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Structures and Stabilities of 1,6-Methano[10]annulene and Its Derivatives

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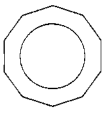
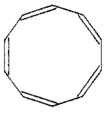
Abstract: Ab initio molecular orbital calculations with the STO-2G, STO-3G, and 4-31G basis sets have been carried out for valence isomers of 1,6-methano[10]annulene and some of its 11-monosubstituted (CN, F) and 11,11-disubstituted (CN, CH_3, F, Cl) derivatives. Both annulenic (**8**) and norcaradienic (**9**) structures have been considered. For the parent system (1,6-methano[10]annulene), the annulenic structure (**8**) is preferred, and the fully optimized structure for **8** agrees well with experiment. The barrier separating the norcaradienic form (**9**) from the annulenic isomer (**8**) is found to be very small. The 11,11-dimethyl and 11,11-dicyano derivatives reverse the position of the annulene–norcaradiene equilibrium, the norcaradiene form being now favored. The importance of steric interactions for methyl and chloro substituents is demonstrated. The effect of substituents in the 1,6-methano[10]annulene system is compared with corresponding substituent effects in cyclopropane.

Hückel's rule,[1] that systems with $(4n + 2)$ π electrons should exhibit a special stability, is well tested for the case of six π electrons. It is, however, less well obeyed in larger π-electron systems. In particular, the simplest higher member, [10]annulene ($C_{10}H_{10}$), is found to be extremely reactive.[2] Recent ab initio calculations[3,4] have shown that if the all-cis (*CCCCC*) isomer of [10]annulene is artificially constrained to be planar, the potential surface in the vicinity of the bond-equalized D_{10h} structure (**1**) is very flat; the energy required for small distortions in the direction of bond alternation, as in D_{5h} structures **2**, is very small. However, the energy is lowered substantially when distortions from planarity are allowed, leading to the all-cis isomer *CCCCC* (**3**), the *TCCCC* isomer (**4**), and two *TCTCC* isomers (**5** and **6**). All the nonplanar structures (**3**–**6**) have alternating single and double bonds and hence may be described as 1,3,5,7,9-cyclodecapentaenes.


CCCCC
1 (D_{10h})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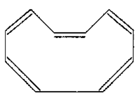
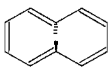
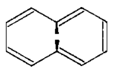
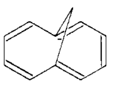

CCCCC
3 (C_s)

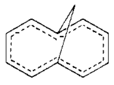

TCCCC
4 (C_2)

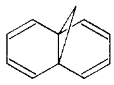

TCTCC
5 (C_2)


TCTCC
6 (C_s)

Interestingly, the pioneering work of Vogel[5] has shown that locking the ring conformation in **6** by means of a bridging methylene group provides an effective means of conferring aromatic character to the [10]annulene system. This conclusion is based on NMR spectral analyses,[5] X-ray crystal structure determinations,[6–14] and a gas-phase electron diffraction study[15] of the resulting molecule 1,6-methano[10]annulene (which we represent initially as **7**) and its simple derivatives. This molecule is of interest also in that it can, in principle, exist in either of two valence isomers,[5] which, following previous usage,[6] we will refer to as "annulenic" (**8**) or "norcaradienic" (**9**). In the former case, it is conceivable that an alternating bond structure (**7**) could be preferred to the delocalized structure (**8**), but this is not supported by the experimental evidence.[5] Although it is clear from NMR results,[5] an electron diffraction study,[15] and X-ray crystal data[12] that the parent hydrocarbon is itself annulenic, substitution on the bridge carbon can cause the norcaradienic form to be favored.[5,9,11]


7 (C_s)


8 (C_{2v})


9 (C_{2v})

The 1,6-methano[10]annulene molecule and its derivatives have been the subject of some theoretical attention but, because of the large size of these systems, most of the previous theoretical studies have been carried out by semiempirical techniques: extended Hückel theory,[16] force-field approaches,[17-19] a combined π-SCF-MO and force-field study,[20] and CNDO/INDO.[21] The force-field methods have been directed toward finding the geometry of the parent hydrocarbon and generally give an annulenic structure in good agreement with that determined from experiment. Comparison of annulenic and norcaradienic forms has been systematically performed[16] only with the extended-Hückel method, with geometries either taken from crystal structures[16] or in a comparison of 1,6-methano[10]annulene and its 11,11-dimethyl derivative by using geometries obtained from force-field calculations.[17] It was found that the predicted form of lower energy (i.e., annulenic or norcaradienic) agreed in all cases studied with the observed crystal structure. A single previous ab initio calculation has been reported,[21] using the molecular fragment

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Table I. Calculated Total Energies (hartrees) and Relative Energies (kJ mol^{-1}) for Valence Isomers of 1,6-Methano[10]annulene

	STO-2G//STO-2G		STO-3G//STO-2G		4-31G//STO-2G	
structure	total	rel	total	rel	total	rel
annulenic C_s (7)	−404.911 21	82.4	−417.142 49	73.4	−421.674 65	7.7
annulenic C_{2v} (8)	−404.903 23	103.4	−417.132 93	98.5	−421.677 59	0.0
norcaradienic C_{2v} (9)	−404.942 60	0.0	−417.170 44	0.0	−421.667 52	26.4

Table II. Calculated Total Energies (hartrees) of 11,11-Disubstituted 1,6-Methano[10]annulenes (STO-3G//std)

substituents	annulenic (8)	norcaradienic (9)
H, H	−417.132 93	−417.170 44
H, F	−514.580 98	−514.621 10
F, F	−612.041 93	−612.082 02
H, CN	−507.669 87	−507.718 66
Cl, Cl	−1325.094 25	−1325.156 98
CN, CN	−598.198 24	−598.258 19
CH_3, CH_3	−494.242 09	−494.322 05

technique with no geometry optimization; the main conclusion was that 1,6-methano[10]annulene possesses weak or intermediate aromaticity.

We felt it desirable to carry out a more extensive ab initio study of 1,6-methano[10]annulene including full geometry optimization and an examination of substituent effects. The results of such a study are reported here.

Theoretical Approach

A similar approach is used in the present work to that previously employed[3] to study [10]annulene. Calculations were performed by using ab initio single-determinant self-consistent-field molecular orbital theory with a modified version[22] of the GAUSSIAN80 system of programs.[23] Geometric parameters for structures **7**–**9** of 1,6-methano[10]annulene were optimized by using a gradient procedure[24] with the minimal STO-2G basis set.[25] Because of the use of symmetry constraints in the optimization procedure, it was necessary to ascertain the nature of the resulting stationary points by determining the second derivative (force constant) matrix and examining the number of negative eigenvalues (i.e., zero for minima, one for saddle points). 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[26] (denoted 4-31G//STO-2G) in order to provide more reliable energy comparisons. In general, the geometries of substituted 1,6-methano[10]annulenes were based on the optimized structures for the parent system together with standard parameters[27] for substituent groups, the calculations being carried out with the STO-3G set (denoted STO-3G//std). The geometry of 11,11-dimethyl-1,6-methano[10]annulene was fully optimized. Calculated total energies for 1,6-methano[10]annulene are shown in Table I and for 11,11-disubstituted derivatives in Table II.

Results and Discussion

1,6-Methano[10]annulene. Optimization of the geometry of 1,6-methano[10]annulene with the STO-2G basis set and a C_{2v} symmetry constraint leads to two distinct minima in the potential-energy surface, corresponding to structures **8** and **9**. However, **8** is not a true minimum in the STO-2G surface, distorting to **7** when the symmetry constraint is removed. It is known that in these circumstances the distortion may be a result of broken symmetry in the wave function at the more symmetric geometry. That is, at the SCF level the best wave function may have lower symmetry than the nuclear framework. This happens, for example, with the cyclobutadiene radical cation.[28] However, it is *not* the case in the present calculations: from a guess made deliberately asymmetric, a wave function of C_{2v} symmetry is obtained for structure **8**.

Table III. Important Geometrical Parameters for 1,6-Methano[10]annulene and Related Systems from X-ray Crystal Structure Determinations

compound	C_1–C_6, Å	C_1–C_{11}, Å	∠$C_1C_{11}C_6$, deg	ref
1,6-methano[10]annulene	2.235	1.485	97.6	12
11,11-difluoro-1,6-methano[10]annulene	2.269	1.479	101.0	10
1,6-epoxy[10]annulene			102.0^a	8
1,6-methano[10]annulene-2-carboxylic acid	2.26	1.477	99.6	7
10-bromo-1,6-methano-2-aza[10]annulene	2.202	1.493, 1.482^b	95.5	13
11,11-dimethyl-1,6-methano[10]annulene	1.808^c	1.515^c	73.2^c	9
11-cyano-11-methyl-1,6-methano[10]annulene	1.817^c	1.510^c	74.0^c	11
	1.622^d			14

^{a} ∠C_1–OC_6. ^{b} C_6–C_{11}. ^{c} Averaged values since there are two nonequivalent sites in the crystal. ^{d} A second crystalline phase.

Geometrical parameters of all three structures (together with the electron diffraction results[15] for **8**) are displayed in Figure 1. For additional comparison, key parameters obtained from X-ray crystal structure determinations for a number of related systems are presented in Table III. There is good agreement for the annulenic structure (**8**), except for some overestimation of bond lengths, a normal feature of STO-2G calculations.[29] However, in the norcaradienic structure (**9**), although there is again generally satisfactory agreement between theoretical and experimental structures, there is a serious discrepancy for the bridgehead C_1–C_6 distance for which the calculated value (1.556 Å) is considerably smaller than most of the relevant experimental values (1.808 Å,[9] 1.817 Å[11]). It is interesting that force-field calculations[17] also yield a small value for the C_1–C_6 distance. A very recent experimental study[14] has revealed a new, lower energy crystalline form for the 11-methyl-11-cyano derivative, which dramatically improves the agreement between theory and experiment for the norcaradienic structure. Thus, if comparisons are made with our results for the 11,11-dimethyl derivative (see below), C_1–C_6 is 1.62 Å compared with 1.55 (theory) and 1.81 Å (previous experiment) while ∠$C_1C_{11}C_6$ is 63.9° compared with 60.5° (theory) and 73.2° (previous experiment). The apparent disagreement between the theoretical and other experimental norcaradienic structures may therefore be attributed at least in part to crystal packing forces.

The STO-3G//STO-2G relative energies are very similar to the STO-2G//STO-2G values. There are large changes, however, at the 4-31G//STO-2G level, and, in particular, structure **7** now lies higher in energy than **8**. Since such an energy comparison is nonisodesmic[30] and since, in addition, minimal basis sets are known to exaggerate single–double bond alternation,[29,31] the 4-31G

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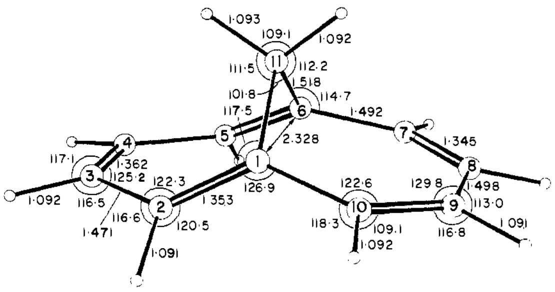


$\angle C_1C_{11}C_6C_7 = -\angle C_6C_{11}C_1C_{10} = 87.9$

$\angle C_3C_2C_1C_{10} = -\angle C_4C_5C_6C_7 = 154.3$

$\angle C_3C_2C_1C_{11} = -\angle C_4C_5C_6C_{11} = -13.7$

$\angle C_6C_7C_8C_9 = -\angle C_1C_{10}C_9C_8 = -7.1$

$\angle C_7C_8C_9C_{10} = \angle C_2C_3C_4C_5 = 0$

$\angle H_{10}C_{10}C_9C_8 = -\angle H_7C_7C_8C_9 = -169.5$

$\angle H_9C_9C_{10}C_1 = -\angle H_8C_8C_7C_6 = 179.2$

$\angle C_6C_{11}C_1C_2 = -\angle C_1C_{11}C_6C_5 = 81.6$

$\angle C_5C_6C_7C_8 = -\angle C_2C_1C_{10}C_9 = 131.8$

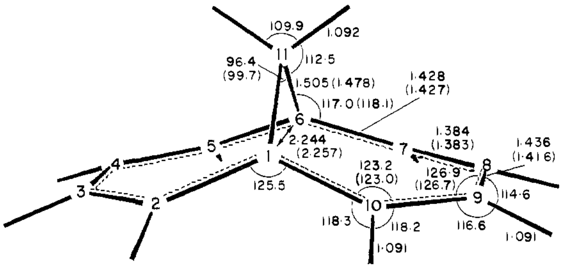
$\angle C_{11}C_6C_7C_8 = -\angle C_{11}C_1C_{10}C_9 = -36.5$

$\angle C_1C_2C_3C_4 = -\angle C_6C_5C_4C_3 = -33.0$

$\angle H_5C_5C_4C_3 = -\angle H_2C_2C_3C_4 = -137.9$

$\angle H_4C_4C_5C_6 = -\angle H_3C_3C_2C_1 = -159.7$

7



$\angle C_1C_{11}C_6C_7 = -\angle C_1C_{11}C_6C_5 = -\angle C_6C_{11}C_1C_{10} = \angle C_6C_{11}C_1C_2 = 86.2$

$\angle C_3C_2C_1C_{10} = -\angle C_2C_1C_{10}C_9 = -\angle C_4C_5C_6C_7 = \angle C_5C_6C_7C_8 = 144.2\ (139.6)$

$\angle C_3C_2C_1C_{11} = -\angle C_{11}C_1C_{10}C_9 = -\angle C_4C_5C_6C_{11} = \angle C_{11}C_6C_7C_8 = -27.4$

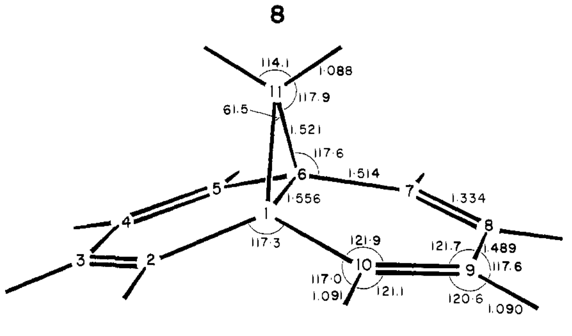
$\angle C_6C_7C_8C_9 = -\angle C_1C_{10}C_9C_8 = -\angle C_6C_5C_4C_3 = \angle C_1C_2C_3C_4 = -20.2\ (-27.3)$

$\angle C_7C_8C_9C_{10} = \angle C_2C_3C_4C_5 = 0\ (0)$

$\angle H_{10}C_{10}C_9C_8 = -\angle H_2C_2C_3C_4 = -\angle H_7C_7C_8C_9 = \angle H_5C_5C_4C_3 = -153.5$

$\angle H_9C_9C_{10}C_1 = -\angle H_3C_3C_2C_1 = -\angle H_8C_8C_7C_6 = \angle H_4C_4C_5C_6 = -176.6$

8



$\angle C_1C_{11}C_6C_7 = -\angle C_1C_{11}C_6C_5 = -\angle C_6C_{11}C_1C_{10} = \angle C_6C_{11}C_1C_2 = 105.6$

$\angle C_3C_2C_1C_{10} = -\angle C_2C_1C_{10}C_9 = -\angle C_4C_5C_6C_7 = \angle C_5C_6C_7C_8 = 148.8$

$\angle C_3C_2C_1C_{11} = -\angle C_{11}C_1C_{10}C_9 = -\angle C_4C_5C_6C_{11} = \angle C_{11}C_6C_7C_8 = -62.3$

$\angle C_6C_7C_8C_9 = -\angle C_1C_{10}C_9C_8 = -\angle C_6C_5C_4C_3 = \angle C_1C_2C_3C_4 = -5.2$

$\angle C_7C_8C_9C_{10} = \angle C_2C_3C_4C_5 = 0$

$\angle H_{10}C_{10}C_9C_8 = -\angle H_2C_2C_3C_4 = -\angle H_7C_7C_8C_9 = \angle H_5C_5C_4C_3 = -174.1$

$\angle H_9C_9C_{10}C_1 = -\angle H_3C_3C_2C_1 = -\angle H_8C_8C_7C_6 = \angle H_4C_4C_5C_6 = -179.4$

9

Figure 1. STO-2G (experimental electron diffraction values[15] in parentheses) optimized structures for possible valence isomers **7**, **8**, and **9** of 1,6-methano[10]annulene.

results are to be preferred and indeed are consistent with experiment. In view also of our results for [10]annulene, we believe that the distortion of **8** to the less symmetrical **7** is an artifact of using too small a basis set. We conclude that the preferred annulenic structure is the C_{2v} form **8**.

The ordering of energies of **8** and **9** is also reversed with the 4-31G basis set, which predicts, in line with experimental results, that **8** is the more stable. Addition of polarization functions to the basis set and incorporation of electron correlation are likely to have opposite effects. Polarization functions might be expected[32] to preferentially favor the more strained norcaradienic structure **9** while electron correlation is likely to favor the delocalized annulenic structure **8**. The extent of such corrections is difficult to assess, but there should be some cancellation of errors. For the moment, our best prediction is based on the 4-31G result, favoring the annulenic structure (**8**) for 1,6-methano[10]annulene.

There remains the question of how large an energy barrier separates the annulenic and norcaradienic structures. If this barrier were large and the energy difference between the two structures not too great, then each form could, in principle, be separately isolated. On the other hand, if the barrier were small, then only one valence isomer would be isolatable or, at best, a mixture of the two if both isomers were of comparable energy. To this end, calculations were performed to map out an approximate potential-energy curve for the interconversion of the valence isomers **8** and **9** by using geometrical parameters linearly interpolated from those optimized at the end points. This procedure should yield an upper bound to the barrier. Both STO-2G and 4-31G results indicate at most a very small barrier (~5 kJ mol^{-1}) for such a rearrangement. We conclude that isolation of *both* the annulenic and norcaradienic forms of a particular 1,6-methano[10]annulene would be most unlikely. On the other hand, the potential surface appears quite flat in the vicinity of the annulenic and norcaradienic structures so that either form might be the preferred stable structure for a particular substituent.

Derivatives of 1,6-Methano[10]annulene. The effect of substituents on the annulene (**8**)–norcaradiene (**9**) equilibrium in 1,6-methano[10]annulene has been interpreted[16,17] in terms of a theory of substituent effects in cyclopropane due originally to Hoffmann.[33] According to this theory, π-acceptor substituents should strengthen the C–C bond opposite the substituted carbon atom but weaken adjacent bonds; π-donor substituents should weaken all C–C bonds. Hoffmann's qualitative predictions have been subjected to extensive experimental[34] and theoretical[35] examination. It is found that for π-electron acceptors, the quantitative experimental and theoretical data confirm the shortening of the opposite bond and lengthening of the adjacent bond. On the other hand, although Hoffmann's prediction of lengthening of all the ring bonds is supported in the case of strong anionic π-donors (e.g., O$^-$, CH$_2^-$), it does not hold for conventional neutral π-donors (e.g., F, OH, NH$_2$, Cl). For these substituents, the opposite bond is lengthened but the adjacent bond is shortened. The following conclusions have been drawn.[35g] (a) Hoffmann's theory describes well the effect of π-acceptor substituents; (b) the cyclopropyl group is itself a poor π-acceptor and the effect of neutral π-donors is therefore dominated by other factors; (c) the electronegativity of the substituent is unimportant; and (d) more important are local effects at the substituted carbon atom where

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Table IV. Calculated Total Energies (hartrees) and Relative Energies (kJ mol^{-1}) for Valence Isomers of 11-Fluoro-1,6-methano[10]annulene

	STO-2G//std		STO-3G//std		4-31G//std	
structure	total	rel	total	rel	total	rel
annulenic (**8**)	−499.414 46	114.2	−514.580 98	105.3	−520.401 89	0.0
norcaradienic (**9**)	−499.457 95	0.0	−514.621 10	0.0	−520.391 95	26.1

Table V. Calculated Relative Energies (STO-3G//std, kJ mol^{-1}) for 11,11-Disubstituted 1,6-Methano[10]annulenes

		E (norcaradienic) − *E* (annulenic)	
substituents	exptl obsvn	uncorrected	corrected
H, H	annulenic[a-c]	−98.5	26.4
H, F		−105.3	19.6[d]
F, F	annulenic[a,e]	−105.3	19.6
H, CN	annulenic[a]	−128.1	−3.2
Cl, Cl	mixture[a]	−164.7	−39.8
CN, CN	norcaradienic[f]	−157.4	−32.5
CH_3, CH_3	norcaradienic[a,g]	−209.9	−85.0

[a] From NMR spectral analysis, ref 5. [b] From photoelectron spectrum: Boschi, R.; Schmidt, W.; Gfeller, J. C. *Tetrahedron Lett.* 1972, 4107. [c] From crystal structure, ref 12. [d] An explicit 4-31G calculation gives 26.1 kJ mol^{-1}. [e] From crystal structure, ref 10. [f] Most probable isomer, ref 5. [g] From crystal structure, ref 9.

changes in hybridization and steric interaction result in changes in the geometry of the ring.

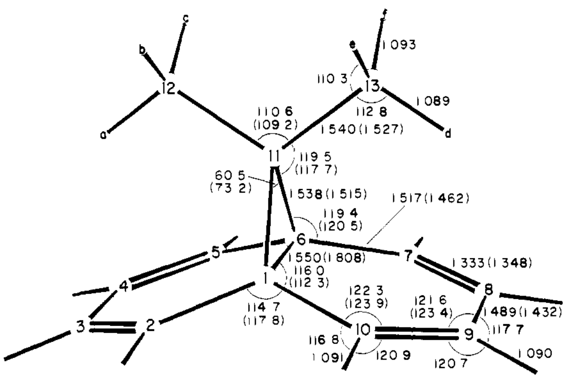
If these considerations are applied to the annulene–norcaradiene equilibrium in 1,6-methano[10]annulene, substituents that lengthen the opposite bond in cyclopropane (e.g., F, Cl) would be expected to favor the annulenic structure (**8**) while substituents that shorten the opposite bond in cyclopropane (e.g., CN) would be expected to favor the norcaradienic structure (**9**). Ab initio calculations were therefore carried out to test these predictions for the 11-fluoro-, 11,11-difluoro-, 11-cyano-, 11,11-dichloro-, 11,11-dicyano-, and 11,11-dimethyl-1,6-methano[10]annulenes.

In order to obtain meaningful estimates of the relative energies of norcaradienic and annulenic isomers, STO-3G relative energies were adjusted by an amount corresponding to the difference between STO-3G and 4-31G relative energies for the parent hydrocarbons. This is equivalent to assuming that the minimal basis set correctly predicts the effect of substituents. The results would, in addition, be subject to any error in the 4-31G energy difference in the parent systems.

This procedure was tested by explicitly calculating the energies of the annulenic and norcaradienic forms of 11-fluoro-1,6-methano[10]annulene with all three basis sets. The results are presented in Table IV. It may be seen that all calculations concur in indicating a very small substituent effect for fluorine with relative stabilizations of the norcaradienic forms of just 10.8, 6.8, and 0.3 kJ mol^{-1} at the STO-2G, STO-3G and 4-31G levels, respectively. The results lend confidence to our (corrected) STO-3G predictions for the remaining substituted systems.

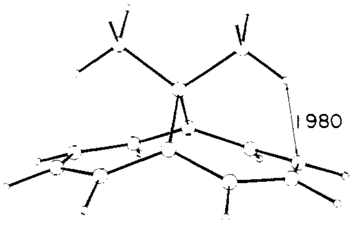
The corrected relative energies (Table V) give predictions of the more stable isomers which are in substantial agreement with experimental results. The trend in mono- and dicyano-substituted compounds is correct although the calculations predict the monocyano compound to be slightly more stable in the norcaradienic form, in contrast to NMR evidence. The only serious disagreement occurs for 11,11-dichloro-1,6-methano[10]annulene, where the calculations predict that the norcaradienic form should be strongly favored whereas NMR evidence[5] suggests that the two forms have comparable energies. This discrepancy may be due to artificially large steric interactions in the theoretical calculations for the annulenic form (see below). It is important to note nevertheless that the difference from the difluoro derivative is in the correct direction.

The change in relative energies induced by methyl substitution is surprisingly large. Examination of the structures produced by using standard geometric parameters shows that there is a very short internuclear distance between some of the nonbonded atoms in the annulenic form. Thus the H_a–C_3 distance is only 1.980 Å (**10**) compared with 2.372 Å in the norcaradienic form (**11**). Thus methyl substitution appears to favor the norcaradienic form at least in part because of steric (as opposed to electronic) effects.



$$\angle C_1C_{11}C_6C_7 = -\angle C_1C_{11}C_6C_5 = -\angle C_6C_{11}C_1C_{10} = \angle C_6C_{11}C_1C_2 = 104{\cdot}9$$
$$\angle C_3C_2C_1C_{10} = -\angle C_2C_1C_{10}C_9 = -\angle C_4C_5C_6C_7 = \angle C_5C_6C_7C_8 = 142{\cdot}1\ (140{\cdot}1)$$
$$\angle C_3C_2C_1C_{11} = -\angle C_{11}C_1C_{10}C_9 = -\angle C_4C_5C_6C_{11} = \angle C_{11}C_6C_7C_8 = -66\ 3$$
$$\angle C_6C_7C_8C_9 = -\angle C_1C_{10}C_9C_8 = -\angle C_6C_5C_4C_3 = \angle C_1C_2C_3C_4 = -2{\cdot}2\ (-8{\cdot}1)$$
$$\angle C_7C_8C_9C_{10} = \angle C_2C_3C_4C_5 = 0{\cdot}0\ (-0{\cdot}7)$$
$$\angle H_aC_{12}C_{11}C_{13} = \angle H_dC_{13}C_{11}C_{12} = 180{\cdot}0$$
$$\angle H_bC_{12}C_{11}C_{13} = -\angle H_cC_{12}C_{11}C_{13} = -\angle H_eC_{13}C_{11}C_{12} = \angle H_fC_{13}C_{11}C_{12} = 59{\cdot}6$$
$$\angle H_{10}C_{10}C_9C_8 = -\angle H_2C_2C_3C_4 = -\angle H_7C_7C_8C_9 = \angle H_5C_5C_4C_3 = -175{\cdot}2$$
$$\angle H_9C_9C_{10}C_1 = -\angle H_3C_3C_2C_1 = -\angle H_8C_8C_7C_6 = \angle H_4C_4C_5C_6 = -179{\cdot}0$$

Figure 2. STO-2G (experimental crystal structure values[9] in parentheses) optimized structure for 11,11-dimethyl-1,6-methano[10]annulene [*E* (STO-2G) = −479.87098 hartrees].



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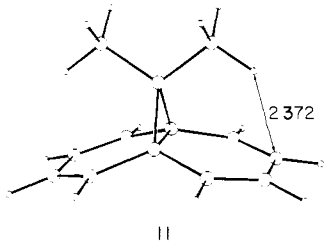

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In order to alleviate this unfavorable interaction, a full geometry optimization of both forms was carried out. The resulting structure for the norcaradienic isomer compares well with the experimental structure, as shown in Figure 2, except for the bridgehead C_1–C_6 distance for which the predicted value (1.550 Å) is considerably smaller than the experimental value[9] (1.808 Å, see above). The annulenic structure is found to collapse in the course of the optimization to the norcaradienic isomer; i.e., there is no barrier separating the two forms.

With the exception of the 11,11-dichloro system, results for the 1,6-methano[10]annulenes are consistent with expectations based on results for corresponding cyclopropanes. Thus difluoro substitution, which lengthens the opposite bond in cyclopropane, does indeed favor the annulenic form of 1,6-methano[10]annulene, whereas dicyano substitution, which shortens the opposite bond in cyclopropane, does indeed favor the norcaradienic structure. For dichloro substitution, both theory and experiment predict a lengthening of the opposite bond in cyclopropane, similar to that observed for the difluoro derivative. On the other hand, dichloro substitution in the 1,6-methano[10]annulene system is found both theoretically and experimentally to favor, relative to the difluoro systems, the norcaradienic structure. The most plausible explanation for the different behavior of the fluoro and chloro substituents in the 1,6-methano[10]annulene system comes from noting that chlorine is considerably bulkier than fluorine and comparable in size to methyl: van der Waals' radii are[36] respectively 1.73, 1.47, and 1.80 Å. Thus steric interaction between the chloro substituents and carbon atoms 3, 4, 8, and 9 would contribute, just as in the case of methyl, to a preference for the norcaradienic structure, as observed. The theoretical calculations, in the absence of geometry reoptimization, would be expected to overemphasize such steric interaction in the annulenic form and this is also consistent with the results.

Concluding Remarks

Two minima have been located in the potential-energy surface of 1,6-methano[10]annulene that correspond to annulenic (**8**) and norcaradienic (**9**) structures. However, the barrier separating these forms is very small so that only the more stable annulenic valence isomer (**8**) is expected to be observable. The calculated structure for **8** agrees well with that obtained experimentally. The effect of substituents on the annulene (**8**)–norcaradiene (**9**) equilibrium is generally well described by the calculations. Hyperconjugative and hybridization effects similar to those operative in substituted cyclopropanes may be used to rationalize the observed preferences for norcaradienic and annulenic structures for cyano and fluoro substituents, respectively. For methyl and chloro substituents, steric effects are found to be important. In particular, for the dichloro derivative, this leads to a relative favoring of the norcaradienic structure, not expected on the basis of results for the model cyclopropane system.

Note Added in Proof. Since this paper was submitted, we have become aware of recently completed calculations, carried out at higher levels of theory, on the 1,6-methano[10]annulene system.[37] These higher level calculations show that (i) geometry optimization at the STO-3G (as opposed to STO-2G used here) level has a very small effect on the relative energies of **8** and **9**: values of 98 (Table I) and 97 (ref 37) kJ mol^{-1} are obtained at the STO-3G//STO-2G and STO-3G//STO-3G levels, respectively; (ii) geometry optimization at the 6-31G level also has a relatively small effect (thus the relative energies of **8** and **9** are 26 (Table I) and 23 (ref 37) kJ mol^{-1} at the 4-31G//STO-2G and 6-31G//6-31G levels, respectively); (iii) finally, incorporation of electron correlation leads, as expected, to a relative stabilization of the annulenic isomer **8**. The relative energy of **9** at MP2/6-31G//6-31G is 65 kJ mol^{-1}. This value is likely to be reduced at higher correlation levels (since MP2 generally overestimates correlation effects) and through addition of polarization functions to the basis set. Consequently, the energy difference between **8** and **9** is likely to lie between our 4-31G//STO-2G estimate of 26 kJ mol^{-1} and the MP2/6-31G value of 65 kJ mol^{-1}.

Registry No. 7, 2443-46-1; 11-fluoro-1,6-methano[10]annulene, 71671-89-1; 11,11-difluoro-1,6-methano[10]annulene, 19026-91-6; 11-cyano-1,6-methano[10]annulene, 10474-26-7; 11,11-dichloro-1,6-methano[10]annulene, 19026-92-7; 11,11-dicyano-6-methano[10]annulene, 61997-35-1; 11,11-dimethyl-1-methano[10]annulene, 58863-22-2.

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Analysis of the Kinetics of Electron Transfer between Blue Copper Proteins and Inorganic Redox Agents. Reactions Involving Bis(dipicolinate) Complexes of Cobalt(III) and Iron(II) and Stellacyanin, Plastocyanin, and Azurin

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Abstract: The kinetics of electron-transfer reactions involving bis(dipicolinato)cobaltate(III) (Co(dipic)$_2^-$) and bis(dipicolinato)ferrate(II) (Fe(dipic)$_2^{2-}$) with Japanese *Rhus vernicifera* stellacyanin, *Phaseolus vulgaris* plastocyanin, and *Pseudomonas aeruginosa* azurin have been studied. Second-order rate constants (M^{-1} s^{-1}; 25 °C; pH 7.0 (phosphate), μ = 0.2 M), $\Delta H^\ddagger$ (kcal/mol), and $\Delta S^\ddagger$ (eu) values are as follows: 6.8 (2) × 10^4, 6.7 (5), and −14 (2) for stellacyanin(II)–Fe(dipic)$_2^{2-}$; 2.04 (8) × 10^4, 4.8 (4), and −23 (1) for plastocyanin(II)–Fe(dipic)$_2^{2-}$; 4.57 (7) × 10^2, 4.5 (2), and −31.2 (8) for plastocyanin(I)–Co(dipic)$_2^-$; and 9.8 (2) × 10^2, 4.5 (4), and −30 (1) for azurin(II)–Fe(dipic)$_2^{2-}$. The oxidation of stellacyanin(I) by Co(dipic)$_2^-$ was found to be too fast to measure, and rate saturation was observed for the azurin(I)–Co(dipic)$_2^-$ reaction. Protein reactivity parameters extracted from an analysis of the kinetics data for the oxidations of plastocyanin(I) and azurin(I) by Co(dipic)$_2^-$ and Co(phen)$_3^{3+}$ are interpreted in terms of a bimolecular electron-transfer mechanistic model in which protein–reagent binding is a dead-end (K = 46 (5) M^{-1} for azurin(I)–Co(dipic)$_2^-$). Estimated protein electron-transfer distances are about the same (∼2–3 Å) for these reactions, suggesting that the hydrophobic π-conducting ligands penetrate the hydrophobic region around the copper–histidine redox units (His-87 in plastocyanin; His-117 in azurin); the distances based on reactions with hydrophilic reagents, however, are 2–3 Å larger for azurin than for plastocyanin, which is consistent with available structural data and the assumption that these redox agents cannot penetrate the three residues (Met-13, Met-44, Phe-114) that isolate copper (His-117) in azurin.

Previous studies in our laboratory have shown that the blue copper centers in the proteins Japanese *Rhus vernicifera* stellacyanin, *Phaseolus vulgaris* (bean) plastocyanin, and *Pseudomonas aeruginosa* azurin differ markedly in their reactivity with various

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