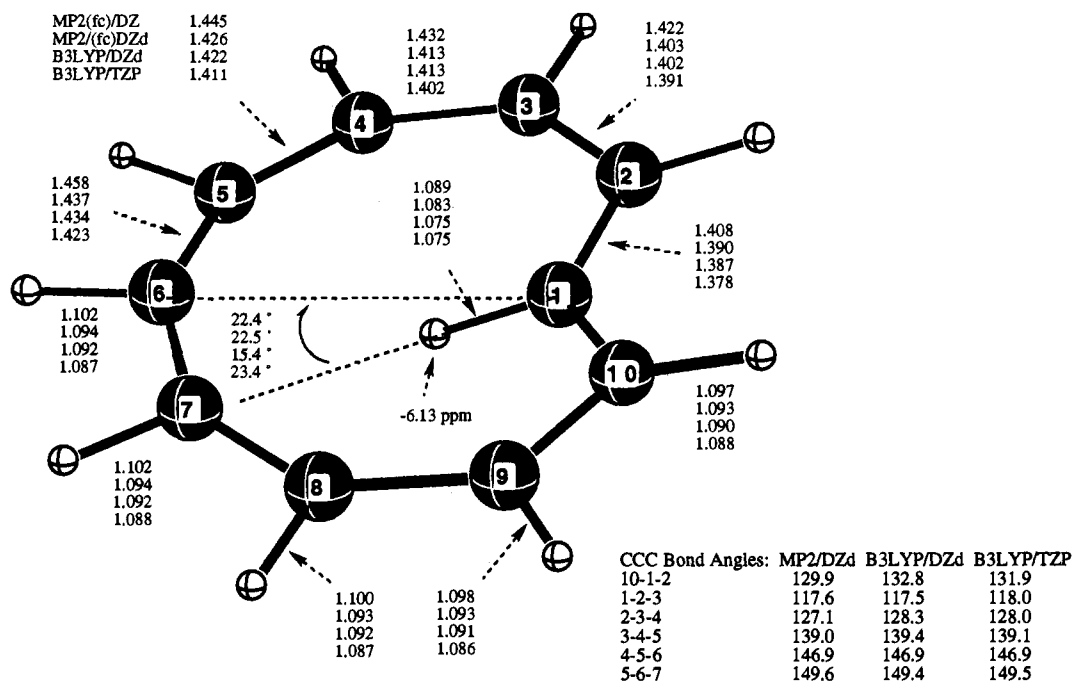


Figure 2. Geometrical data (in Å and degree) for the new aromatic structure **IIb** of [10]annulene with the MP2(fc)/DZ, MP2(fc)/DZd, Becke3LYP/DZd, and Becke3LYP/TZP methods.

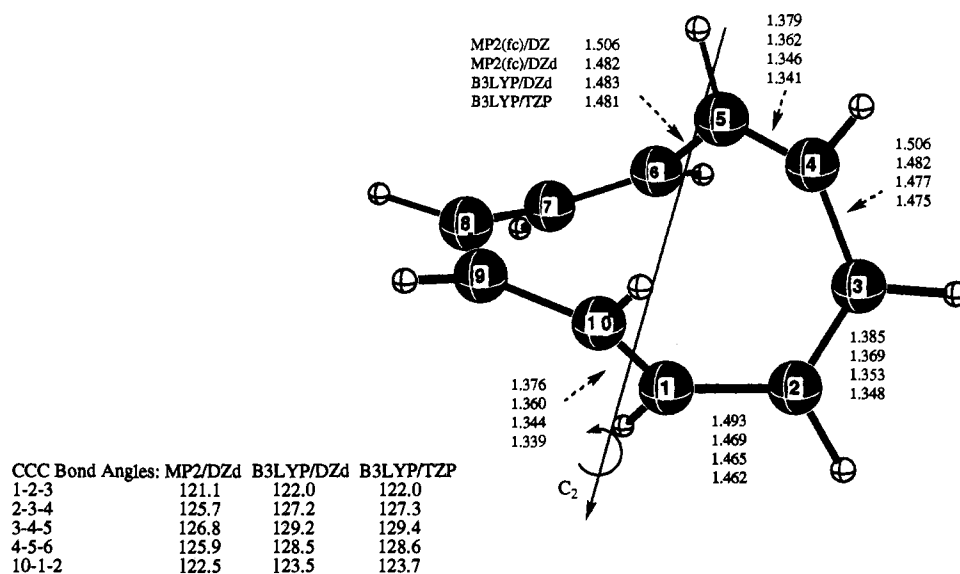


Figure 3. Geometrical data (in Å and deg) for Masamune's structure **IIa** of [10]annulene from the MP2(fc)/DZ, MP2(fc)/DZd, Becke3LYP/DZd, and Becke3LYP/TZP methods.

The magnetic susceptibility exaltation (Λ) and anisotropy (χ_{anis}) are excellent measures of aromaticity.^{18,21} Structure **IIb** exhibits $\Lambda = -66.9$ ppm cgs with respect to the sum of the χ increment values for ten olefinic $=\text{CH}-$ groups. This $\Lambda = -66.9$ is much larger in magnitude than the corresponding value of -28.2 for naphthalene and the value of -46.0 for Vogel's 1,6-methano-[10]annulene (**VI**) which have the same number of π electrons (Table 5). The χ_{anis} values are -196.3 (**IIb**), -131.6 (**VI**), and -130.3 (naphthalene). These demonstrate the *strongly aromatic character* of **IIb**.

(21) (a) Pauling, L. *J. Chem. Phys.* **1936**, *4*, 763. (b) Haberditzl, W. *Angew. Chem., Int. Ed. Engl.* **1966**, *2*, 288. (c) Dauben, H. J., Jr.; Wilson, J. D.; Laity, J. L. *J. Am. Chem. Soc.* **1968**, *90*, 811. (d) Dauben, H. J., Jr.; Wilson, J. D.; Laity, J. L. *J. Am. Chem. Soc.* **1969**, *91*, 1991. (e) Dauben, H. J., Jr.; Wilson, J. D.; Laity, J. L. *Nonbenzenoid Aromatics*; Snyder, J. P., Ed.; Academic Press: New York, 1971; Vol. II, p 187. (f) Labarre, J. F.; Crasnier, F. *Top. Curr. Chem.* **1971**, *23*, 37. (g) Haddon, R. C.; Haddon, V. R.; Jackman, L. M. *Top. Curr. Chem.* **1971**, *16*, 122.

With $\chi_{\text{anis}} = -24.4$ and $\Lambda = +8.6$, structure **IIa** ($\chi_{\text{tot}} = -93.9$) is nonaromatic. Cyclooctatetraene in D_{2d} symmetry has a similar ($\Lambda = +7.2$ ppm cgs) small positive deviation from the increment estimate.²² In agreement with our ASEs, structure **I** (D_{10h}) is even more aromatic than **IIb**: $\Lambda = -80.1$, $\chi_{\text{anis}} = -215.9$ (Table 5).

The ^1H NMR chemical shift of the inner hydrogen (-6.2 ppm) is highly shielded (GIAO-SCF/TZP//MP2/DZd, relative to TMS),¹⁴ while the NMR chemical shifts of the other hydrogen atoms are in the benzene-like 7.9–8.6 ppm range. The average ^1H NMR chemical shift of all hydrogens is 6.7 ppm. Thus, NMR experiments, unable to resolve the distinct proton signals, would be unable to determine if the protons in **IIb** have olefinic or aromatic character. However, Masamune's low-temperature

(22) Jiao, H.; Schleyer, P. v. R. *Proceedings of the First European Conference on Computational Chemistry*; Troyanowsky, C., Ed.; American Institute of Physics: Jericho, New York, 1994.

Table 4. Total Energies, Strain, Uncorrected Aromatic Stabilization Energies (ASEs), and Strain Corrected ASEs at the MP2/DZd Level^a

compd	total energy, hartree	strain, hartree (kcal/mol) [from Table 1]	ASE, hartree (kcal/mol) ^b	strain corrected ASE, ^c hartree (kcal/mol)
I	-385.626 67	0.121 34 (76.14)	-0.079 67 (-50.00)	+0.041 67 (+26.14)
IIb	-385.664 15	0.070 38 (44.16)	-0.042 19 (-26.48)	+0.028 19 (+17.68)
sum of increments ^d	-385.706 34			

^a The core molecular orbitals were frozen and the corresponding highest virtual orbitals were deleted. ^b ASE_{uncorrected} = -(E_{Compound} - E_{increments}); a positive ASE corresponds to aromatic stabilization. ^c Derived from eq 2. ^d Derived from eq 1.

¹³C NMR spectra of **B** showed only five signals,⁵ rather than the six required by **IIb**, and the average ¹H NMR chemical shift was only 5.9 ppm. Moreover, our ¹³C computed chemical shifts²³ for **IIa** are in better agreement with Masamune's experiments than those for **IIb** (Table 2), despite the opposite relative energy ordering.

Conclusions

The present and the earlier^{8,9} computational results reopen the [10]annulene problem. Masamune's isomer **A** very likely does have the nonaromatic all-*cis* (**I**) configuration. Although

(23) The GIAO-MP2 level should give improved values relative to GIAO-SCF (see for example: Schleyer, P. v. R.; Gauss, J.; Bühl, M.; Greatrex, R.; Fox, A. M. *J. Chem. Soc., Chem. Commun.* **1993**, 1766).

Table 5. IGLO/DZ//MP2/DZd Computed Magnetic Susceptibilities (χ_{tot}), Magnetic Anisotropies (χ_{anis}), and Diamagnetic Susceptibility Exaltations (Λ , ppm cgs)

	I	IIa	IIb	VI ^a	naphthalene ^a
χ_{tot}	-182.6	-93.9	-169.4	-156.2	-123.6
χ_{anis}	-215.9	-24.4	-196.3	-131.6	-130.3
Λ	-80.1	+8.6	-66.9	-46.0	-28.2

^a Employing Becke3LYP/6-31G* optimized geometries.

lower in energy,⁸ *trans,trans* **III** may cyclize too rapidly (into **V**) to be observable experimentally. However, both B3LYP and MP2 which take electron correlation into account agree that aromatic structure **IIb** should be the global minimum on the [10]annulene energy hypersurface. While the UV spectrum of Masamune's compound **B** is similar to those found experimentally for aromatic analogs, its ¹³C NMR spectrum agrees much better with our computed chemical shifts for the nonaromatic conformer **IIa** than for **IIb**. This ambiguity and our present and earlier computational findings⁸ stress the desirability of a modern experimental reinvestigation of [10]annulene.

Acknowledgment. The research in Georgia was supported by the U.S. Department of Energy, Office of Basis Energy Sciences, Division of Chemical Sciences, Fundamental Interactions Branch, Grant DE-FG05-94ER14428. The work in Erlangen was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Deutschen Chemischen Industrie (fellowship for H.M.S.), and the Convex Computer Corporation. H. Jiao thanks the Shanxi Normal University (the People's Republic of China) for a scholarship.

JA942930M