[10]Annulene: The Wealth of Energetically Low-Lying Structural Isomers of the Same $(CH)_{10}$ Connectivity

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Received April 5, 1993. Revised Manuscript Received December 7, 1993[®]

Abstract: *Ab initio* quantum mechanical methods, as well as molecular mechanics (MM2 and MM3) and semiempirical theoretical methods (AM1), have been used to predict the molecular structures and energetics of the plausible isomers of [10]annulene. Standard double-ζ (DZ) and double-ζ plus polarization (DZP) basis sets have been used for the *ab initio* self-consistent-field (SCF) studies. Full geometry optimizations have been carried out by these different methods. The harmonic vibrational frequencies and their infrared intensities are also predicted for all these isomers. The most likely observable isomers are the two structures with C_2 symmetry, one of which could be called naphthalene-like and the other twisted. Isomers with C_s (including a low-lying boat-like structure) and C_1 (including a low-lying azulene-like structure) symmetries are also discussed. The aromatic character for the planar isomers, which are not local minima, has been studied using second-order perturbation theory. A random conformational searching procedure based on the MM3 method was also carried out to avoid losing any possible energetically low-lying conformations. The latter procedure uncovered one low-lying structure that had never been suggested previously. A comparison with the experimental conclusions of Masamune and co-workers is made.

Introduction

Since the structure of benzene (or [6]annulene) was determined in 1865, aromatic compounds have been a very important part of organic chemistry. And so the attempt to find other cyclic, conjugated polyenes has become a popular subject. Disappointing to many, the properties of the next closed-shell candidate, cyclooctatetraene ([8]annulene)—which was prepared in 1911—are quite different from those of aromatic compounds. After Huckel's $4n + 2$ rule had been put forward in 1932, [10]-annulene was expected to be the next homolog of benzene. However, the latter was not synthesized until 8 years after [18]-annulene was reported by Sondheimer[1] in 1959. The transient existence of cyclodecapentaene ([10]annulene) was first reported by van Tamelen and Burkoth in 1967.[2] In 1969, Masamune and co-workers[3-5] reported that they isolated two isomers of [10]-annulenes in crystalline form, and they qualitatively assigned the geometries of these structures on the basis of the NMR and UV spectra. They concluded that the [10]annulenes are not planar in structure, and accordingly have no aromatic character.

In the 1970s several empirical and semiempirical theoretical studies on [10]annulenes were published.[6,7] The first systematic *ab initio* study on plausible structures of [10]annulenes was made by Farnell, Kao, Radom, and Schaefer[8] in 1981. They optimized (but kept all C–H bond lengths fixed at 1.09 Å) six structurse of isomeric [10]annulenes at the STO-2G and STO-3G SCF levels of theory and predicted the relative stabilities of these isomers. However, with a decade's hindsight, the minimum basis sets may be seen to be inadequate, and so full geometry optimizations at a higher level of theory are certainly in order. Moreover, the vibrational character of the lower symmetry $C_{10}H_{10}$ stationary points has never been established. Although Haddon and Raghavachari carried out much improved *ab initio* calculations with split valence basis sets,[9,10] their work was limited to the planar structures, which we will demonstrate are not local minima on the potential surface. The present paper will study both the planar structures of [10]annulene with their aromatic purported character and the other energetically lower-lying structures which might be observable in the laboratory.

Theoretical Approach

In this research, full geometry optimizations and harmonic vibrational frequency analyses were carried out by the self-consistent-field (SCF) method in conjunction with two basis sets for eight possible isomers of [10]annulenes. The first basis was the double-ζ (DZ) set of Huzinaga[11] and Dunning,[12] which may be designated as C(9s5p/4s2p) and H(4s/2s). The second basis was the DZ set appended with pure angular momentum (i.e., five functions for the d shell) polarization functions (DZP) with $\alpha_d(C) = 0.75$ and $\alpha_P(H) = 0.75$. Single-point energies were also evaluated by using second-order Møller–Plesset perturbation theory (MP2) to study the effects of electron correlation. The *ab initio* research reported here was carried out by using the programs TURBOMOLE (the direct SCF approach of Ahlrichs and co-workers[13]), PSI, developed in our research group,[14] and Gaussian 92.[15]

In addition, two kinds of empirical molecular mechanics[16] (MM2 and MM3) methods and one semiempirical (AM1[17]) method were employed

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[®] Abstract published in *Advance ACS Abstracts*, February 1, 1994.

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Chart 1

Structure 1 (D_{10h})

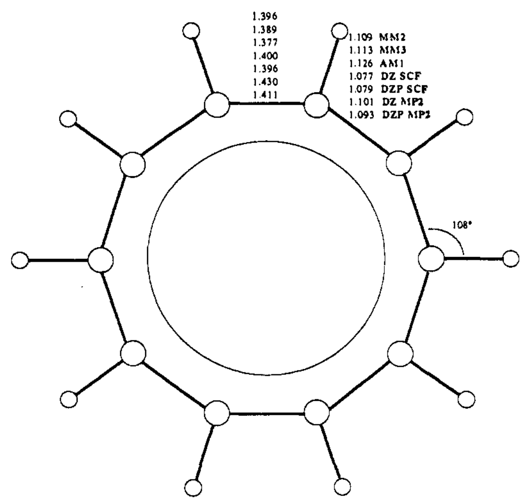
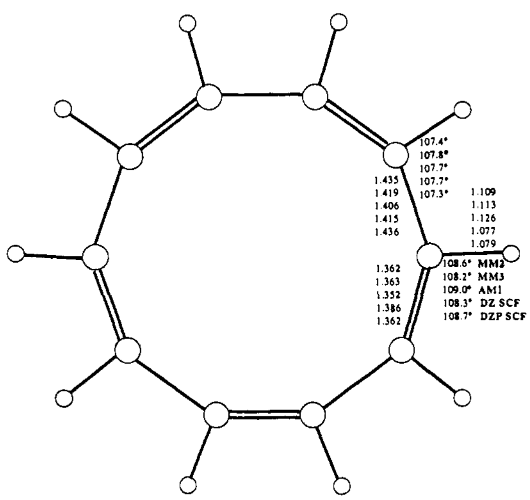


Chart 2

Structure 2 (D_{5h})



for comparison. The MM3 program[18,19] (92 version) was also used to do random conformational searching.

Results and Discussion

Planar Structures. The planar *all-cis* structures **1** (D_{10h}) and **2** (D_{5h}) have drawn the most attention from previous theoretical researchers.[9,10] While benzene is the first stable aromatic species ($n = 1$ from Huckel's $4n + 2$ rule), the planar [10]annulene should be the next one ($n = 2$). The optimized geometrical parameters of structures **1** and **2** at various levels of theory are shown in Charts 1 and 2, while their vibrational frequencies are given in Tables A and B (supplementary material), and energies in Table 4. Due to the D_{10h} symmetry constraint, the ring structure of **1** has identical C–C bond lengths. The theoretical results are qualitively in agreement among the different methods, and are encouragingly close to those of benzene. Electron correlation effects increase the C–C bond length from 1.400 (DZ SCF) to 1.430 Å (DZ MP2), the latter value being artificially long due to the incompleteness of the DZ basis set. The addition of polarization functions has little effect on the *ab initio* SCF structures. However, polarization functions make a significant change for the MP2 structure, decreasing the C–C bond length to 1.411 Å (DZP MP2). The empirical MM2 and MM3 results (1.396 and 1.389 Å) are basically in agreement with the *ab initio* predictions, while the AM1 C–C bond length (1.377 Å) is slightly shorter. The stationary point geometry for structure **2** (D_{5h}) has alternating single C–C and double bonds at the SCF level of theory, although the extent of bond alternation is much less than one might expect from standard single and double bond distances (1.35, 1.54 Å). These bond lengths are close to those in cyclobutadiene and cyclooctatetraene. Similar to the results of ref 9, our work shows that the SCF treatment favors the bond alternating structure **2**, but the energy difference between **1** and **2** is very small (<1 kcal/mol; see Table 4). Using the empirical and semiempirical methods, the D_{5h} structure also has a slightly lower energy than the D_{10h}. Accordingly, structure **1** (D_{10h})—in addition to the degenerate imaginary frequency related to the ring puckering modes for structure **2** (D_{5h})—has one more imaginary vibrational frequency related to the C–C stretch mode. Rather surprisingly, the C–C stretching fundamental of b_{2u} symmetry for the D_{10h} structure (1953 cm^{-1}) is not predicted to be imaginary with the MM3 method, while its total energy is still higher than that of the D_{5h} structure. Since the energy differences between **1** and **2** are very small—i.e., only 2.18 (MM2), 1.18 (MM3), 0.67 (AM1), 0.02 (DZ SCF), and 0.66 (DZP SCF) kcal/mol, respectively—it is possible that the order of energy might be reversed at higher levels of theory.

As a matter of fact, the MP2 single point energies at the DZ and DZP SCF stationary point geometries for the D_{10h} structure are lower than those of the D_{5h} structure (0.89 kcal/mol with the DZ basis set, and 6.89 kcal/mol with the DZP basis set). When we optimize the geometries at the DZ MP2 and DZP MP2 levels, the D_{5h} structure is no longer a stationary point; it collapses to the same D_{10h} structure with longer C–C (1.430 Å) and C–H (1.101 Å) bond lengths. If the MP2 results are correct, then the MM2, MM3, AM1, and SCF methods all inproperly characterize this D_{5h} feature of the $C_{10}H_{10}$ potential energy hypersurface. This is consistent with the statement made in refs 7 and 10 that SCF and semiempirical methods prefer the localized π bonding structure, while electron correlation favors the delocalized one. Unfortunately, although these two planar structures are favorable for π electron occupation (predicted aromatic by Huckel's $4n + 2$ rule), their σ skeletons exhibit such severe angle strain that the ring structures tend to twist or pucker. That is whay our theoretical study gives two imaginary vibrational frequencies (see Tables A and B in the supplementary material) and quite high relative energies (see Table 4). Therefore, these very high symmetry structures will not be observable in the laboratory.

We emphasize that in going from the DZ to the DZP basis set, the D_{10h} C–C bond distance at the MP2 level decreases from an unreasonably long 1.430 Å to 1.411 Å. Thus the predicted carbon–carbon distances for other [10]annulene DZ MP2 structures should reasonably be reduced by ~0.02 Å if comparison with experimental structures becomes possible in the future.

C_2 Symmetry Structures. Following the previous lower-level theoretical results of ref 8, we have obtained two energetically favorable structures with C_2 symmetry (**4** and **5**). Structure **4** (TCCCC) may be called twisted or propeller-shaped and structure **5** (TCTCC) naphthalene-like. Charts 4 and 5 show that both optimized geometries, with all methods we used, exhibit alternating single and double bonds. An inset to structure **5** demonstrates that the naphthalene-like structure is also chair-like. The geometrical parameters optimized at different theoretical levels are in reasonable agreement. Since correlation effects would probably favor the delocalized π bonding structure,[6,7] as in the comparison between structures **1** and **2**, the alternating C–C single and double bonds in structures **4** and **5** should more closely approach parity when correlation is properly taken into account. However, such an effect should not be as strong as for the planar structures, so this remains a question to be resolved by further study with high-level theoretical treatments. The probable

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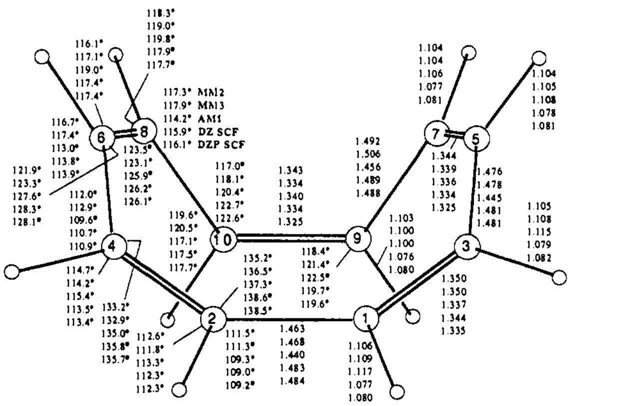
Chart 3

Structure 3 (C_s)

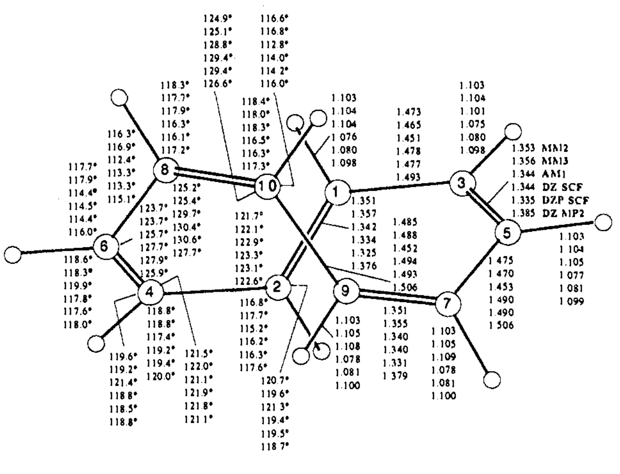


Dihedral Angles:

$\tau_{4-2-1-3}$	$\tau_{2-1-3-5}$	$\tau_{1-3-5-7}$	$\tau_{3-5-7-9}$	$\tau_{5-7-9-10}$	$\tau_{7-9-10-8}$	$\tau_{6-4-2-H}$	$\tau_{1-2-4-H}$	$\tau_{10-8-6-H}$	$\tau_{4-6-8-H}$	$\tau_{7-9-10-H}$
0.0°	12.0°	-66.1°	16.0°	88.8°	0.0°	178.9°	164.3°	-169.2°	153.0°	155.0°
0.0°	12.5°	-63.6°	13.9°	89.9°	0.0°	175.8°	165.7°	-176.5°	167.2°	175.8°
0.0°	-0.2°	-68.3°	11.3°	87.4°	0.0°	179.2°	-178.3°	176.1°	172.0°	178.7°
0.0°	4.7°	-61.0°	8.2°	87.9°	0.0°	-179.4°	-174.0°	-179.6°	172.8°	177.7°
0.0°	4.0°	-61.8°	8.5°	87.9°	0.0°	-179.6°	-174.4°	-179.4°	172.5°	177.3°

Chart 4

Structure 4 (C_2)



Dihedral Angles:

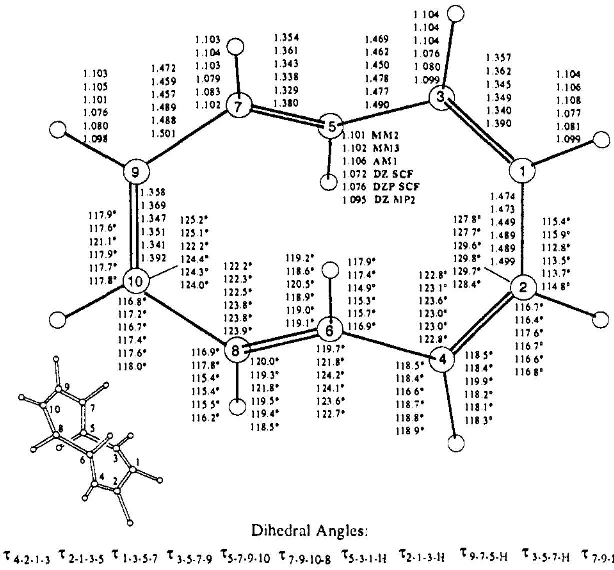
$\tau_{4-2-1-3}$	$\tau_{2-1-3-5}$	$\tau_{1-3-5-7}$	$\tau_{3-5-7-9}$	$\tau_{5-7-9-10}$	$\tau_{7-9-10-8}$	$\tau_{6-4-2-H}$	$\tau_{8-6-4-H}$	$\tau_{10-8-6-H}$	$\tau_{9-10-8-H}$	$\tau_{7-9-10-H}$
152.9°	-42.5°	-1.9°	-37.3°	-17.3°	129.6°	127.9°	174.0°	145.2°	169.0°	-53.2°
151.2°	-40.9°	-3.5°	-36.9°	-16.8°	128.3°	130.0°	172.4°	150.0°	166.7°	-55.7°
155.1°	-51.7°	7.1°	-49.0°	-6.7°	107.9°	119.9°	-177.2°	134.2°	174.1°	-75.8°
151.3°	-50.1°	4.3°	-47.2°	-7.0°	104.4°	117.6°	179.7°	136.1°	173.5°	-80.0°
151.3°	-50.8°	5.2°	-48.3°	-6.4°	103.3°	116.6°	179.7°	135.5°	173.7°	-81.4°
151.5°	-46.7°	3.4°	-48.0°	-8.1°	112.5°	121.2°	179.5°	135.5°	173.7°	-70.5°

unimportance of such higher order effects is indicated by the fact that the MM2 and MM3 methods predict longer C–C double bonds and shorter single bonds than those predicted by *ab initio* methods. Table 4 shows that structures **4** and **5** have lower energy than the other $C_{10}H_{10}$ structures, with a very small difference between the two.

To consider the point raised in the previous paragraph, structures **4** and **5** were reoptimized at the DZ MP2 level of theory. As speculated above, there is some decrease in the extent of bond alternation. As expected, all C—C bond distances increase in going from DZ SCF to DZ MP2. However the C=C double bond distances increase by about 0.040 Å, while the C—C single bond distances increase by about 0.015 Å. Thus the extent of bond alternation is decreased by about 0.025 Å. Nevertheless, the extent of bond distance alternation remains substantial, in the range 0.11–0.14 Å.

Chart 5

Structure 5 (C_2)



Dihedral Angles:

$\tau_{4-2-1-3}$	$\tau_{2-1-3-5}$	$\tau_{1-3-5-7}$	$\tau_{3-5-7-9}$	$\tau_{5-7-9-10}$	$\tau_{7-9-10-8}$	$\tau_{5-3-1-H}$	$\tau_{2-1-3-H}$	$\tau_{9-7-5-H}$	$\tau_{3-5-7-H}$	$\tau_{7-9-10-H}$
-31.2°	-5.2°	130.4°	-148.5°	33.4°	0.8°	176.6°	169.4°	10.9°	20.3°	-175.5°
-27.5°	-5.5°	131.8°	-149.9°	29.6°	3.7°	174.5°	170.1°	12.7°	21.3°	-173.1°
-30.1°	0.8°	117.7°	-159.0°	44.1°	-7.2°	179.6°	179.8°	13.1°	13.4°	176.6°
-35.8°	0.8°	121.5°	-151.1°	41.7°	-7.4°	179.6°	177.0°	13.6°	15.5°	178.4°
-37.8°	1.6°	121.0°	-150.8°	42.8°	-8.3°	-179.8°	177.1°	13.3°	15.4°	178.2°
-35.8°	-0.2°	125.5°	-151.5°	40.1°	-7.1°	178.7°	175.8°	15.2°	14.5°	178.6°

Empirical and semiempirical methods predict that the energy of the naphthalene-like **5** is lower than that of the twisted **4**, i.e., by 3.62 (MM2), 4.82 (MM3), and 0.68 (AM1) kcal/mol, respectively. The *ab initio* SCF results, in contrast, show that structure **4** has the lower energy. But the MP2 single-point energies significantly reduce the difference (from 2.96 to 1.94 kcal/mol with the DZ basis set, and from 2.91 to 0.51 kcal/mol with the DZP basis set). It would not be surprising if higher levels of theory (larger basis sets and more complete descriptions of electron correlation) reverse the energetic order of these two structures. In any case, both species are likely to be observable.

The theoretical harmonic vibrational frequencies and their infrared intensities are shown in Tables 1 and 2. The assignments in these tables are based on the potential energy distributions (PED) from the SCF results. The fact that all the vibrational frequencies are real numbers indicates that both structures **4** and **5** are genuine minima. The results are in qualitive agreement among the different theoretical methods, but the MM3 and AM1 frequencies are slightly lower. It is known that DZP SCF frequencies are about 10% higher than the experimental fundamentals, while the empirical and semiempirical results (with parameters obtained by fitting to the experimental data) are generally closer in absolute value to the observed fundamentals. Since structures **4** and **5** are genuine minima with low energies, they are most likely to be observed. The twisted structure **4** has some strong infrared absorption bands (with IR intensities about 40–70 km/mole) around 3100 cm^{-1} related to C—H stretching modes, some bands (with IR intensities about 30–60 km/mole) around 700–800 cm^{-1} related to the C—H wagging and ring deformation modes, and also a weaker band representing a C=C stretching mode at about 1700 cm^{-1} (with IR intensity 28 km/mol). The naphthalene-like structure **5** has a very strong infrared absorption band (with IR intensity more than 100 km/mol) around 700–800 cm^{-1} related to the C–H wagging mode, and then some intense IR bands around 3100 cm^{-1} corresponding to C–H stretching modes.

***C_s* Symmetry Structures.** Structures **3** (CCCCC) and **6** (CTCTC) are predicted to have energies slightly higher than those of structures **4** or **5**. At the SCF level of theory the energy of the boat-like structure **3** is even lower than that of structure

Table 1. Harmonic Vibrational Frequencies and Infrared Intensities for Structure **4** (C_2 Symmetry)

sym	no.	description	MM3	AM1	DZ SCF	DZP SCF
			freq in cm^{-1} (and intensities in km/mol)			
b	1	C—H stretch	3046	3178	3371 (7)	3345 (6)
a	2	C—H stretch	3047	3178	3370 (98)	3344 (73)
b	3	C—H stretch	3036	3166	3354 (71)	3331 (46)
a	4	C—H stretch	3043	3151	3351 (12)	3330 (10)
b	5	C—H stretch	3034	3151	3346 (33)	3327 (21)
a	6	C—H stretch	3036	3146	3344 (66)	3324 (45)
b	7	C—H stretch	3030	3132	3332 (<1)	3313 (<1)
a	8	C—H stretch	3031	3128	3331 (16)	3313 (10)
a	9	C—H stretch	3023	3118	3313 (<1)	3299 (<1)
b	10	C—H stretch	3020	3113	3313 (4)	3299 (3)
a	11	C=C stretch	1691	1940	1874 (1)	1879 (1)
a	12	C=C stretch	1688	1890	1858 (28)	1868 (28)
b	13	C=C stretch	1636	1881	1821 (6)	1829 (5)
a	14	C=C stretch	1615	1840	1809 (1)	1823 (<1)
b	15	C=C stretch	1590	1836	1793 (4)	1808 (3)
a	16	C—H bend	1510	1507	1586 (<1)	1573 (<1)
b	17	C—H bend	1476	1498	1564 (4)	1549 (4)
a	18	C—H bend	1440	1406	1553 (<1)	1531 (1)
b	19	C—H bend	1422	1378	1526 (3)	1494 (4)
a	20	C—H bend	1272	1302	1454 (1)	1431 (3)
b	21	C—H bend	1384	1298	1438 (2)	1408 (<1)
a	22	C—H bend	1240	1265	1405 (<1)	1370 (<1)
b	23	C—H bend	1263	1253	1382 (2)	1350 (3)
a	24	C—H bend	1187	1223	1343 (<1)	1315 (<1)
b	25	C—H bend	1197	1216	1340 (1)	1311 (<1)
b	26	C—C stretch	1045	1193	1161 (<1)	1140 (<1)
a	27	C—H wag	1046	1161	1152 (1)	1129 (<1)
a	28	C—H wag	989	1131	1152 (<1)	1120 (<1)
b	29	C—H wag	968	1107	1147 (<1)	1111 (<1)
b	30	C—H wag	947	1053	1136 (1)	1107 (1)
a	31	C—H wag	942	1020	1130 (15)	1107 (17)
a	32	C—H wag	936	990	1098 (32)	1079 (18)
a	33	C—C stretch	921	987	1046 (23)	1037 (20)
b	34	C—C stretch	896	969	1018 (11)	995 (4)
a	35	C—C stretch	866	950	1005 (11)	989 (7)
b	36	C—H wag	816	937	999 (13)	972 (15)
b	37	C—C stretch	750	900	925 (10)	911 (12)
a	38	C—H wag	777	892	889 (<1)	879 (<1)
b	39	C—H wag	649	841	851 (3)	839 (2)
b	40	C—H wag	607	822	861 (68)	838 (57)
a	41	ring deformation	635	741	819 (42)	796 (33)
a	42	ring deformation	609	740	780 (30)	766 (19)
a	43	ring deformation	518	666	715 (41)	698 (36)
b	44	ring deformation	513	554	614 (5)	600 (5)
b	45	ring deformation	463	501	556 (10)	538 (9)
a	46	ring deformation	446	479	538 (7)	530 (5)
a	47	ring deformation	412	421	492 (22)	481 (20)
b	48	ring deformation	344	351	390 (1)	382 (<1)
a	49	ring deformation	269	276	309 (<1)	304 (<1)
b	50	ring deformation	316	245	306 (1)	302 (1)
b	51	ring deformation	242	200	240 (1)	235 (1)
a	52	ring deformation	223	173	213 (<1)	210 (<1)
b	53	ring deformation	178	148	180 (<1)	177 (<1)
a	54	ring deformation	191	80	153 (<1)	149 (<1)

Table 2. Harmonic Vibrational Frequencies and Infrared Intensities for Structure **5** (C_2 Symmetry)

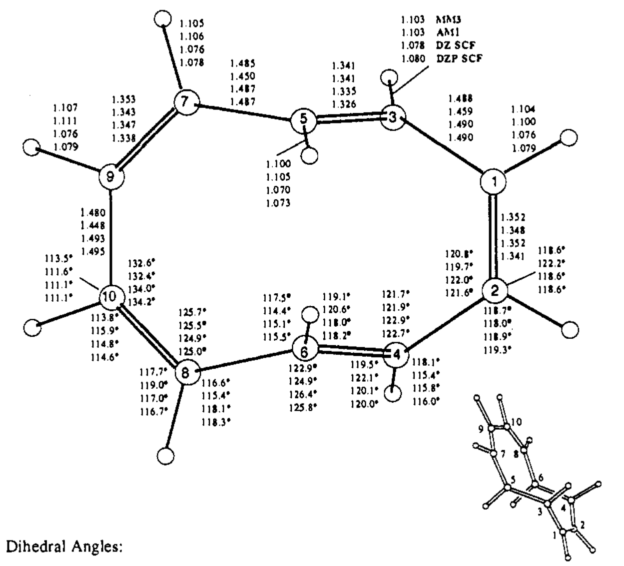
sym	no.	description	MM3	AM1	DZ SCF	DZP SCF
			freq in cm^{-1} (and intensities in km/mol)			
a	1	C—H stretch	3059	3181	3398 (7)	3379 (4)
b	2	C—H stretch	3058	3170	3397 (13)	3379 (7)
a	3	C—H stretch	3041	3169	3372 (10)	3347 (25)
b	4	C—H stretch	3039	3167	3364 (53)	3344 (35)
a	5	C—H stretch	3037	3160	3370 (130)	3344 (70)
b	6	C—H stretch	3036	3159	3341 (12)	3323 (11)
a	7	C—H stretch	3033	3135	3343 (18)	3321 (13)
b	8	C—H stretch	3023	3133	3329 (5)	3312 (5)
a	9	C—H stretch	3020	3131	3320 (2)	3300 (1)
b	10	C—H stretch	3014	3124	3319 (35)	3299 (27)
b	11	C=C stretch	1710	1882	1857 (10)	1866 (10)
a	12	C=C stretch	1714	1895	1851 (<1)	1859 (<1)
a	13	C=C stretch	1634	1865	1785 (8)	1794 (6)
b	14	C=C stretch	1591	1831	1773 (9)	1786 (7)
a	15	C=C stretch	1599	1826	1770 (6)	1782 (6)
a	16	C—H bend	1495	1328	1572 (<1)	1557 (1)
b	17	C—H bend	1491	1298	1550 (5)	1534 (4)
b	18	C—H bend	1452	1273	1546 (<1)	1521 (2)
a	19	C—H bend	1371	1306	1466 (<1)	1438 (1)
b	20	C—H bend	1370	1253	1463 (2)	1434 (4)
a	21	C—H bend	1294	1274	1433 (1)	1403 (<1)
b	22	C—H bend	1242	1206	1424 (3)	1391 (3)
a	23	C—H bend	1265	1229	1371 (3)	1336 (1)
b	24	C—H bend	1203	1143	1357 (2)	1325 (2)
a	25	C—H bend	1197	1198	1196 (2)	1181 (2)
a	26	C—C stretch	1128	1503	1196 (2)	1181 (2)
b	27	C—C stretch	1095	1482	1187 (<1)	1179 (<1)
b	28	C—H wag	1049	1004	1169 (86)	1144 (61)
a	29	C—H wag	1055	998	1165 (1)	1139 (<1)
a	30	C—H wag	994	975	1142 (<1)	1112 (<1)
b	31	C—H wag	1032	984	1135 (3)	1100 (3)
a	32	C—H wag	980	954	1133 (<1)	1095 (<1)
b	33	C—C stretch	953	1407	1111 (20)	1093 (27)
a	34	C—C stretch and C—H wag	905	1145	1033 (15)	1016 (6)
b	35	C—H wag	834	982	1017 (16)	977 (16)
a	36	C—H wag and C—C stretch	854	920	985 (26)	965 (22)
a	37	C—C stretch and C—H wag	805	1077	953 (9)	937 (28)
b	38	ring deformation	797	860	921 (14)	901 (14)
a	39	C—H wag	676	845	874 (22)	851 (23)
b	40	C—H wag and ring deformation	717	826	850 (10)	837 (4)
b	41	C—H wag	627	792	855 (135)	828 (106)
b	42	C—H wag and ring deformation	592	677	718 (11)	686 (9)
a	43	ring deformation	574	600	650 (4)	639 (6)
a	44	ring deformation	528	589	626 (<1)	618 (<1)
a	45	ring deformation	498	523	596 (2)	583 (2)
b	46	ring deformation	423	444	465 (3)	459 (2)
a	47	ring deformation	432	369	419 (<1)	408 (<1)
b	48	ring deformation	359	360	408 (17)	401 (14)
a	49	ring deformation	333	315	344 (<1)	337 (<1)
a	50	ring deformation	309	273	291 (1)	284 (2)
b	51	ring deformation	302	257	277 (3)	271 (3)
b	52	ring deformation	247	189	224 (1)	218 (1)
b	53	ring deformation	191	181	206 (<1)	202 (<1)
a	54	ring deformation	163	123	160 (<1)	158 (<1)

5 (see Table 4), which supports the explanation of the NMR measurements.[3,4] However, the MP2 method raises the boat-like structure **3** significantly above the naphthalene-like structure **5** in energy. Molecular mechanics methods and AM1 also show that structure **3** is of higher relative energy. The energy of structure **6** is even higher (MM2 failed to optimize the C_s geometry of structure **6**, diverting instead of structure **8**). Both structures **3** and **6**, like structures **4** and **5**, involve alternating single and double bonds. The bond lengths are basically similar to those of structures **4** or **5** at all levels of theory. Similar to structures **4** and **5**, the MM2 and MM3 methods predict longer C–C double bonds and shorter single bonds than those predicted by *ab initio* methods. However, both structures **3** and **6** are transition states with the imaginary vibrational frequency related to the ring deformation mode (except for the AM1 method, which predicts that **6** is a minimum; see Tables C and D in the supplementary material). This seems contrary to the experimental reports[3-5] concerning the observation of the boat-like structure **3**. However, since the magnitudes of the imaginary vibrational frequencies are quite small (only 20–30i cm^{-1} for structures **3**; slightly larger for structures **6**, but real for AM1), the imaginary frequencies might conceivably become real at higher theoretical levels. In addition, the energies of structures **3** and **6** are only about 10 kcal/mol above those of structures **4** and **5**, so we cannot absolutely exclude the possibility of their observation (especially structure **3**) by experiment.

In light of the visual similarity of the boat-like structure **3** to cyclooctatetraene (COT), some comparison is in order. In fact,

Chart 6

Structure 6 (C_s)

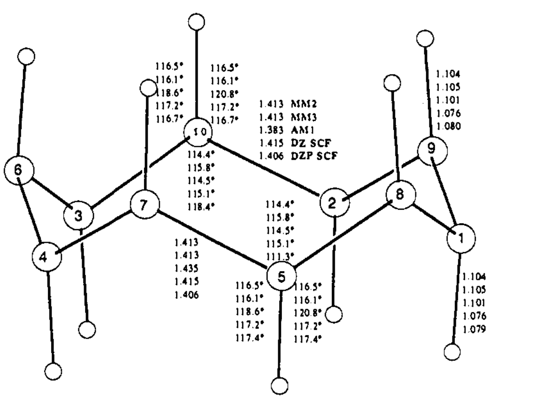


Dihedral Angles:

$\tau_{4\text{-}2\text{-}1\text{-}3}$	$\tau_{2\text{-}1\text{-}3\text{-}5}$	$\tau_{1\text{-}3\text{-}5\text{-}7}$	$\tau_{3\text{-}5\text{-}7\text{-}9}$	$\tau_{5\text{-}7\text{-}9\text{-}10}$	$\tau_{7\text{-}9\text{-}10\text{-}8}$	$\tau_{6\text{-}4\text{-}2\text{-}H}$	$\tau_{8\text{-}6\text{-}4\text{-}H}$	$\tau_{2\text{-}4\text{-}6\text{-}H}$	$\tau_{9\text{-}10\text{-}8\text{-}H}$	$\tau_{6\text{-}8\text{-}10\text{-}H}$
0.0°	-63.2°	156.3°	-107.1°	7.0°	0.0°	-132.5°	14.1°	15.1°	170.9°	178.5°
0.0°	-65.0°	158.8°	-104.3°	-2.9°	0.0°	-118.9°	11.6°	18.6°	177.8°	178.7°
0.0°	-61.7°	154.3°	-105.2°	4.5°	0.0°	-126.7°	12.4°	17.8°	176.0°	178.8°
0.0°	-63.7°	154.5°	-103.0°	3.7°	0.0°	-124.5°	11.9°	16.9°	177.1°	179.2°

Chart 7

Structure 7 (D_{5d} for MM2, MM3 and DZ SCF)
(D_5 for AM1)
(C_{5v} for DZP SCF)

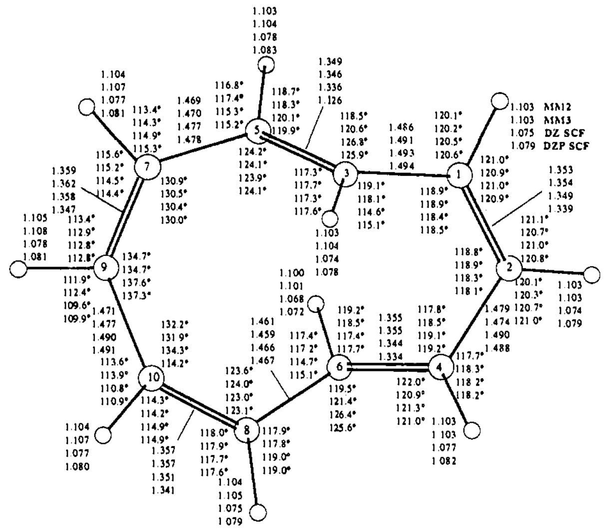


Dihedral Angles:

$\tau_{1\text{-}9\text{-}2\text{-}10}$	$\tau_{8\text{-}1\text{-}9\text{-}2}$
110.3°	-110.3°
108.9°	-108.9°
110.7°	-109.9°
109.6°	-109.6°
110.2°	-110.2°

Chart 8

Structure 8 (C_1)



Dihedral Angles:

$\tau_{4\text{-}2\text{-}1\text{-}3}$	$\tau_{2\text{-}1\text{-}3\text{-}5}$	$\tau_{1\text{-}3\text{-}5\text{-}7}$	$\tau_{3\text{-}5\text{-}7\text{-}9}$	$\tau_{5\text{-}7\text{-}9\text{-}10}$	$\tau_{7\text{-}9\text{-}10\text{-}8}$	$\tau_{9\text{-}10\text{-}8\text{-}6}$	$\tau_{10\text{-}8\text{-}6\text{-}4}$	$\tau_{8\text{-}6\text{-}4\text{-}2}$	$\tau_{6\text{-}4\text{-}2\text{-}1}$
7.6°	-113.3°	150.1°	-33.2°	-0.9°	-23.7°	-1.7°	133.7°	-139.5°	40.3°
5.0°	-109.7°	153.4°	-36.1°	-2.5°	-20.5°	-0.4°	133.9°	-140.0°	38.7°
1.4°	-114.0°	153.8°	-40.1°	2.6°	-18.0°	2.0°	126.6°	-147.9°	44.2°
0.5°	-111.1°	154.1°	-42.8°	3.7°	-19.6°	2.7°	125.1°	-148.0°	46.7°

the extent of bond distance alternation is quite similar. With the DZP SCF method, the COT bond distances are 1.329 and 1.481 Å. For our boat-like $C_{10}H_{10}$ structure **3** the C=C double bond distances (DZP SCF) are 1.325–1.335 Å, while the C—C single bond distances are 1.481–1.488 Å. By this criterion, [10]annulene is no more "aromatic" than cyclooctatetraene. Another appropriate comparison is with the prototypical linear polyene hexatriene. For hexatriene the DZP SCF C=C double bond distances are 1.329 and 1.334 Å, while the C—C single bond distance is 1.466 Å. Thus the prototypical linear polyene shows somewhat less bond alternation than [10]annulene.

A Structure with a C_5 Axis of Symmetry. The optimization of structure **7** began with the C_5 structure in ref 8 (number 12 in ref 8). Our result showed that the final structure differs greatly from the initial one. With all the different computational methods used in this research, this structure is crown-shaped with C–H bonds in the axial positions. The symmetry of this structure depends strongly on the theoretical method employed (see Chart 7). Only AM1 gave the structure with alternant C–C single and double bonds (D_5 symmetry), while the other methods (empirical and *ab initio* studies) gave equivalent C–C bond structures (D_{5d} symmetry for the MM2, MM3, and DZ SCF methods; C_{5v} for the DZP SCF method). Although all the vibrational frequencies of this interesting structure **7** (Table E in the supplementary material) are real for all theoretical methods, its energies are so high (≥47 kcal/mol; see Table 4) that it is unlikely to be observed by experiment.

The MM3 Searching Method and New Structures. Finally, a stochastic conformational searching[17] has been used in an attempt to locate any previously undetected conformations. This searching method of Saunders, available in MM3 (92 version),[18] samples conformation space by randomly pushing atoms in the molecule and then minimizing the structure through the MM3 force field.

Structure **6** was used here as the starting structure. From this structure, the next structure has been created by randomly pushing all 20 atoms (moving the positions of atoms and checking the validation of the bond length) in the molecule within a certain range. Then this structure is energy optimized. If the resulting structure has not been found before, it will be considered as a new conformation. For the next iteration, the computer randomly selects the starting geometry from either the original starting geometry or the last geometry that was found.

Because all possible conformations will eventually be randomly chosen as the starting structure, the selection of the first one will not affect the total number of conformations that could be found if the total number of structure perturbations is large enough. The moments of inertia and the total energy are used as the criteria to detect a new conformation. A new structure that has different moments of inertia or different total energy from the structures that have been found previously will be treated as a new conformation. If the newly optimized structure has the same moments of inertia and the same total energy as one of the conformations previously determined, this structure will be considered as identical with the old one and discarded. In order to eliminate transition-state structures the MM3 *block-diagonal and subsequent full-matrix* optimization (option 8 in the MM3 program '92 version) has been used to minimize the molecular structures. With this option the nonconjugated system with the same conformation can be guaranteed to have exactly the same moments of inertia and total energy. Since the valence electronic self-consistent-field (VESCF) method has been applied prior to geometry optimization and will not be repeated, unless the geometry has been improved significantly, the conjugated system with the same conformation may have slightly different moments of inertia and total energy and be considered as a different conformation. Thus, reoptimization is necessary to force MM3 to recalculate the VESCF and to group them together.

After 2000 iterations of random searching and 12–20 cycles of reoptimization for each conformation (the optimization for each of those conformations has been retained until there is no further change in the total energy), a total of 16 minima were found. Besides the three minima which had been found by *ab initio* methods, 13 new minima were revealed to have heats of formation below the highest $\Delta H_f°$ that was previously found (i.e. structure **7**).

In order to confirm the result of the MM3 search method, we chose the new conformation with the lowest energy (the azulene-like structure **8**, which actually bears more resemblance to homoazulene, synthesizd by Scott[20] in 1981) as a starting point to carry out geometry optimizations using the AM1 and SCF methods. While the result of the AM1 optimization collapsed to structure **6** (note that structure **6** is found as a minimum only by the AM1 method), the *ab initio* results with the DZ and DZP SCF basis sets have qualitively the same geometries as MM3 with an energy even lower than that of structure **6**. The geometrical parameters of the azulene-like structure **8** are shown in Chart 8. This is a C_1 symmetry ten-membered ring with alternating single and double C–C bonds. Its relative energy and harmonic vibrational frequencies are shown in Tables 3 and 4. The energy of **8** is 8.14 kcal/mol higher than that of the twisted structure **4** at the DZP SCF level. It is very close energetically to structure **6**. An interesting result is that at the DZP SCF/MP2 level, the relative energy of the azulene-like structure **8** is 5.25 kcal/mol lower than that of structure **6**. After ZPVE correction, the relative energy of structure **8** is still 4.85 kcal/mol lower than that of structure **6**, and even 0.91 kcal/mol below that of structure **3**. It is a genuine minimum with 136 cm^{-1} as its smallest harmonic vibrational frequency at the DZP SCF level. The discovery of the azulene-like structure **8** is an encouraging example of finding a new conformation independently via the molecular mechanics searching program. This method is, no doubt, a very helpful means for locating new minima on complicated potential energy hypersurfaces, and it is especially useful for larger molecular systems.

All of the other 12 structures located also have C_1 symmetry. Their geometrical shapes, heats of formation, and energies relative to the twisted structure **4** with the MM3 method are shown in Chart 9. Since all of them have higher energies than the azulene-like structure **8**, it is not of comparable importance to investigate them with the AM1 or *ab initio* methods.

Table 3. Harmonic Vibrational Frequencies and Infrared Intensities for Structure **8** (C_1 Symmetry)

			freq in cm^{-1} (and IR intensities in km/mol)[a]		
sym	no.	description	MM3	DZ SCF	DZP SCF
a	1	C—H stretch	3079	3438 (9)	3416 (5)
a	2	C—H stretch	3060	3389 (57)	3358 (38)
a	3	C—H stretch	3051	3374 (6)	3354 (4)
a	4	C—H stretch	3047	3369 (69)	3348 (45)
a	5	C—H stretch	3041	3361 (9)	3335 (10)
a	6	C—H stretch	3030	3351 (82)	3332 (53)
a	7	C—H stretch	3030	3336 (9)	3319 (17)
a	8	C—H stretch	3007	3334 (40)	3311 (19)
a	9	C—H stretch	3000	3321 (17)	3302 (8)
a	10	C—H stretch	2985	3311 (2)	3296 (7)
a	11	C═C stretch	1727	1860 (15)	1872 (15)
a	12	C═C stretch	1713	1835 (2)	1848 (1)
a	13	C═C stretch	1682	1777 (3)	1791 (1)
a	14	C═C stretch	1620	1765 (21)	1776 (22)
a	15	C═C stretch	1578	1748 (5)	1767 (4)
a	16	C—H bend	1538	1601 (1)	1578 (1)
a	17	C—H bend	1494	1571 (1)	1545 (1)
a	18	C—H bend	1426	1528 (2)	1513 (1)
a	19	C—H bend	1372	1485 (<1)	1450 (<1)
a	20	C—H bend	1356	1476 (2)	1440 (4)
a	21	C—H bend	1347	1451 (1)	1419 (<1)
a	22	C—H bend	1266	1424 (6)	1398 (5)
a	23	C—H bend	1234	1405 (1)	1372 (1)
a	24	C—H bend	1210	1372 (3)	1339 (1)
a	25	C—H bend	1180	1302 (1)	1273 (1)
a	26	C—C stretch	1125	1225 (3)	1209 (2)
a	27	C—C stretch	1053	1164 (8)	1148 (6)
a	28	C—H wag	1031	1171 (52)	1142 (44)
a	29	C—H wag	977	1159 (1)	1127 (1)
a	30	C—C stretch and C—H wag	1078	1146 (17)	1121 (16)
a	31	C—H wag	950	1123 (5)	1102 (2)
a	32	C—H wag	930	1137 (10)	1096 (9)
a	33	C—C stretch	994	1089 (14)	1071 (11)
a	34	C—C stretch	981	1078 (1)	1064 (5)
a	35	C—H wag	818	1012 (1)	975 (1)
a	36	C—H wag	799	999 (70)	958 (73)
a	37	ring deformation	756	934 (6)	915 (6)
a	38	C—H wag and C—C stretch	723	910 (10)	891 (1)
a	39	C—H wag	782	899 (8)	877 (17)
a	40	C—H wag	677	852 (145)	824 (114)
a	41	C—H wag	622	789 (4)	777 (2)
a	42	ring deformation	615	726 (7)	705 (4)
a	43	ring deformation	520	691 (4)	672 (4)
a	44	ring deformation	499	634 (3)	619 (3)
a	45	ring deformation	468	566 (2)	558 (2)
a	46	ring deformation	462	508 (3)	501 (2)
a	47	ring deformation	399	427 (16)	415 (12)
a	48	ring deformation	376	422 (3)	401 (2)
a	49	ring deformation	342	348 (3)	341 (3)
a	50	ring deformation	309	298 (1)	290 (1)
a	51	ring deformation	266	280 (2)	275 (2)
a	52	ring deformation	192	205 (2)	201 (2)
a	53	ring deformation	171	157 (<1)	151 (<1)
a	54	ring deformation	133	142 (2)	135 (1)

[a] AM1: collapses to structure **6**.

Concluding Remarks

(1) The planar structures (D_{10h} and D_{5h} symmetry) of [10]-annulene are the logical next candidates after benzene following Huckel's rule. They are suitable examples for studying conjugation effects and resonance energies theoretically, even though both are transition states with relatively high energies and therefore not observable. While the SCF studies show that the D_{5h} (with C–C bond length alternation) structure has a slightly lower energy than the D_{10h} (with equal bond lengths) structure, the MP2 methods favor the D_{10h} structure, which implies that conjugation effects are still favorable in planar 10-membered ring polyenes. It is noteworthy that single-point 6-31G* MP2 calculations on [18]annulene also reverse the order of the structures, making the D_{6h} form the more stable.[21]

(2) Table 4 shows the relative energies for the structures considered with all methods. The zero-point vibrational energy correction does not change the relative energies significantly. The two structures with C_2 symmetry [structures **4** (twisted) and

(20) Scott, L. T.; Brunsvold, W. R.; Kirms, M. A.; Erden, I. *J. Am. Chem. Soc.* **1981**, *103*, **103**, 5216. Scott, L. T.; Oda, M.; Erden, I. *J. Am. Chem. Soc.* **1985**, *107*, 7213.

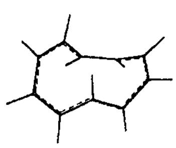
(21) Schulman, J. M.; Disch, R. L. *J. Mol. Struct. Theochem* **1991**, *234*, 213.

Table 4. Relative Energies with Respect to Structure 4 (in kcal/mol)[a]

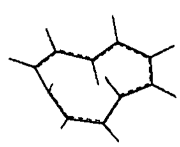
compd. no.	sym	MM2	MM3	AM1	DZ SCF	DZP SCF	DZ SCF/MP2[c]	DZ MP2[d]	DZP SCF/MP2[c]	ZPVE	after ZPVE correction[e]
7	$(C_s)^b$	47.31	64.85	103.36	117.09	108.87	85.18		70.99	109.74	69.53
		(143.02)	(160.33)	(190.84)	(−384.084434)	(−384.271426)	(−385.102808)		(−385.768035)		
2	D_{5h}	58.28	67.03	40.75	28.09	31.21	22.75	collapses to D_{10h}	20.68	113.13	22.04
		(153.99)	(162.51)	(128.23)	(−384.226263)	(−384.395183)	(−385.202286)		(−385.848219)		
1	D_{10h}	61.46	69.17	41.42	28.11	31.87	21.86	22.84	13.79	111.77	13.79
		(157.17)	(164.65)	(128.90)	(−384.226233)	(−384.394035)	(−385.203704)	(−385.084637)	(−385.859192)		
6	C_s		7.24	2.87	10.04	8.13	9.55		10.18	111.55	9.96
			(102.72)	(90.35)	(−384.255030)	(−384.431959)	(−385.223331)		(−385.223331)		
3	C_s	11.82	15.53	2.40	1.95	1.88	6.11		6.15	111.64	6.02
		(107.53)	(111.01)	(89.88)	(−384.267915)	(−384.441919)	(−385.228802)		(−385.871369)		
8	C_1	5.46	7.41		8.40	8.14	6.66		4.93	111.95	5.11
		(101.17)	(102.89)		(−384.257679)	(−384.431948)	(−385.227936)		(−385.873311)		
5	C_2	−3.62	−3.55	−0.68	2.96	2.91	1.94	2.37	0.51	111.88	0.62
		(93.09)	(91.93)	(86.80)	(−384.266305)	(−384.440277)	(−384.235458)	(−385.117263)	(−385.880351)		
4	C_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	111.77	0.0
		(95.71)	(95.48)	(87.48)	(−384.271028)	(−384.444919)	(−385.238543)	(−385.121039)	(−385.881170)		

[a] Total energies (for *ab initio* results, in hartrees) or heats of formation (for MM2, MM3, and AM1, in kcal/mol) are given in parentheses. [b] The symmetry for structure 7 varies at different levels (see text). [c] SCF/MP2 indicates the full (i.e. no frozen core) MP2 single-point energies at appropriate SCF geometries. [d] Ten cores and ten counterpart virtual orbitals were frozen for the DZ MP2 optimization. [e] The energy at the DZP SCF/MP2 level corrected by the zero-point vibrational energies at the DZP SCF level.

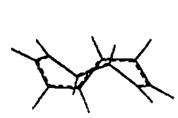
Chart 9



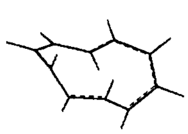
structure 9
108.0 kcal/mol
(12.5 kcal/mol)



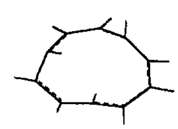
structure 13
123.8 kcal/mol
(28.4 kcal/mol)



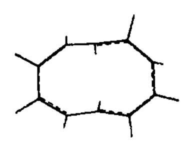
structure 17
133.4 kcal/mol
(37.9 kcal/mol)



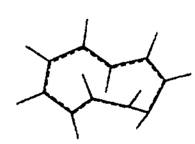
structure 10
116.5 kcal/mol
(21.0 kcal/mol)



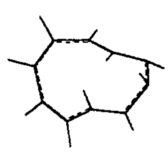
structure 14
124.5 kcal/mol
(29.0 kcal/mol)



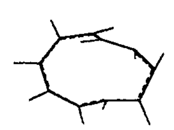
structure 18
137.1 kcal/mol
(41.6 kcal/mol)



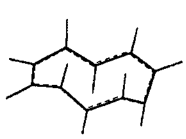
structure 11
120.3 kcal/mol
(24.8 kcal/mol))



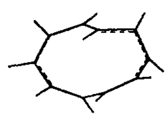
structure 15
125.9 kcal/mol
(30.4 kcal/mol)



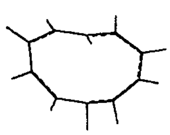
structure 19
150.7 kcal/mol
(55.2 kcal/mol)



structure 12
120.3 kcal/mol
(24.8 kcal/mol)



structure 16
126.8 kcal/mol
(31.3 kcal/mol)



structure 20
158.9 kcal/mol
(63.5 kcal/mol)

5 (naphthalene-like)] are the genuine minima with the lowest relative energies among the stationary points. Both are C–C bond-length alternating; the energetic order between them varies somewhat with different computational methods. They are the most likely to be observable of the [10]annulene structures. The C_s symmetry structures appear to be transition states. This is contrary to previous experimental assignments.[5] However, in light of the small values of the imaginary vibrational frequencies, and the slightly higher relative energies than structures **4** (twisted) and **5** (naphthalene-like), the possibility of observation (especially the boat-like structure **3**) cannot be absolutely ruled out. An isomer with C_1 symmetry (the azulene-like structure **8**) is also a minimum with energy very close to that of boat structure **3**. The crown-shaped structure (structure **7**) is another minimum on the potential hypersurface, but with significantly higher energy.

(3) In most cases, the MM3 method gives similar results for the geometries, relative energies, and vibrational frequencies. An exception is the relative energy of the D_{10h} structure **1**, which appears to be artificially high with the MM3 method. Comparing the relative energies between MM3 and *ab initio* methods in Table 4, it is noteworthy that for the larger basis sets the relative energy difference becomes smaller. According to MM3, the ground state of [10]annulene should be the naphthalene-like structure **5**. In contrast to this, the different *ab initio* methods all give the twisted structure **4** as the [10]annulene global minimum, but the energy difference is decreased when higher levels of theory are used.

(4) Random conformation searching via MM3 is a useful tool for finding other possible comformations in addition to those readily imagined. For [10]annulene, Saunders' MM3 searching method located several new conformations within the given energy range. Some of them (e.g. structures **8** and **9**) have heats of formation not far from the [10]annulene minimum (i.e., 5 and 13 kcal/mol, respectively, above the twisted structure **4**).

(5) Masamune and Darby[5] have assigned their two observed [10]annulene moieties to the structures we have labeled boat-like (**3**) and twisted (**4**). They designate our boat-like structure **3** as *cis*^{5}-[10]annulene and our twisted structure **4** was *trans-cis*^{4}-[10]annulene. The match with the present theoretical predictions is good in that the highest level *ab initio* method predicts the twisted structure **4** to be the global minimum among [10]annulene structures. However, the agreement is less satisfactory in that theory predicts the boat-like structure **3** to be a transition state. Structure **3** is, however, predicted to be only 6.1 kcal/mol above the global minimum. Also somewhat puzzling is Masamune's suggested exclusion of our naphthalene-like chair structure **5** as one of the two observed [10]annulene structures. Masamune considered **5** to be "unlikely" due to the apparent absence of a low-energy process to make all like nuclei equivalent. We hope that the present fairly exhaustive theoretical study of [10]annulene structures will stimulate new experiments on this fascinating and important molecular system.

(6) Experimental infrared spectra of the two observed [10]-annulene structures might be highly informative in light of the theoretical infrared intensities reported here. For example, the naphthalene-like structure **5** (labeled "unlikely" by Masamune) has no significant predicted IR features in the range 400–630 cm^{-1}, while both the twisted structure **4** and the boat-like structure

3 (predicted by us to be a transition state but identified in the laboratory by Masamune) have fundamentals with substantial IR intensity in this range. Similarly, our structure **5** has features with large IR intensity at 1030 (61 km/mol) and 984 cm^{-1} (27 km/mol), while Masamune's structure **3** has no IR intensities above 1 km/mol in this range. Should the homoazulene-like structure **8** prove observable, its IR spectrum would be identifiable due to the C–H wag mode at 742 cm^{-1}, which has the strongest IR intensity (114 km/mol). Also, there are three C–H stretches at 3022, 3013, and 2999 cm^{-1} with modest IR intensities (38, 45, and 53 km/mol, respectively). All of the above vibrational frequencies have been reduced by 10% from the DZP SCF values to account for the limitations of the basis set, as well as for the effects of correlation and anharmonicity.

Acknowledgment. This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences Fundamental Interactions Branch, Grant No. DE-FG09-87ER13811. Some of the computations reported here were performed using the IBM RS/6000s at the Cornell National Supercomputer Facility. Y.X. thanks Dr. Cynthia Meredith for helpful discussions.

Supplementary Material Available: Tables of harmonic vibrational frequencies and infrared intensities for **1**, **2**, **3**, **6**, and **7** (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.