Quim. Nova, Vol. 24, No. 6, 719-723, 2001. *Artigo*

DISJOINT NONCLASSICAL HYDROCARBONS HAVE VERY UNSTABLE LOWEST-LYING SINGLET STATES: A PM3 STUDY

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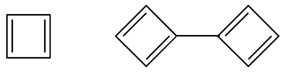
Recebido em 19/5/00; aceito em 4/5/01

Earlier workers have suggested that disjoint hydrocarbons have nearly-degenerate lowest-lying singlet and triplet states while non-disjoint (or joint) hydrocarbons should be ground-state triplets. PM3 results for an appropriate selection of alternant hydrocarbons are inconsistent with that generalization: disjoint, nonclassical, alternant hydrocarbons show the strongest predilection for triplet ground states.

Keywords: disjoint; PM3 calculations; ground state; alternant hydrocarbons; PMO analyses.

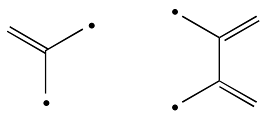
INTRODUCTION

There are two types of even hydrocarbons which have extended π-systems and nonbonding electrons at the Hückel level. The first type has a 4N circuit embedded in the compound's carbon framework. Familiar examples[1,2] include cyclobutadiene **1** and biscyclobutadiene **2** (see Figure 1). This type of molecule is very important theoretically and is generally referred to as antiaromatic[3-5]. The second type has a Lewis structure which must show two nonbonding electrons. Familiar examples are trimethylenemethane **3** and tetramethylenethane **4** (see Figure 2). This type of molecule presents an important challenge for modern theory and is commonly described as Y-antiaromatic[6-11] or nonclassical[12].



1 **2**

Figure 1



3 **4**

Figure 2

In part because it was the first to successfully rationalize the very substantial difference in stability between cyclobutadiene **1** and benzene, Hückel theory has been very widely disseminated, particularly amongst organic chemists. At the Hückel level, the instability of cyclobutadiene **1** is ascribed to the presence of two nonbonding electrons. Assuming that Hund's rule applies to molecules, one then expects that cyclobutadiene **1** should be a ground-state triplet. The experimental fact is that cyclobutadiene **1** is a ground-state singlet[13]. In sharp contrast, the nonclassical hydrocarbon, trimethylenemethane **3**, is expected to be a ground-state triplet at the Hückel level and the experimental fact is that **3** is a ground-state triplet[14].

All of the molecules described herein, which have two nonbonding electrons on their Lewis structures, also have a pair of nonbonding orbitals at the Hückel level. The connection between dots on the Lewis structure and nonbonding orbitals at the Hückel level is only obvious when the structure is alternant[12]. Non-alternant hydrocarbons (those which have an odd-membered ring in their structures) that have a pair of nonbonding electrons on their Lewis structures need not have any Hückel nonbonding orbitals (see ref. 15 for an example). Hence, the present discussion of Lewis structures with dots will be restricted to alternant hydrocarbons.

Because Hückel theory is so familiar to chemists and because it fails to correctly predict ground-state multiplicity for some molecules, there have been some attempts[16,17] to develop simple, conveniently-applied corrections to such Hückel predictions. We are concerned, here, with the method of Borden and Davidson[17].

When a pair of molecular orbitals are degenerate, the coefficients for those molecular orbitals cannot be chosen uniquely[18]. Thus, for the molecules under consideration, there is no unique representation for the nonbonding molecular orbitals. A valid pair of such orbitals must be orthonormal and must satisfy the homogeneous linear equations (see Chapter 3, reference 18). As an example, there are two commonly-used representations for the degenerate pair of nonbonding molecular orbitals of cyclobutadiene **1** (see Figure 3).

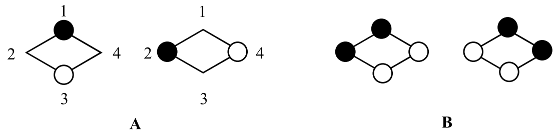


Figure 3. *Two pairs of representations for the non-bonding molecular orbitals of cyclobutadiene.*

In Figure 3, the **A** pair of representations for the nonbonding orbitals of **1** has the following feature - a non-zero coefficient for a given vertex in one nonbonding molecular orbital is always paired with a zero coefficient for that same vertex in the other orbital. Such a pair of nonbonding orbitals is said to be disjoint[17]. If a hydrocarbon has a legitimate disjoint representation for its nonbonding orbitals, the hydrocarbon itself is said to be disjoint,[17] the possibilty of non-disjoint representations notwithstanding.

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When a structure cannot have a disjoint representation for its nonbonding orbitals, the hydrocarbon is said to be non-disjoint[17]. Trimethylenemethane **3** is a familiar example (see Figure 4). To avoid such clumsy and imprecise terminology, I propose to call structures like **3** - joint.

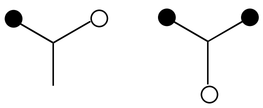
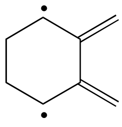


Figure 4. *Non-disjoint non-bonding orbitals for trimethylenemethane.*

At the Hückel level, both **1** and **3** are predicted to be ground-state triplets. Cyclobutadiene **1** is disjoint (see **A**, Figure 3), while trimethylenemethane **3** is joint (see Figure 4). Borden and Davidson[17] propose that a disjoint hydrocarbon like **1** will, in reality, have lowest singlet and triplet states that are very nearly degenerate. In contrast, they propose that a joint hydrocarbon like **3** will have a lowest-lying triplet state which lies well below the corresponding open-shell singlet at the SCF level[17]. In their paper,[17] they point out that **1** (disjoint) is known to be a ground-state singlet and **3** (joint) is known to be a ground-state triplet in accord with their proposal.

In their publication,[17] planar tetramethylenethane **4** was shown to be disjoint and, based on molecular orbital calculations, predicted to be a ground-state singlet. In 1970,[19] Dowd had produced a triplet state of **3** via irradiation at 77°K. It was not clear whether the triplet state produced was, in fact, the ground state. In 1986,[20] Dowd et al. exploited an alternative synthesis, produced **3** and established experimentally that it is a ground-state triplet. Because it was unclear whether the triplet ground-state of **3** is planar, Dowd et al.[21] prepared the conformationally restrained system **5** and showed that it too is a ground-state triplet. They then concluded that planar **5** is a ground-state triplet.[21] Subsequently, Borden and Du reported[22] that *ab initio* calculations predict that both planar and nonplanar **3** have a singlet ground state. The singlet was predicted to prefer the perpendicular geometry. Finally, Dowd et al.[23] have reported *ab initio* results for the lowest-lying triplet states of **5** and **6**, both of which have been shown experimentally to be ground-state triplets[21,24-26]. **5** was calculated to deviate from planarity by 25° while **6** was predicted to have a planar structure[23].



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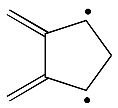


6

From the mix of experiments and computations provided by Dowd and his colleagues, it now seems clear that both planar and twisted tetramethylenethanes are, indeed, ground-state triplets.

A convenient summary[27] of experimental results for half a dozen alternant diradicals, including **3** and **4** shows that they are all ground-state triplets regardless of their status as joint or disjoint hydrocarbons.

In spite of the obvious difficulties the Borden and Davidson approach[17] has encountered in anticipating experimentally-determined ground-state multiplicities, one could still expect that it would correctly anticipate computational results.

My interest in these issues arose in connection with ongoing studies of antiaromatic bicycles. To pursue my study, I elected to use calculated energy differences (ΔE_{ST}) between the lowest-lying singlet state and the lowest-lying triplet state. In accord with the analysis offered in a recent paper,[28] the most antiaromatic molecules should have the largest calculated ΔE_{ST} values. As the work progressed, it became desireable to know whether joint or disjoint nonclassical hydrocarbons would generally be most antiaromatic. The present report addresses that question.

METHODS

PM3 computations[29] were carried out using the MOPAC6 program. All computations were fully optimized using the PRECISE command[30]. Triplets were examined with both RHF and UHF methods.

For some time now, we have been applying calculated ΔE_{ST} values to the exploration of hydrocarbon structures. In our experience, semiempirical (MNDO, AM1, PM3) numbers have reproduced *ab initio* (STO 3-21G, MP2/6-31(d)) trends when differences are large (i.e. more than 5 kcal/mol)[28,31]. Hence, larger PM3 calculated $\Delta\Delta E_{ST}$ values (see Table 1 and compare **11** with **12** or **8** with **15**) should be reasonable. We have recently published a PM3 study featuring PM3 calculated ΔE_{ST} values[32].

RESULTS AND DISCUSSION

Given the proposal advanced by Borden and Davidson,[17] I began this study with the expectation that disjoint nonclassical hydrocarbons would have significantly smaller ΔE_{ST} values than similar joint nonclassical hydrocarbons. As a consequence, disjoint nonclassical hydrocarbons should be much less antiaromatic. Before turning to PM3 computational results, it would be useful to examine the advice given earlier,[17] regarding hydrocarbon classification.

Borden and Davidson have suggested[17] that facile classification of a hydrocarbon as joint or disjoint can be done by employing a perturbation molecular orbital (PMO) analysis. To properly employ a PMO analysis, one should disconnect an even alternant hydrocarbon into two odd alternant fragments. From the Pairing Theorem,[21] each fragment will have at least one nonbonding molecular orbital (NBMO). The number of NBMO's (Hückel level) for an odd acyclic alternant hydrocarbon is equal to the number of nonbonding electrons on the Lewis structure, after one has maximized the number of π bonds in the structure. To obtain an unambiguous PMO prediction, each fragment should have a single NBMO. Consequently, useful disconnections will produce odd alternant fragments each of which shows only one dot on its Lewis structure. After an appropriate disconnection has been carried out, one can deduce the form of the NBMO for each fragment by (i) embedding,[34] (ii) using the zero sum rule[17] or (iii) carrying out zeroth order Hückel calculations[35].

To illustrate the method, consider tetramethylenethane **4**. It may be disconnected into two allyl fragments as shown in Figure 5.

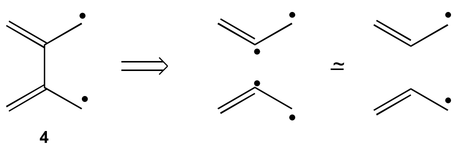


Figure 5. *Disconnection of 4 into a pair of allyl radicals.*

Because Hückel theory is constrained to π systems, each diradical produced by a disconnection is approximated by a radical in which the unpaired σ electron is ignored. The recombination of allyl radicals to regenerate **4** is depicted using the NBMO of each as shown in Figure 6.

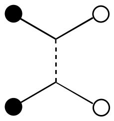


Figure 6. *The recombination of allyl fragments to regenerate **4**.*

According to the earlier paper,[17] when the recombination connects "inactive" centers (those with a zero coefficient in their NBMO), the product will be disjoint. Hence **4** is expected to be disjoint, whether or not Hückel calculations on **4** happen to provide a disjoint representation for the NBMO's. Therefore, **4** should have nearly degenerate lowest-lying singlet and triplet states[17].

Recombination of the allyl fragments leads to a different classification for a different hydrocarbon as shown in Figure 7.

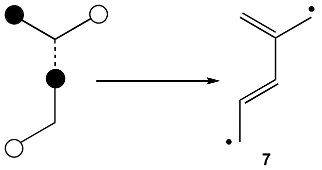
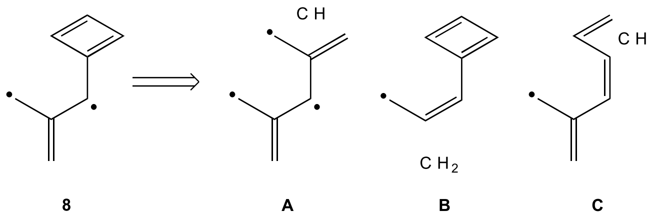


Figure 7. *The recombination of allyl fragments to regenerate **7**.*

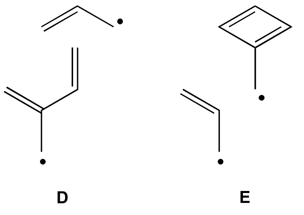
Since that recombination involves interaction of an "active" center (one which has a non-zero coefficient in the NBMO) with an inactive center, **7** is expected to be a joint hydrocarbon. Therefore, **7** should be a ground state triplet.

Both the presentation in Figures 5, 6 and 7 and the discussion in reference 17 make the PMO approach seem simple and convenient. In reality, it provides ambiguous, inconsistent answers unless it is applied thoroughly. Figure 8 presents all of the possible PMO disconnections for the nonclassical hydrocarbon **8**.

Disconnection **A** (Figure 8) produces a C_7 fragment which, even when s radical electrons are ignored, must show three nonbonding electrons. It has three NBMO's at the Hückel level which precludes a unique prediction for **8** and is thus not useful. Disconnections **B** and **C** (Figure 8) lead to the same conclusion, i.e. **8** should be a joint hydrocarbon (see Figure 9).



All possible 7 + 1 disconnections for **8**.



Both possible 5 + 3 disconnections for **8**.

Figure 8. *All PMO disconnections for **8**.*

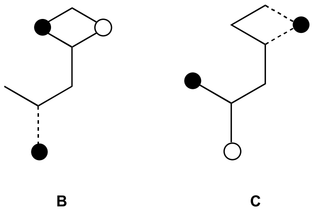


Figure 9. *Recombinations **B** and **C** lead to the conclusion that **8** is joint.*

In sharp contrast, both disconnections **D** and **E** lead to the conclusion that **8** must be a disjoint hydrocarbon (see Figure 10).

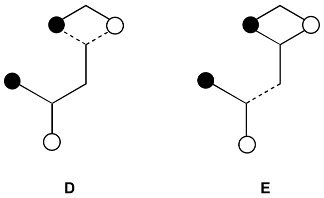
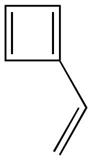


Figure 10. *Recombinations **D** and **E** lead to the conclusion that **8** is disjoint.*

In order to reach the correct conclusion, each structure must be subjected to all possible disconnections and each recombination examined until the structure is found to be disjoint. Only if all possible recombinations find the structure to be joint, can one reach the PMO-based conclusion that the structure is, in fact, joint. Note that even the simple structure **4** is incorrectly classified as a joint hydrocarbon if one only applies a 5+1 disconnection for its PMO analysis.

As outlined in the introduction, a convenient method for comparing hydrocarbons with respect to aromatic character would be PM3 calculations of ΔE_{ST} values. Aromatic singlets are expected to have large highest occupied molecular orbital - lowest unoccupied molecular orbital (HOMO-LUMO) splittings, estimates of which are available from ${}^{S}\Delta E_{FMO}$ values provided by PM3 calculations on lowest-lying singlet states. Antiaromatic hydrocarbons are expected to have negligible splittings between singly occupied molecular orbital (SOMO) energies, so that ${}^{T}\Delta E_{SOMO}$ values should provide another measure of antiaromatic character. Tabulated PM3 results for hydrocarbons include all three parameters.

Consider the isoconjugate hydrocarbons **4**, **7**, **9** and **10**. Hexatriene **10** has no NBMO (it lacks a 4N ring and has no nonbonding electrons on its Lewis structure) and is, therefore, neither joint nor disjoint. Such structures will be termed ajoint. Figures 6 and 7 show that hydrocarbons **4** and **7** are disjoint and joint, respectively. Figure 11 demonstrates that **9** must be classified as disjoint.



9

10

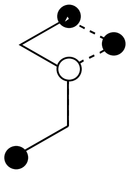


***Figure 11.** A recombination which shows that **9** must be disjoint.*

Based on the Borden and Davidson proposal,[17] one would expect ΔE_{ST} to have (i) a large negative value for hexatriene **10**, (ii) a value near zero for the disjoint systems **4** and **9** and (iii) a large positive value for the joint hydrocarbon **7**. Table 1 presents the PM3 results for these compounds.

Table 1. PM3 calculated ΔE_{ST}, ${}^{S}\Delta E_{FMO}$ and ${}^{T}\Delta E_{SOMO}$ for hydrocarbons

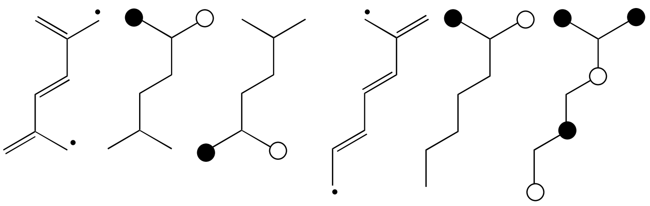
Compound	Type[a]	ΔE_{ST}[b] (kcal/mol)	${}^{S}\Delta E_{FMO}$ (eV)	${}^{T}\Delta E_{SOMO}$[b] (eV)
4	D/NC	44.9	4.1	0.0
7	J/NC	45.7	4.1	0.0
9	D/C	-4.3	7.9	0.0
10	A/C	-34.3	8.7	2.1
11	D/NC	61.5	2.6	0.0
12	J/NC	42.8	3.8	0.0
14	A/C	-30.4	8.0	1.7
1	D/C	-4.3	8.6	0.0
3	J/NC	53.0	4.5	0.0
13	A/C	-39.2	9.2	2.6
8	D/NC	52.3	3.8	0.1
15	J/NC	29.7	5.0	0.3
16	D/C	-5.0	7.5	0.0
17	A/C	-35.6	8.7	2.0
18	D/NC	48.3	3.2	0.2
19	D/NC	44.5	3.6	0.0
20	J/NC	34.5	4.4	0.3
21	D/C	-5.9	7.1	0.0
22	A/C	-18.1	7.1	1.6

[a] D = disjoint, J = joint, A = ajoint, C = classical, NC = nonclassical
[b] Reported numbers use RHF results for the lowest triplet state.

The ΔE_{ST} results in Table 1 categorically reject the Borden and Davidson proposal as it applies to expected differences between nonclassical structures **4** and **7**. On the other hand, the classical antiaromatic system **9** has a ΔE_{ST} value close to zero as they would predict. Note that Table 1 results correctly anticipate experimentally-established ground-state multiplicity for both **4** and **7**. Of the two additional parameters reported in Table 1, the frontier orbital splitting for the lowest-lying singlet (${}^{S}\Delta E_{FMO}$) correlates better with calculated ΔE_{ST} values.

Based on the results for **4**, **7** and **9**, one might now propose that *all* alternant nonclassical hydrocarbons exhibit a strong preference for triplet ground states and that *only classical disjoint alternant hydrocarbons consistently have nearly-degenerate lowest-lying triplet and singlet states*. Such a conclusion is also entirely compatible with our experience with computational studies of non-alternant monocycles: the π-ylides[31,36].

Structures **11**, **12** and **14** constitute another set of compounds encompassing all categories: disjoint, joint and ajoint. Like hexatriene **10**, octatetraene **14** is ajoint. Figure 12 presents representations for the NBMO's of **11** and **12** which show them to be disjoint and joint, respectively.



11

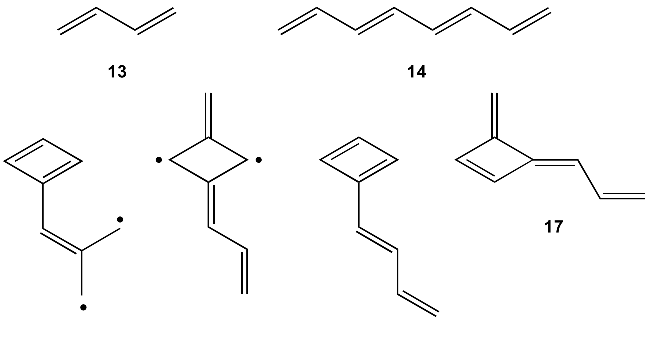
12

***Figure 12.** NBMO representations for **11** and **12** showing that **11** is disjoint and **12** is joint.*

Once again, Borden and Davidson would expect the disjoint nonclassical structure **11** to have nearly-degenerate singlet and triplet states and the joint nonclassical structure **12** to exhibit a strong preference for the triplet state. The PM3 calculated ΔE_{ST} values in Table 1 show that both **11** and **12** are expected to exhibit pronounced preference for triplet ground states. Moreover, it is the disjoint system **11** which is predicted to have the larger ΔE_{ST}, *not* the joint system **12**.

PM3 results (Table 1) for cyclobutadiene **1** and trimethylenemethane **3**, along with those for butadiene **13** are in accord with the results reported for them by Borden and Davidson[17]. They are also compatible with my generalization that only classical disjoint structures should be expected to have nearly-degenerate lowest-lying singlet and triplet states.

A modest selection of monocycles, which includes classical and nonclassical as well as disjoint, joint and ajoint structures is made up of compounds **8, 15-17** (see Figure 13).



13 **14**

17

8 **15** **16**

Figure 13

The PM3 results for compounds **8, 15-17** are consistent with the earlier results in Table 1. Both the disjoint and joint nonclassical hydrocarbons **8** and **15** are calculated to be ground-state triplets. In direct opposition to Borden and Davidson,[17] it is the nonclassical disjoint system **8** which has the largest ΔE_{ST} value. In accord with their proposal,[17] the classical disjoint hydrocarbon **16** shows a weak preference for the singlet ground state.

Table 1 presents results for a selection of alternant hydrocarbon bicycles **18-22** (see also Figure 14).

These results are consistent with all others in Table 1 and fully support the conclusions reached above. Note again that ${}^{S}\Delta E_{FMO}$ (FMO stands for frontier molecular orbital) correlates better with ΔE_{ST} than does ${}^{T}\Delta E_{SOMO}$.

I have examined an assortment of isoconjugate structural isomers which are not included in Table 1 and they all give PM3 results consistent with the results reported herein.

Table 1 ΔE_{ST} values were calculated with RHF singlet and RHF triplet descriptions. There are those who believe that "antiaromatic" structures like **1** and **3** should be examined computationally, using UHF methods. The most noteworthy changes in going from RHF-triplet based ΔE_{ST} values to UHF-triplet based ΔE_{ST} values were obtained for the classical

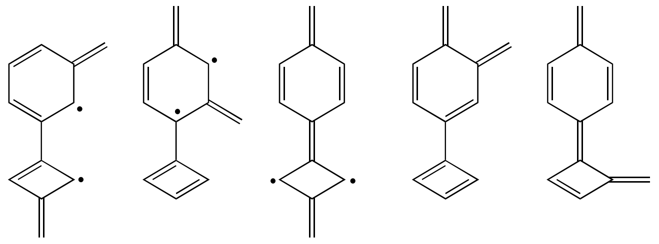

18 19 20 21 22

Figure 14

antiaromatics **9** and **16**. **9** and **16** (like cyclobutadiene **1**) were expected to be ground-state singlets using RHF-triplet based ΔE_{ST} values. Both **9** and **16** are expected to be ground-state triplets using UHF-triplet based ΔE_{ST} values. None of the discussion of isoconjugate nonclasical disjoint, joint pairs in Table 1 is affected by a change to UHF-triplet based ΔE_{ST} values. For example, the nonclassical structural pair **8** and **15** have RHF-triplet based ΔE_{ST} values of 52.3 and 29.7 kcal/mol, respectively, suggesting that **8** has a stronger predilection for a triplet ground state. **8** and **15** have UHF-triplet based ΔE_{ST} values of 74.8 and 50.8 kcal/mol, respectively, leading to the same conclusion.

The proposal[17] that both classical and nonclassical hydrocarbons should strongly prefer triplet ground states when the compound is joint but should have nearly-degenerate lowest-lying singlet and triplet states when the compound is disjoint is inconsistent with PM3 results for an appropriate selection of small hydrocarbons. Instead, PM3 results show that only classical disjoint structures have nearly-degenerate lowest-lying singlet and triplet states. When there is a significant difference between disjoint and joint hydrocarbon ΔE_{ST} values, it is usually *the disjoint hydrocarbon* which shows the stronger preference for a triplet ground state i.e. *is more Y-antiaromatic*.

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