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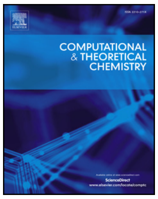

Computational search for metastable high-spin C_5H_n (n = 4, 5, 6) species

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ABSTRACT

A search for small hydrocarbon radicals with two electronic spin states of comparable stability has identified 9 candidates among singlet and triplet states of various isomers of cyclic C_5H_4, cyclic C_5H_6, and acyclic C_5H_6. No quartet states of C_5H_5 were found to be comparable in energy to the doublet state of the same structural isomer. Equilibrium geometries, term energies, and vertical excitation energies have been predicted by CCSD(T)-F12a/cc-pVDZ-F12 calculations. Relative coupled cluster energies are in fair agreement with small active space MCSCF calculations, which were then used for rough predictions of the intersystem crossing (ISC) barriers. Results suggest that only 1,3-cyclopentadienylidene, with a calculated barrier of 71 kJ mol^{-1}, is likely to be experimentally observable in both high-spin and low-spin electronic states. The other candidates found to have ISCs in this work have potential energy curves that pose barriers of less than 35 kJ mol^{-1} for relaxation to the ground state. Surface hopping calculations on the 1,3-cyclopentadienylidene surface have further characterized the dynamics of the ISC for that system.

1. Introduction

Several reactive C_5H_n molecules play prominent roles as chemical intermediates in combustion processes. A variety of their cations, anions, and free radical isomers have been observed by mass spectrometry in hydrocarbon-rich flames [1–7]. There have been also a number of computational studies [1,6,8–22] to predict properties such as electronic structure, electron affinity, isomerization energies, reaction pathways, and reactivity. Among the reasons for this interest is that multiple C_5H_n isomers may participate in the formation of polycyclic aromatic hydrocarbons and soot. Furthermore, high-spin states of organic species may play an important role in environmental photochemistry [23]. There are few prior computational studies of these intermediates, perhaps given the need for multireference ab initio methods and anharmonic vibrational analysis [24,25].

With expansion of unsaturated hydrocarbons beyond four carbons, the π-electron system becomes capable of supporting high-spin states, with multiple unpaired electrons, at energies nearly as low as the ground electronic state. This often appears in computational chemistry as spin contamination of the low-spin states, a problem that increases with the size of the unsaturated carbon chain [26]. For hydrocarbons, the *global* minimum on the vibronic potential energy surface generally corresponds to lowest possible spin multiplicity, either singlet (for an even number of electrons) or doublet (for an odd number), and for the smallest hydrocarbons the high-spin state is rarely more stable than the low-spin state at any geometry.

However, certain carbon-skeleton systems may isolate single unpaired electrons along the backbone, making the high-spin state the most stable for the given structural or configurational isomer. While triplet/singlet spin systems have long been studied in many classes of molecules, studies of quartet states have largely been confined to very small systems, particularly diatomic or triatomic molecules [27–29].

It is in the larger, unsaturated chain and ring systems that the high-spin states are both relevant to the bonding and capable of competing for stability with the low-spin ground state at suitable geometries. Interest in quartet-state hydrocarbons has been of long standing [30] and high-spin electronic states of organic molecules are receiving renewed attention as potential media for spintronic devices [33]. However, few accounts of experimental studies exist in the literature. For example, ESR and ENDOR studies of quartet spin phenylmethylene ions were reported in the 1990s [31,32]. Matrix isolation and molecular beam experiments provide avenues for the formation and study of reactive intermediates such as these, but tend to concentrate on the more stable electronic ground states. Identification of the molecular carrier and interpretation of the data become increasingly challenging with excitation. Generally the intrinsic difficulties in working with such highly reactive species suggest that exploratory computational studies could assist further experiments.

In this work we search for stable and metastable triplet and quartet geometries of selected, low molecular weight hydrocarbons with molecular formulas C_5H_4, C_5H_5, and C_5H_6. These highly unsaturated hydrocarbons may allow the high-spin states to localize unpaired electrons on different carbons, while still having the flexibility of π-bonding to rearrange and recombine the orbitals for the low-spin states.

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2. Methods

An initial survey of C_5H_4, C_5H_5, and C_5H_6 structural isomers was carried out by calculating optimized QCISD/cc-pVDZ [34–36] geometries for both low-spin and high-spin states, followed by single-point energies of each spin state at the optimized geometry of the other spin state. To keep the scope of the project within our resources, the search was limited to all of the cyclopentene/yne rings and to all of the symmetrically hydrogenated, acyclic, unbranched isomers $CH_kCH_mCH_nCH_mCH_k$. This amounted to a total of 35 molecules in the survey over 6 distinct molecular systems (7 cyclic C_5H_4, 7 cyclic C_5H_5, 7 cyclic C_5H_6, 5 acyclic C_5H_4, 3 acyclic C_5H_5, and 6 acyclic C_5H_6 structural isomers). Previous work in our group on similar small, unsaturated hydrocarbon free radicals [37–39] had suggested that this level of theory and basis would be adequate for a rough assessment of the relative energies of these states. However, subsequent calculations found discrepancies between QCISD and CCSD(T)-F12a relative energies of up to about 60 kJ mol^{-1}, so most of these survey energies were recalculated at the CCSD(T)-F12a/cc-pVDZ-F12 level and basis [40,41]. We did not pursue calculations on molecules where the lowest QCISD energy was at least 400 kJ mol^{-1} above the global minimum energy for that molecular formula (the minimum energy isomers are 1,3-pentadiyne for C_5H_4, cyclopentadienyl for C_5H_5, and cyclobutadiene for C_5H_6). Despite our concerns over possible spin contamination in the single-reference calculations, $S^2 - S_z(S_z + 1)$ in the CCSD(T)-F12a calculations was less than 0.03 in all cases.

Coupled cluster calculations based on an unrestricted reference wavefunction should be reliable for the high-spin states, because use of the $M_S = S$ spin component in the determinants excludes mixing with the lower spin state. However, for the present systems that exhibited a spin crossing, we wished to carry out at least a crude examination of the potential energy surface near the intersection of high-spin and low-spin states. The degeneracy of the two states at the intersection contaminates the lower spin state in a single-reference calculation, so for cases exhibiting a spin crossing at the coupled cluster level, we performed multireference (MCSCF/aug-cc-pVDZ) calculations on the lowest energy of these isomers ($E_{\text{iso}} < 400$ kJ mol^{-1}) to optimize the conic intersection of the low-spin and high-spin surfaces. Only C_5H_4 and C_5H_6 were found to have these spin crossings, and the MCSCF calculations employed (6,6) active spaces, which were adequate to encompass all π and unpaired electrons. We took advantage of the MCSCF reference states to carry out MRCISD/cc-pVDZ calculations on a small set of these species, and found that relative adiabatic term energies agreed with values from CCSD(T)-F12a/cc-pVDZ-12 to within 12 kJ mol^{-1}, although vertical excitation energies differed by up to 33 kJ mol^{-1}.

Frequency corrections for the relative equilibrium energies were provided by QCISD/cc-pVDZ calculations. In many cases these geometries initially converged to unstable symmetric geometries and required reoptimization after strongly breaking the symmetry. In addition, many calculations required the quadratic optimization algorithm, additional damping factors, or orbital switching to optimize the HF wave functions. All CCSD(T) calculations were carried out with MolPro [42], multi-reference calculations with GAMESS [43], and QCISD calculations with Gaussian 09 [44]. Orbital selection for the MCSCF active spaces was made possible by use of the Molekel visualization package [45].

3. Results and discussion

The three levels of theory used in this study result in relative energies which are qualitatively consistent but subject to discrepancies of tens of kJ mol^{-1}, as shown in Table 1. We note that the QCISD relative energies are not in substantially better agreement with the CCSD(T)-F12a values than the MCSCF energies, although previous work on the ground states of similar systems has found QCISD to be a reliable approximation of CCSD(T) relative energies. This reflects the enhanced importance of the higher level excitations when studying excited states. Spin contamination as high as 10% was also observed in isolated QCISD triplet state calculations, suggesting a related reason for the discrepancies. Nevertheless, in 6 of the 9 cases in Table 1, the three methods predict adiabatic energy differences all agreeing to within 22 kJ mol^{-1}.

Table 1
Uncorrected adiabatic energy differences (triplet–singlet) in kJ mol^{-1} for the 9 spin-crossing cases investigated in this work.

Method	MCSCF(6,6)	QCISD	CCSD(T)-F12a
Basis set	aug-cc-pVDZ	cc-pVDZ	cc-pVDZ-F12
Species	$\Delta E_{\text{T-S}}$	$\Delta E_{\text{T-S}}$	$\Delta E_{\text{T-S}}$
1 (c-CHCHCHCHC)	−18.4	−57.1	−29.1
2 (c-CH_2CH_2CCC)	49.9	75.9	85.3
2B (c-CH_2CH_2CCC)[a]	17.5	20.0	28.4
3 (c-CH_2CH_2CHCHC)	4.7	2.8	24.7
4 (c-CH_2CH_2CHCCH)	9.2	53.6	28.7
5 (c-$CH_2CHCHCH_2C$)	13.0	11.1	33.2
6 (c-CH_2CHCH_2CHC)	9.9	−20.2	13.3
7 (c-$CH_2CH_2CCH_2C$)	25.1	9.3	28.9
8 ($CH_2CHCCHCH_2$)	−38.5	−45.5	−26.1
9 (CH_3CCCCH_3)	−31.4	−46.8	−28.2

[a] Secondary minimum singlet geometry; see text.

This study identified nine species with spin crossings as well as three more in which the high-spin state is the most stable, even at the low-spin optimized geometry. All of the spin crossings were found for structural isomers of C_5H_4 or C_5H_6, so all involve singlet/triplet state combinations. For one of the C_5H_4 and both of the acyclic C_5H_6 species, the triplet state is predicted to be the ground electronic state; the singlet state is the global minimum for all of the other spin-crossing systems. Table 2 summarizes these results and the labeling scheme used for these molecules in the rest of the discussion. For example, in structure **1**, the triplet state is more stable than the singlet by 27 kJ mol^{-1}, including zero-point, and the vertical transition from the triplet to the singlet state at the triplet optimized geometry is predicted to be 181 kJ mol^{-1}. The triplet state of **1** is 104 kJ mol^{-1} higher in energy than the most stable C_5H_4 isomer, 1,3-pentadiyne. The MCSCF conic intersection calculation estimates that the singlet state would have to overcome a barrier of 71 kJ mol^{-1} to relax to the triplet state.

Three more of the highest energy acyclic species were identified as having persistent high-spin ground states, lower in energy than the low-spin state at both optimized geometries: CHCHCHCHCH (quartet state isomer energy 355 kJ mol^{-1}), $CHCHCH_2CHCH$ (463 kJ mol^{-1}), and $CH_2CCH_2CCH_2$ (439 kJ mol^{-1}). Their geometries and other properties are listed in the SI. The acyclic C_5H_6 isomer $CCH_2CH_2CH_2C$ was found to have a spin crossing, but with a relative isomer energy of over 900 kJ mol^{-1} it is too unstable for likely relevance to combustion chemistry. One cyclic C_5H_5 structure was found to have a spin crossing at the QCISD level, but not at the CCSD(T)-F12a level.

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.comptc.2018.07.010.

Most of the molecules in our survey (including all the acyclic structures, by design) can adopt two-fold symmetry, and several converge on C_{2v} or C_s geometries. In those cases, the singlet states, with MOs all doubly occupied, are $^1A_1$ or $^1A'$ symmetry, while the triplet states are all $^3B_1$ or $^3A''$ symmetry (where b_1 is chosen to be antisymmetric with respect to the plane of the carbon atoms). In each of the triplet cases, the symmetry arises from the unpaired electrons being split between one in-plane a_1 or a′ MO and one out-of-plane b_1 or a″ MO.

C_5H_4isomers. Structure 1 (c-CHCHCHCHC). Species **1**, 1,3-cyclopentadienylidene, is the most stable isomer of the species studied, only 79 kJ mol^{-1} above 1,3-pentadiyne (the C_5H_4 global minimum), and **1** is the only cyclic system in this study which is more stable in the high-spin electronic state. The singlet adopts an asymmetric geometry, reducing