JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

Registered in U.S. Patent Office. © Copyright, 1981, by the American Chemical Society

VOLUME 103, NUMBER 9 MAY 6, 1981

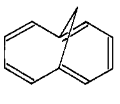
Structures and Stabilities of Isomeric [10]Annulenes

Leslie Farnell, James Kao, Leo Radom,* and Henry F. Schaefer III*[1]

Contribution from the Research School of Chemistry, Australian National University, Canberra, A.C.T. 2600, Australia. *Received June 27, 1980.*
Revised Manuscript Received December 19, 1980

Abstract: Ab initio molecular orbital theory has been used to predict the structures and relative stabilities of several $(CH)_{10}$ isomers. Calculations were carried out with minimal (STO-2G and STO-3G) and split-valence (4-31G) basis sets. The planar D_{10h} (**1**) and D_{5h} (**2**) structures are not local minima in the $C_{10}H_{10}$ surface but are of interest from the viewpoint of theories of aromaticity. The potential surface describing a bond-alternating distortion in the vicinity of the regular decagon structure (**1**) is predicted to be very flat; the best calculations (4-31G) predict a very slight energy lowering in moving to bond-alternating D_{5h} structures (**2**) but the energy lowering is too small to be regarded as definitive. On the other hand, it is clear that the energy is lowered substantially when distortions from planarity are allowed. The geometries of several nonplanar structures were examined including the all-cis isomer *CCCCC* (**3**), the *TCCCC* isomer (**4**), and two distinct *TCTCC* isomers (**5** and **6**). Structures **3–6** all have alternating single and double bonds and hence may be described as 1,3,5,7,9-cyclodecapentaene. The lowest energy structure is **4** although **5** and **3** lie only slightly higher in energy. Our theoretical results are discussed in the light of available experimental data.

Hückel's idea that systems with $(4n + 2)$ π electrons should have a special stability[2] has proved particularly valuable in organic chemistry since its introduction in 1931. Among its most obvious successes is the observation of particularly stable 6π-electron species, namely cyclopentadienyl anion $C_5H_5^-$, benzene C_6H_6, and the tropylium cation $C_7H_7^+$. For the case of $n = 2$ (i.e., 10π electrons), the success of the $(4n + 2)$ rule is less clear-cut. Although the cyclononatetraenide anion, $C_9H_9^-$, exhibits a measure of stability,[3,4] the isoelectronic neutral [10]annulene, $C_{10}H_{10}$, is extremely reactive.[5-8] This casts some doubt on Hückel's prediction of aromaticity for the planar all-cis isomer (**1**, Figure 1) of this species. Interestingly, if the conformation of the [10]-annulene ring is locked by a bridging methylene group (**13**), the resulting molecule does exhibit aromatic character.[9] NMR evidence suggests that 9-membered heterocycles, analogous to furan and pyrrole, are sometimes aromatic and sometimes not.[10]



13

Much of the experimental work on the [10]annulenes has been carried out by the groups of van Tamelen[5,6] and Masamune.[7,8] Specifically, van Tamelen and Burkoth[11] reported the synthesis of the bridged $C_{10}H_{10}$ molecule *trans*-9,10-dihydronaphthalene and proposed that its UV photolysis at −190° gave rise to an undetermined isomer of [10]annulene. However, it remained for Masamune et al.[12] to isolate isomers of [10]annulene in crystalline form. Their NMR spectra confirmed the earlier suggestion of Masamune and Seidner[13] that two distinct forms of [10]annulene were present.

One of the two observed [10]annulene isomers appears to be the all-cis isomer, symbolically designated as **2** (Figure 1). Although the NMR is consistent with a planar structure, the UV spectrum seems to rule this out. Among several all-cis conformers, Masamune favors **3** which has a tub-shaped portion attached to a near-planar diene fragment. Pseudorotation in **3** leads to equivalencing of all the hydrogen atoms.

Masamune identified the second crystalline form as the *TCCCC* isomer, represented schematically as **4** (Figure 1). Equivalencing of the hydrogen atoms can take place via bond alternation and rotation.

Only three monocyclic $(CH)_{10}$ isomers were considered by Masamune to be geometrically feasible. The third isomer, the *TCTCC* arrangement (**5** and **6**), was considered to be inconsistent with the observed ^{13}C NMR spectra because of the absence of a low-energy process which would make all the nuclei equivalent.

Clearly, it would be very desirable to have crystal structures for the various [10]annulene isomers. However, in the absence

---

(1) University of California, Berkeley.
(2) Hückel, E. *Z. Phys.* **1931**, *70*, 204.
(3) Katz, T. J.; Garratt, P. J. *J. Am. Chem. Soc.* **1964**, *86*, 5194.
(4) LaLancette, E. A.; Benson, R. E. *J. Am. Chem. Soc.* **1965**, *87*, 1941.
(5) Burkoth, T. L.; van Tamelen, E. E. In "Nonbenzenoid Aromatics"; Snyder, J. P., Ed.; Academic Press: New York, 1969; Chapter 3.
(6) van Tamelen, E. E. *Acc. Chem. Res.* **1972**, *5*, 186.
(7) Masamune, S.; Darby, N. *Acc. Chem. Res.* **1972**, *5*, 272.
(8) Kemp-Jones, A. V.; Masamune, S. In "Topics in Nonbenzenoid Aromatic Chemistry"; Nozoe, T., Breslow, R., Hafner, K., Ito, S., Murata, I., Eds.; Halsted Press: New York, 1973; Chapter 6.
(9) Vogel, E. *Chem. Soc. Spec. Publ.* **1967**, *21*, 113.
(10) Anastassiou, A. G. *Pure Appl. Chem.* **1975**, *44*, 691.
(11) van Tamelen, E. E.; Burkoth, T. L. *J. Am. Chem. Soc.* **1967**, *89*, 151. See also: van Tamelen, E. E.; Greeley, R. H. *Chem. Commun.* **1971**, 601.
(12) Masamune, S.; Hojo, K.; Hojo, K.; Bigam, G.; Rabenstein, D. L. *J. Am. Chem. Soc.* **1971**, *93*, 4966.
(13) Masamune, S.; Seidner, R. T. *Chem. Commun.* **1969**, 542.

0002-7863/81/1503-2147$01.25/0 © 1981 American Chemical Society

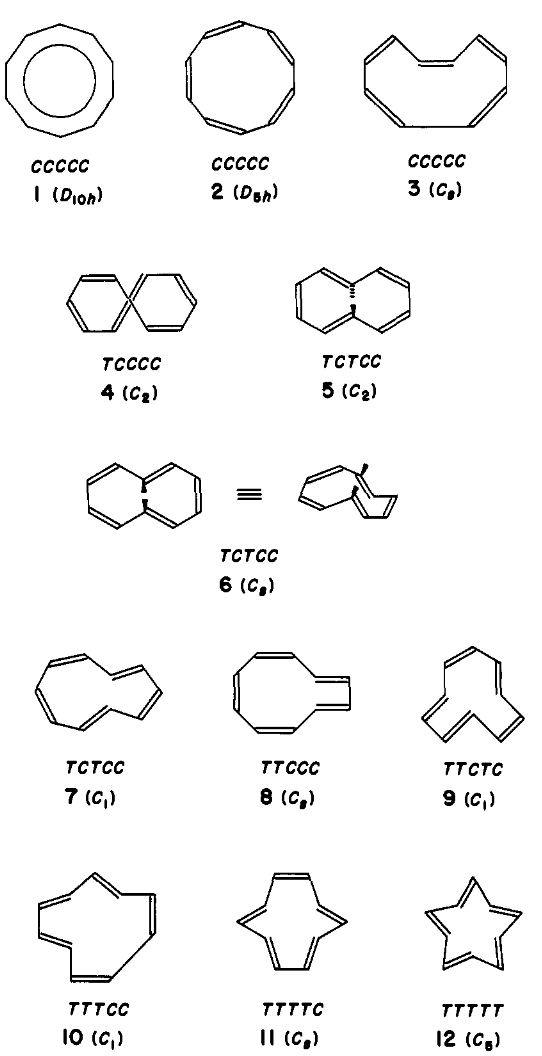


Figure 1. Possible isomeric structures for $(CH)_{10}$. The labels *T* and *C* denote the ring configuration (trans or cis) about the C═C double bonds. Molecular point groups are given in parentheses.

of experimental structures, theory should be of considerable help in providing a more complete picture of the equilibrium geometries of these fascinating species. Furthermore, theory can provide certain insights which might ultimately prove inaccessible to experiment. For example, if the planar all-cis isomer (**1**) is neither a minimum nor a saddle point on the $C_{10}H_{10}$ potential surface, then its energy relative to the stable isomers cannot be determined from experiment. Nevertheless, such energetic quantities would be quite helpful in organizing one's thoughts on the broader aspects of aromaticity.[14] For these reasons, we report in the present paper ab initio geometrical structures for the lower lying isomers of [10]annulene. It is hoped that these predictions will stimulate further experimental studies.

Theoretical Background and Present Approach

Although a number of types of theoretical calculations have been reported for [10]annulene, most of these have assumed a planar all-cis structure in the hope of relating $C_{10}H_{10}$ to other $(4n + 2)$ π-electron systems. Among the different topics discussed in these systematic studies are aromaticity,[15,16] localized orbitals,[17] resonance energies,[18] semiempirical estimates of correlation energies,[19] and ring currents.[20] The only detailed study of the geometries of the [10]annulenes is that of Leska and Loos,[16,21] who used an empirical potential scheme due to Dashevskii[22] and the MINDO/2 and MINDO/3 semiempirical molecular orbital procedures of Dewar.[23] They obtained widely differing results with these three procedures.[16] The empirical procedure predicts structure **4** to be most stable with **3** lying 78 kJ mol^{-1} higher in energy and **5** a further 76 kJ mol^{-1} higher. MINDO/2 yields lowest energy for **3** with a 52 kJ mol^{-1} gap to **4**, a further 13 kJ mol^{-1} to **5**, and a further 60 kJ mol^{-1} to **2**. Finally, MINDO/3 surprisingly predicts **2** to be the lowest energy structure with **3** lying 121 kJ mol^{-1} higher, **5** a further 125 kJ mol^{-1} higher, and **4** a further 26 kJ mol^{-1} higher in energy. It is clearly highly desirable to resolve these conflicting predictions with the use of more reliable theoretical procedures.

To the best of our knowledge, not a single ab initio study of the [10]annulenes has appeared in the literature.[24] This is no doubt in large part due to the size of $C_{10}H_{10}$. Furthermore, we must concede from the outset that the size of the $C_{10}H_{10}$ system and the low symmetry of several of the isomeric forms has severely restricted the level of theory that we ourselves apply here. In fact, most of the present research was carried out with the use of the crudest levels of ab initio theory likely to provide meaningful predictions. Specifically, the different structures were optimized with the use of the minimal STO-2G basis set[25] and single-determinant self-consistent-field (SCF) theory with a modified version[26] of the GAUSSIAN 70 system of programs.[27] Poppinger has shown[28] that this approach gives structures almost as well as the very widely used STO-3G basis set, except that bond lengths are somewhat overestimated. Both STO-2G and STO-3G slightly exaggerate the extent of single–double bond alternation.[28,29]

In order to assess which isomers warranted ab initio study, preliminary molecular mechanics calculations[30] were carried out on all the structures shown in Figure 1. These calculations identified **3**–**6** as the lowest energy isomers and the geometries of these isomers were then optimized at the ab initio STO-2G level. Except for the highly symmetric planar structures **1** and **2** for which the optimization is quite straightforward, the optimization procedure was carried out in two parts for computational efficiency. Geometric parameters describing the ring were optimized with the use of a gradient procedure[31] while angles determining the orientation of the hydrogen atoms were optimized separately by the axial iteration technique. The latter parameters are sufficiently uncoupled that very few passes are required, particularly near the final structure. C–H lengths were held fixed at 1.092 Å, the optimized value for **1**, throughout. The gradient and axial iteration optimizations were alternated until the axial iteration produced an improvement in energy of less than 1 kJ mol^{-1}. We believe that the optimized geometric parameters have converged to within 0.005 Å in bond lengths, 0.5° in bond angles, and 3° in dihedral angles.

Single calculations on the STO-2G optimized structures were carried out with the larger minimal STO-3G basis set[25] (denoted STO-3G//STO-2G) and with the split-valence 4-31G basis set[32] (denoted 4-31G//STO-2G) in order to provide more reliable

---

[14] Garratt, P. J. "Aromaticity"; McGraw-Hill: London, 1971.

[15] Baird, N. C. *J. Am. Chem. Soc.* **1972**, *94*, 4941.

[16] Loos, D.; Leska, J. *Collect. Czech. Chem. Commun.* **1980**, *45*, 187.

[17] Kleier, D. A.; Dixon, D. A.; Lipscomb, W. N. *Theor. Chim. Acta* **1975**, *40*, 33.

[18] Aihara, J. *J. Am. Chem. Soc.* **1976**, *98*, 2750.

[19] Baumann, H. *J. Am. Chem. Soc.* **1978**, *100*, 7196.

[20] Haddon, R. C. *J. Am. Chem. Soc.* **1979**, *101*, 1722.

[21] Leska, J.; Loos, D. *J. Mol. Struct.* **1974**, *21*, 245.

[22] Dashevskii, V. G.; Naumov, V. A.; Zaripov, N. M. *J. Struct. Chem.* **1970**, *11*, 687.

[23] (a) Dewar, M. J. S.; Haselbach, E. *J. Am. Chem. Soc.* **1970**, *92*, 590. (b) Dewar, M. J. S. et al. *QCPE* **1975**, *11*, 279.

[24] See, for example: Richards, W. G.; Scott, P. R.; Colbourn, E. A.; Marchington, A. F. "Bibliography of *Ab Initio* Molecular Wave Functions"; Clarendon Press: Oxford, 1978.

[25] Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

[26] Poppinger, D.; Vincent, M. A.; Hinde, A. L.; Radom, L. unpublished.

[27] Hehre, W. J. et al. *QCPE* **1973**, *11*, 236.

[28] Poppinger, D. *Chem. Phys.* **1976**, *12*, 131.

[29] (a) Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 6941; (b) Haddon, R. C.; Starnes, W. H. *Adv. Chem. Ser.* **1978**, *169*, 133.

[30] (a) Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1. (b) Allinger, N. L. et al. *QCPE* **1976**, *11*, 318.

[31] Poppinger, D. *Chem. Phys. Lett.* **1975**, *35*, 550.

[32] Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.

Table I. Calculated Total Energies (hartrees) of Isomeric [10]Annulenes[a]

isomer	structure	symmetry	STO-2G// STO-2G	STO-3G// STO-2G	4-31G// STO-2G
TCCCC	4	C_2	−368.54025	−379.67876	−383.82527
CCCCC	3	C_s	−368.53397	−379.67424	−383.82188
TCTCC	5	C_2	−368.53530	−379.67351	−383.82073
TCTCC	6	C_s	−368.52163	−379.66065	−383.80697
CCCCC	2	D_{5h}	−368.47590	−379.61482	−383.77322
CCCCC	1	D_{10h}	−368.47035	−379.60882	−383.77637
			STO-3G// STO-3G	4-31G// 4-31G	
CCCCC	2	D_{5h}	−379.61714	−383.78148	
CCCCC	1	D_{10h}	−379.61120	−383.78144	

[a] The notation STO-3G//STO-2G, for example, denotes STO-3G energies calculated with the use of STO-2G optimized geometries.

Table II. Calculated Relative Energies (kJ mol^{-1}) of Isomeric [10]Annulenes[a]

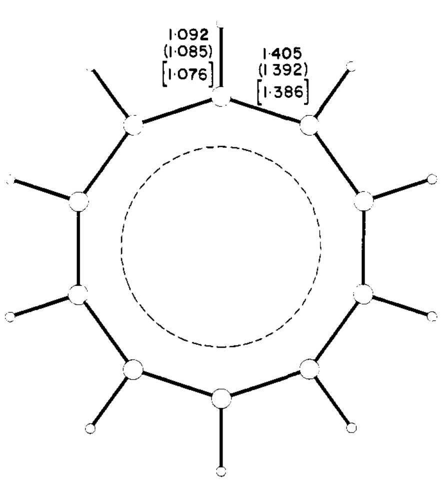
isomer	structure	symmetry	MM[b]	STO-2G// STO-2G	STO-3G// STO-2G	4-31G// STO-2G	exptl
TCCCC	4	C_2	0	0	0	0	obsd
CCCCC	3	C_s	32.6	16.5	11.8	8.9	obsd
TCTCC	5	C_2	13.0[c]	13.0	13.8	11.9	
TCTCC	6	C_s	30.5	48.9	47.5	48.1	
CCCCC	2	D_{5h}	311.0	168.9	167.8	136.7[d]	
CCCCC	1	D_{10h}	313.1	183.5	183.6	128.4[d]	

[a] The notation STO-3G//STO-2G, for example, denotes STO-3G energies calculated with the use of STO-2G optimized geometries. [b] Molecular mechanics results. [c] The optimized molecular mechanics structure actually has C_{2h} symmetry (i.e., is nonalternating). [d] When 4-31G optimized structures are used, 2 lies 0.1 kJ mol^{-1} lower in energy than 1.

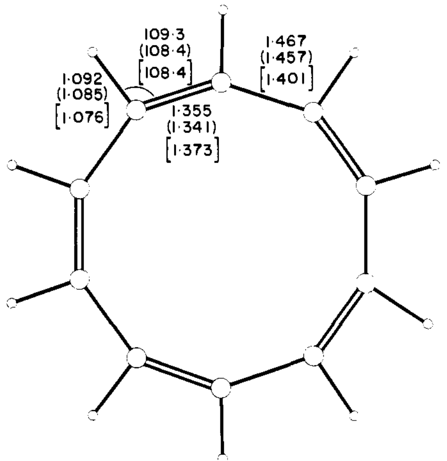
energy comparisons. All the isomers except **1** and **2** turn out to be described by five single C–C and five double C═C bonds so that the energy comparisons are isodesmic[33] and are expected to be reasonably described by the STO-3G and 4-31G basis sets. The intercomparison of **1** and **2** is more sensitive to the level of theory employed and so additional optimizations of these structures were carried out with the STO-3G and 4-31G basis sets. Calculated total and relative energies for all isomers studied are shown in Tables I and II, respectively.

Results and Discussion

Planar *all-cis*-[10]Annulenes (1, 2). The question of bond alternation in polyenes and annulenes has a long history.[34] Restricting ourselves to the annulenes, it has been known for many years[35] that benzene does not show bond alternation. Of larger annulenes with ($4n + 2$) π electrons, [18]annulene has been the most exhaustively studied. Unfortunately, however, there is no clear verdict as to whether or not [18]annulene shows bond alternation. The weight of the experimental evidence seems to tilt slightly in favor of a delocalized structure,[36,37] while theory more often predicts bond alternation.[38–40] A similar relationship appears to apply to the less-studied [14]annulene. In the sense that the hypothetical planar *all-cis*-[10]annulene serves as a bridge between benzene and [14]annulene, the question of bond alternation in this system would appear to fill an important gap.



CCCCC
1 (D_{10h})



CCCCC
2 (D_{5h})

Figure 2. STO-2G (STO-3G in parentheses) [4-31G in square brackets] optimized structures for the *CCCCC* isomers **1** and **2** of [10]annulene.

Bond alternation in planar *all-cis*-[10]annulene can be prevented by forcing the molecule to have D_{10h} symmetry. When this is done, the constrained equilibrium geometry (Figure 2) has bond lengths 1.405 Å (C═C) and 1.092 Å (C–H) [STO-2G], 1.392 Å (C═C) and 1.085 Å (C–H) [STO-3G], or 1.386 Å (C═C) and 1.076 Å (C–H) [4-31G]. Comparison with corresponding results for benzene[41] shows that the hypothetical D_{10h} [10]annulene isomer (**1**) has very similar bond lengths to those in benzene. For benzene, the results are C═C = 1.399 Å, C–H = 1.090 Å (STO-2G); C═C = 1.387 Å, C–H = 1.083 Å (STO-3G); and C═C = 1.384 Å, C–H = 1.072 Å (4-31G) which are close to the experimental[35] C═C = 1.397 Å and C–H = 1.084 Å. The good agreement between the theoretical and experimental bond lengths for benzene[41] and other hydrocarbons[29,42,43] lends confidence to the predictions for the systems examined in this paper.

The possibility of bond alternation for planar *all-cis*-$C_{10}H_{10}$ is introduced by reducing the point-group symmetry to D_{5h}. The STO-2G and STO-3G calculations predict substantial bond al-

---

(33) (a) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796. (b) Radom, L.; Hehre, W. J.; Pople, J. A. *J. Chem. Soc. A.* **1971**, 2299.

(34) Salem, L. "The Molecular Orbital Theory of Conjugated Systems"; Benjamin: New York, 1966.

(35) Langseth, A.; Stoicheff, B. P. *Can. J. Phys.* **1956**, *34*, 350.

(36) Bregman, J.; Hirshfeld, F. L.; Rabinovich, D.; Schmidt, G. M. J. *Acta Crystallogr.* **1965**, *19*, 227.

(37) Oth, J. F. M.; Bunzli, J. C.; de Zelicourt, Y. deJ. *Helv. Chim. Acta* **1974**, *57*, 2276.

(38) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1973**, *95*, 3893.

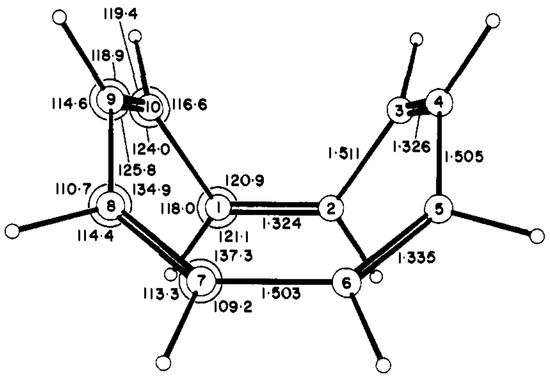
(39) Dewar, M. J. S.; Haddon, R. C.; Student, P. J. *Chem. Commun.* **1974**, 569.

(40) Haddon, R. C. *Chem. Phys. Lett.* **1980**, *70*, 210.

(41) (a) Radom, L.; Schaefer, H. F. *J. Am. Chem. Soc.* **1977**, *99*, 7522. (b) The STO-2G and 4-31G calculations were carried out in the present study and yield total energies of −221.20648 (STO-2G//STO-2G) and −230.37778 (4-31G//4-31G) hartrees.

(42) Lathan, W. A.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 808.

(43) Radom, L.; Lathan, W. A.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 5339.



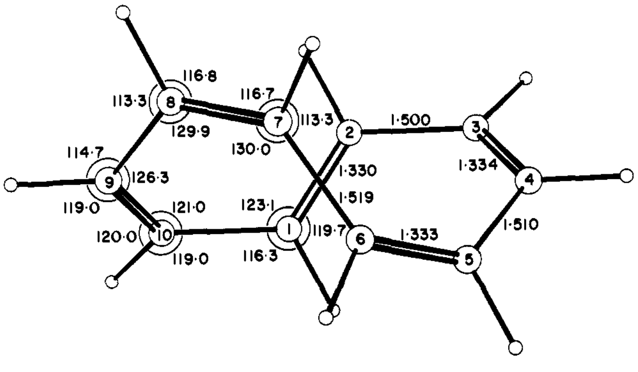
$\angle C_{10}C_1C_2C_3 = \angle C_8C_7C_6C_5 =$ 0·0
$\angle C_1C_2C_3C_4 = -\angle C_2C_1C_{10}C_9 =$ 89·1
$\angle C_2C_3C_4C_5 = -\angle C_1C_{10}C_9C_8 =$ 11·5
$\angle C_3C_4C_5C_6 = -\angle C_{10}C_9C_8C_7 =$ −61·6
$\angle C_4C_5C_6C_7 = -\angle C_9C_8C_7C_6 =$ 9·6

$\angle H_1C_1C_2C_3 = -\angle H_2C_2C_1C_{10} =$ 178·1
$\angle H_{10}C_{10}C_9C_8 = -\angle H_3C_3C_4C_5 =$ 171·8
$\angle H_9C_9C_{10}C_1 = -\angle H_4C_4C_3C_2 =$ 178·9
$\angle H_8C_8C_7C_6 = -\angle H_5C_5C_6C_7 =$ −171·5
$\angle H_7C_7C_8C_9 = -\angle H_6C_6C_5C_4 =$ −176·4

CCCCC

3 (C_s)

Figure 3. STO-2G optimized structures for the nonplanar *CCCCC* isomer 3 of [10]annulene.



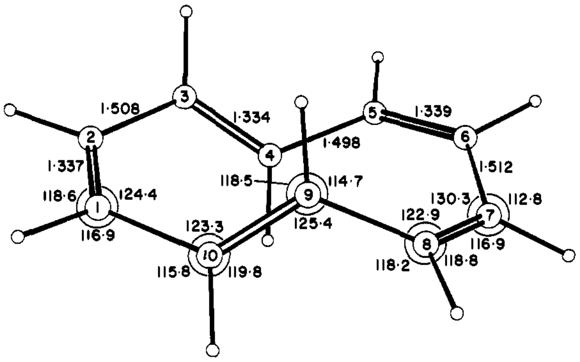
$\angle C_{10}C_1C_2C_3 =$ 155·1
$\angle C_1C_2C_3C_4 = \angle C_9C_{10}C_1C_2 =$ −49·1
$\angle C_2C_3C_4C_5 = \angle C_8C_9C_{10}C_1 =$ 2·0
$\angle C_3C_4C_5C_6 = \angle C_7C_8C_9C_{10} =$ −44·0
$\angle C_4C_5C_6C_7 = \angle C_6C_7C_8C_9 =$ −8·1
$\angle C_5C_6C_7C_8 =$ 131·3

$\angle H_1C_1C_2C_3 = \angle H_2C_2C_1C_{10} =$ −13·4
$\angle H_3C_3C_4C_5 = \angle H_{10}C_{10}C_9C_8 =$ 179·4
$\angle H_4C_4C_3C_2 = \angle H_9C_9C_{10}C_1 =$ 179·8
$\angle H_5C_5C_6C_7 = \angle H_8C_8C_7C_6 =$ 173·4
$\angle H_6C_6C_5C_4 = \angle H_7C_7C_8C_9 =$ 177·6

TCCCC

4 (C_2)

Figure 4. STO-2G optimized structure for the *TCCCC* isomer 4 of [10]annulene.

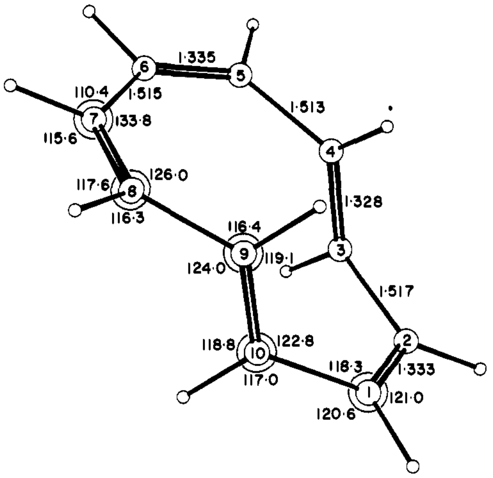


$\angle C_5C_6C_7C_8 =$ −33·7
$\angle C_4C_5C_6C_7 = \angle C_6C_7C_8C_9 =$ 2·1
$\angle C_3C_4C_5C_6 = \angle C_7C_8C_9C_{10} =$ 120·6
$\angle C_2C_3C_4C_5 = \angle C_8C_9C_{10}C_1 =$ −153·2
$\angle C_1C_2C_3C_4 = \angle C_9C_{10}C_1C_2 =$ 37·1
$\angle C_{10}C_1C_2C_3 =$ −1·4

$\angle H_1C_1C_2C_3 = \angle H_2C_2C_1C_{10} =$ −179·5
$\angle H_3C_3C_4C_5 = \angle H_{10}C_{10}C_9C_8 =$ 14·0
$\angle H_4C_4C_3C_2 = \angle H_9C_9C_{10}C_1 =$ 12·5
$\angle H_5C_5C_6C_7 = \angle H_8C_8C_7C_6 =$ 177·5
$\angle H_6C_6C_5C_4 = \angle H_7C_7C_8C_9 =$ −179·3

TCTCC

5 (C_2)



$\angle C_5C_6C_7C_8 = \angle C_{10}C_1C_2C_3 =$ 0·0
$\angle C_9C_{10}C_1C_2 = -\angle C_1C_2C_3C_4 =$ 72·1
$\angle C_8C_9C_{10}C_1 = -\angle C_2C_3C_4C_5 =$ −157·6
$\angle C_7C_8C_9C_{10} = -\angle C_3C_4C_5C_6 =$ 88·0
$\angle C_6C_7C_8C_9 = -\angle C_4C_5C_6C_7 =$ 9·0

$\angle H_1C_1C_2C_3 = -\angle H_2C_2C_1C_{10} =$ −176·3
$\angle H_{10}C_{10}C_9C_8 = -\angle H_3C_3C_4C_5 =$ 8·6
$\angle H_9C_9C_{10}C_1 = -\angle H_4C_4C_3C_2 =$ 14·1
$\angle H_8C_8C_7C_6 = -\angle H_5C_5C_6C_7 =$ −177·4
$\angle H_7C_7C_8C_9 = -\angle H_6C_6C_5C_4 =$ −174·0

CTCTC

6 (C_s)

Figure 5. STO-2G optimized structures for the *TCTCC* isomers **5** and **6** of [10]annulene.

ternation (Figure 2). Alternate CC bonds in the ring are 1.355 and 1.467 Å (STO-2G) or 1.341 and 1.457 Å (STO-3G). Nonetheless, the energy of the D_{5h} structure (2) is only 16 kJ mol^{-1} below that of the delocalized D_{10h} structure (1) at these levels of theory. By way of comparison, [18]annulene shows a much larger energy lowering (150 kJ mol^{-1}, STO-3G) when bond alternation is allowed.[40] We find that bond alternation also occurs in the more reliable 4-31G surface but the extent of geometric distortion (CC lengths of 1.373 and 1.401 Å) is considerably less than with STO-2G and STO-3G, and the energy lowering (0.1 kJ mol^{-1}) is very small indeed. The process of testing for distortions from D_{10h} symmetry requires care since three of the variables (the two C–C lengths and the HCC bond angle) are strongly coupled. The downhill valley corresponds to changes in all three parameters. We conclude that the potential energy surface for *planar* [10]-annulene is very flat in the vicinity of the D_{10h} structure. Higher level calculations would be required to provide a definitive answer to the question of whether or not there is a small degree of bond alternation.

Nonplanar *all-cis*-[10]Annulene (3). Optimization of the boat structure 3 was carried out with a C_s symmetry constraint (i.e., a plane of symmetry which makes carbon atoms 1 and 2 equivalent) yielding the optimized structure shown in Figure 3. One of the more obvious features of this isomer is the suitability of the name 1,3,5,7,9-cyclodecapentaene. There are five well-defined C=C double bonds of length 1.324, 1.326 (two of these), and 1.335 Å (two) and five equally conventional C–C single bonds of length 1.511 (two), 1.505 (two), and 1.503 Å. Thus, it is clear that *all-cis*-[10]annulene should bear few if any signs of aromaticity. The strong tendency to avoid the 144° CCC bond angles of the planar "aromatic" structure is also seen in Figure 3. However, there is still quite a range of CCC angles from 137.3° near the front (as depicted in Figure 3) of the boat to 120.8° at the rear of the boat.

The energy of 3 is about 130 kJ mol^{-1} (4-31G//STO-2G) below that of the planar D_{5h} structure 2. It is clear that there is a large stabilization which accompanies distortions from planarity.

***TCCCC* [10]Annulene (4).** The predicted structure for the propeller-shaped isomer 4, optimized under a C_2 (twofold axis bisecting the bonds C_1=C_2 and C_6—C_7) symmetry constraint, is displayed in Figure 4. This minimum on the $C_{10}H_{10}$ potential energy surface is qualitatively very similar indeed to that suggested by Masamune.[7,8] The range of C=C bond distances in **4** is extremely narrow with the five values being 1.332, 1.333 (two), and 1.334 Å (two). A slightly larger spectrum of C–C distances is predicted, namely 1.519, 1.510 (two), and 1.500 Å (two), with all five lying within the normal range of carbon–carbon single bonds. This isomer is seen to be even more effective than the all-cis form (**3**) in reducing the 144° CCC bond angles required by the D_{10h} aromatic structure. The largest CCC bond angle in **4** is 130.0° while the smallest is 121.0°. In this structure, the $C_{10}C_1C_2C_3$ dihedral angle is found to be 155.1°, significantly different from the 180° for an ideal trans configuration. **4** is predicted to lie 9 kJ mol^{-1} (4-31G//STO-2G) below **3**.

***TCTCC* [10]Annulenes (5 and 6).** Optimized geometries have been obtained for two conformations (**5** and **6**) of the *TCTCC* isomer of [10]annulene (Figure 5). The lower energy form is **5** with C_2 symmetry and a twofold axis bisecting the $C_1{=}C_2$ and $C_6{-}C_7$ bonds. As for the previous isomers **3** and **4**, the name 1,3,5,7,9-cyclodecapentaene is very appropriate. The double bond lengths are 1.339 (two), 1.334 (two), and 1.337 Å, while the single bonds are of lengths 1.512, 1.498 (two), and 1.508 Å (two). None of the CCC angles is particularly strained with the five independent angles falling between 122.9° and 130.3°. The $C_1C_{10}C_9C_8$ and $C_2C_3C_4C_5$ dihedral angles are −153.2°, again significantly distorted from 180°. The predicted structure of **5** contrasts with that determined experimentally[41] for crystals of a derivative of Vogel's methano-bridged system (**13**). Whereas the carbon ring in the methano-bridged system is very similar to that of **5** in being almost planar, the range of CC bond lengths in **13** is only 1.38–1.42 Å, i.e., there is no longer a separation into single and double bonds.

5 is predicted to lie only 12 kJ mol^{-1} (4-31G//STO-2G) above the *TCCCC* isomer **4**. Thus we would predict that **5** may well be an observable isomer of [10]annulene.

The second conformation (**6**) of the *TCTCC* isomer was optimized under a C_s symmetry constraint with the plane of symmetry bisecting the bonds $C_1{=}C_2$ and $C_6{-}C_7$. Strong alternation of bond lengths is again evident. **6** lies 36 kJ mol^{-1} above **5** or 48 kJ mol^{-1} above **4**. As with **5**, the $C_8C_9C_{10}C_1$ and $C_5C_4C_3C_2$ dihedral angles are noticeably different from 180°, namely ±155.2°.

Concluding Remarks

The structures and energies of the [10]annulenes predicted here from ab initio molecular quantum mechanical calculations are for the most part consistent with the picture obtained indirectly from experiment by Masamune and co-workers.[7,8,12,13] The two structures **3** (all-cis) and **4** (*TCCCC*) observed by Masamune are indeed those predicted by the theory to lie lowest in energy. A third low-energy isomer **5** (*TCTCC*), lying just 3 kJ mol^{-1} above **3**, has been identified as a reasonable target for experimental observation. The equilibrium geometries of **3**–**6** are all appropriately described as 1,3,5,7,9-cyclodecapentaene and thus show no structural signs of aromaticity. The energy of the planar D_{10h} structure (**1**) of [10]annulene is found, at the 4-31G level, to decrease slightly in moving to a bond-alternating D_{5h} structure (**2**). The energy lowering, however, is not large enough for this result to be regarded as definitive. Higher levels of theory will be required to resolve the question of whether or not planar [10]annulene exhibits bond alternation. Both **1** and **2** lie considerably higher in energy than the nonplanar structures **3**–**6**.

Acknowledgment. H.F.S was supported by the U.S. National Science Foundation Grant CHE-7622621 and by the NSF U.S.–Australian Cooperative Science Program. We thank Professor E. R. Davidson and Dr. R. C. Haddon for helpful comments on the manuscript.

Molecular Mechanics Calculations and Experimental Studies of Conformations of δ-Valerolactone

Thomas Philip, Robert L. Cook, Thomas B. Malloy, Jr., Norman L. Allinger,*[1] Scott Chang, and Young Yuh

Contribution from the Department of Physics and Department of Chemistry, Mississippi State University, Mississippi State, Mississippi 39762, and the Department of Chemistry, University of Georgia, Athens, Georgia 30602. Received March 4, 1980

Abstract: The microwave spectrum of the title compound has been determined in the gas phase at room temperature, and the Raman spectrum has been determined on the liquid at room temperature and on the solid at 73 K. From the experimental data it is concluded that there are two conformers separated in energy by approximately 0.6 kcal/mol, and only the more stable one persists in the crystal. The more stable conformer has a very small (<0.1 D) μ_c component of the dipole moment, while this component is much greater for the less stable conformer. The rotational constants for the two conformations have been determined and are substantially different. The use of the molecular mechanics (MM2) program indicates two stable conformers, a half-chair and a boat form. The former is calculated to be 0.54 kcal/mol more stable and to have a value of μ_c about 0.02 D. The value for μ_c predicted for the boat conformer is approximately 1 D. The rotational constants calculated for the two conformations are in agreement with the experimental ones only if the half-chair conformation is the more stable.

Introduction

There have been numerous studies, both theoretical and experimental, of the conformations of cyclic molecules. Various experimental techniques including vibrational spectroscopy, rotational spectroscopy, NMR, and electron diffraction yield information relating to the identity of the stable conformations and the presence or absence of metastable conformers. Several reviews of experimental studies have appeared recently. Applications of microwave spectroscopy to small-ring molecules have been given by Gaylord and Gwinn,[2] of laser Raman studies by Wurrey et al.[3] and of Raman and far-infrared spectroscopy by Carreira et al.[4] and Malloy et al.[5] Strauss[6] has recently reviewed spectroscopic

---

(1) To whom correspondence should be addressed at the University of Georgia.

(2) W. D. Gwinn and A. S. Gaylord, *MTP Int. Rev. Sci.: Phys. Chem., Ser. Two*, 3, (1976).

(3) C. J. Wurrey, L. A. Carreira, and J. R. Durig *Vib. Spectra Struct.*, 5, Chapter 4 (1976).

0002-7863/81/1503-2151$01.25/0