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# Conjugated π-Electron Systems in Reactive Molecules: Multiple Minima on $^2A'$ Potential Surfaces of Carbon Chain Free Radicals

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**Abstract:** Favorable, nonequivalent canonical structures for a given free radical may correspond to local minima on the *ab initio* potential surface of the ground electronic state. The isomerization path between two such structures involves the relocation of an unpaired electron and coincident transformation of the donor and acceptor molecular orbital hybridizations. In *ab initio* calculations, this may cause convergence to a local minimum. In experiments, the relatively flat bending potential will complicate the vibrational energy level structure. Self-consistent field (SCF) and configuration interaction (CISD) calculations were employed in a search for multiple minima on the potential energy surfaces of seven $X^2A'$ free radicals: $NC_2O$, $FC_3O$, $ClC_3O$, $HC_3NH$, $HC_4H_2$, $HC_2N_2$, and $FC_4H_2$. Minima were assumed to lie near the acetylenic, cumulenic, or allylic canonical forms. All of the three- and four-carbon compounds in this set exhibit at least two minima on the SCF potential surface. At the CISD level, two stable structures were identified for $ClC_3O$ and $HC_4H_2$, and three were found for $FC_4H_2$. In all cases, bending amplitudes of more than 40° are classically allowed at energies less than 3000 cm$^{-1}$ above the global minimum potential energy. Ramifications of these potential surfaces are discussed, and a crude energy additivity comparison is presented. Predicted stationary point geometries, permanent dipole moments ($\mu$), Fermi contact terms ($a$), and isomerization barriers are given.

## 1. Introduction

**A. $^2A'$ Carbon Chain Free Radicals.** Free radicals with conjugated π-electron systems have been studied in the contexts of diacetylene polymerization,[1] allene cycloaddition and the captodative effect,[2] acetylene pyrolysis,[3] and interstellar chemistry.[4] Because of their importance to the kinetics of these diverse chemical processes, the unusual dynamic properties of these molecules require greater scrutiny.

Free radicals with favorable, nonequivalent canonical geometries may have local minima near each of these geometries on the vibrational potential energy surface. If so, the low-energy interconversion between the geometries will involve significant changes in the molecular orbital (MO) hybrids, the bond orders, and the unpaired electron localization. An example is the $^2A'$ radical of the form $R_{sp}{\equiv}C{-}\dot{S}_{sp^2}$ (structure I), which may transform into the cumulene $\dot{R}_{sp^2}{=}C{=}S_{sp}$ (structure II), where the R- and S-group subscripts denote the σ-bond MO hybridization of the atom bonded to the carbon. A third, linear geometry (structure III) is also possible, with the carbon atom at the center of a three-electron allylic π system[5]: $R_{sp}{\equiv}C{-}\dot{S}_{sp} \leftrightarrow \dot{R}_{sp}{=}C{=}S_{sp}$, with an unpaired electron in p atomic orbitals. These canonical forms are illustrated in Figure 1. These may all appear to be resonance structures of a single isomer, but each may correspond to a stable structure, a minimum on the compound's vibrational potential energy surface. This report presents *ab initio* results for several $^2A'$ carbon-chain radicals and suggests that multiple minima are common among the potential surfaces of these molecules and that large-amplitude bending is typical at energies less than 3000 cm$^{-1}$.

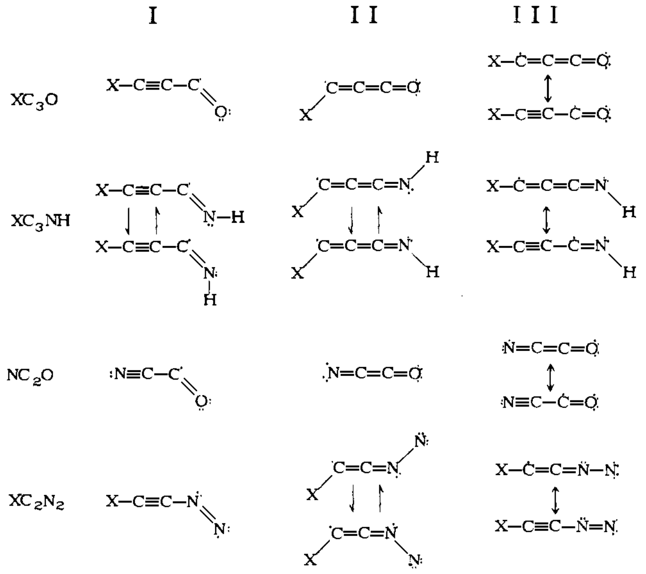

**Figure 1.** Canonical structures for the molecules investigated in the present work, with X = H, F, Cl. For simplicity, the $XC_4H_2$ structures (which are equivalent to the $XC_3O$ structures) and canonical structures with formal charges are omitted.

The transformation of $XC_3O$(I) to $XC_3O$(II) in Figure 1 is characterized by the following concurrent changes, phrased in terms of the local bonding model with the C atoms labeled according to $XC_aC_bC_cO$: (1) the sp MO hybrid of the $C_a$ atom

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(1) Kollmar, C. *Chem. Phys.* **1994**, *182*, 131−147.

(2) Pasto, D. J. *J. Am. Chem. Soc.* **1988**, *110*, 8164−8175.

(3) Kiefer, J. H.; Sidhu, S. S.; Kern, R. D.; Xie, K.; Chen, H.; Harding, L. B. *Combust. Sci. Technol.* **1992**, *82*, 101−130.

(4) Adams, N. G.; Smith, D.; Giles, K.; Herbst, E. *Astron. Astrophys.* **1989**, *220*, 269−271.

(5) The bonding in this structure will be termed "allylic", because it is characterized by three electrons, one unpaired, distributed among the π molecular orbitals formed from three p atomic orbitals centered on sequential atoms. There is one additional, paired electron π orbital with nodal plane coincident with the molecular plane, replacing the center C−H bond of the allyl radical.

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becomes $sp^2$; (2) the $sp^2$ MO hybrid of the $C_c$ atoms becomes sp; (3) an unpaired electron moves from $C_c$ to $C_a$, occupying one of the binding sites of the $sp^2$ hybrid in either location; (4) the geometry of the nuclei changes accordingly (in particular, the XCC and CCO bond angles change by 60°). Similar changes are required for the transformation to the linear structure. Such dramatic alteration in the bonding is possible for the isomerization of a stable molecule only by breaking chemical bonds, and is therefore accompanied by much higher barriers. The potential surfaces of some closed-shell carbenes, however, bear strong resemblance to those of the radicals in the present study.[6]

In order for a chain molecule with a single unpaired electron to isomerize along this path without invoking formal charges, the radical centers involved must be separated by an odd number of atoms. Therefore, the smallest free radicals for which this effect is likely are three-atom chains, not including chain terminations such as the X and O atoms in $XC_3O$. Detailed spectroscopic characterization of free radical geometries has recently been extended to chains of this size, and the possibility of two or more nearly isoenergetic minima in these molecules must now be addressed.

The prototypical candidate for this isomerization problem is $HC_3O$, the subject of recent experiments[7-9] because of its application to combustion science[10] and in interstellar chemistry.[4] There are two minima on the potential energy surface of the $^2A'$ ground electronic state, according to *ab initio* calculations,[11,12] corresponding approximately to canonical structures I and II in Figure 1. Structure III, the linear form, is not predicted to be stable except in the lowest $^2A''$ excited state.[13] The $HC_3O$(I) structure is predicted to be more stable than $HC_3O$(II) by 2000 $cm^{-1}$, with a barrier for isomerization of 2100 $cm^{-1}$.[12] The geometry for the most stable structure has been determined by microwave spectroscopy of the complete set of monosubstituted isotopomers[8] and is in good agreement with the *ab initio* predictions. The predicted minimum near the cumulene remains unconfirmed. Experimental probes of the potential energy surface of $HC_3O$ are at an early stage, but one of the vibrational transitions has already been observed by Jiang and Graham[9]. More recently, the millimeter-wave spectrum of $HC_3S$ has been investigated, prompting *ab initio* calculations which predict that both $HC_3S$(I) and the linear $HC_3S$(III) are minima on the potential surface.[14]

The generality of this isomerization problem is of interest in the following contexts: (1) the interpretation of vibrational spectra in these molecules, given the possibility of large-amplitude bending along the isomerization coordinate (the vibrational mode that couples the two configurations); (2) the effect on the radical's chemical activity of a large temperature-dependence in the unpaired electron distribution; (3) the contribution of resonance stability to these radicals in chemical models; and (4) *ab initio* calculations on these molecules seeking to identify the global minimum on the potential surface. As an illustration of this last point, the first calculations on $HC_3O$[11] were not carried out at the global minimum because initial geometry optimization converged to a higher energy structure. Of the present candidates, only $HC_4H_2$ appears to have a prior literature of *ab initio* calculations, for which a linear carbon chain was assumed.[15]

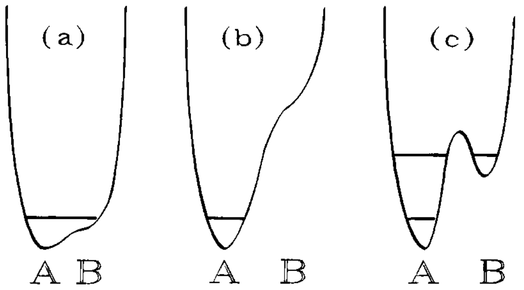

**Figure 2.** Qualitative potential energy surfaces and ground-state energies along a vibrational coordinate coupling two nonequivalent structures A and B: (a) A and B are resonance structures separated by less than the zero-point vibrational amplitude; (b) A and B are resonance structures, with little contribution from B in low energy states; (c) A and B are distinct isomers, effectively with distinct ground states.

**B. Nomenclature.** The near degeneracy of these structures causes ambiguity in the chemical nomenclature. $HC_4H_2$, for example, may be identified either as butenynyl radical (configuration I) or as butatrienyl radical (configuration II). For expedience, only the chemical formulas will be used in this paper.

The present problem is similar to that of conformational isomers; it cannot be assumed at the outset that a given molecule is satisfactorily represented by any single, rigid geometry. Because of their conceptual simplicity, however, a variety of rigid geometries will be invoked in the following discussion. The following definitions are adopted for convenience.

*Geometry* and *structure* refer to rigid arrangements of the atomic nuclei (for example, resonance structures and equilibrium geometries) rather than to any true state of the molecule. A *canonical* structure is an idealized geometry with bond angles and bond lengths fixed by a localized bond structural model; $sp^2$ bond angles are 120°, etc. A *resonance* structure is one of two or more canonical structures differing so little in parameter space that no potential barrier exists between them, as illustrated in Figure 2a. Nonequivalent resonance structures have different stabilization energies, and it may be that the contribution of the less stable structure to a particular vibrational state is negligible (Figure 2b). If there is a barrier between two canonical structures (Figure 2c), these structures will be referred to as distinct *isomers*, without regard to the height of the barrier.

*Configuration* refers to the molecule in some dynamic state that is still well-characterized by a single geometry. Configuration I, for example, is a state of the molecule (real or ideal) with vibrational wave function concentrated in the region of parameter space near structure I in Figure 1. It will be demonstrated later that such a structure need not be the equilibrium structure. The geometries of *ab initio* local minima in this work correspond approximately to canonical structures, and will be labeled by the same scheme: I (acetylenic), II (cumulenic), and III (linear).

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(6) The triplet structure $H—\ddot{C}_{sp^2}—C{\equiv}C_{sp}—H$ and $H—\dot{C}_{sp^2}{=}C{=}\dot{C}_{sp^2}—H$, for example, are both found to be stable: Jonas, V.; Böhme, M.; Frenking, G. *J. Phys. Chem.* **1992**, *96*, 1640–1648.

(7) Cooksy, A. L.; Watson, J. K. G.; Gottlieb, C. A.; Thaddeus, P. *Astrophys. J.* **1992**, *386*, L27–L30.

(8) Cooksy, A. L.; Watson, J. K. G.; Gottlieb, C. A.; Thaddeus, P. *J. Chem. Phys.* **1994**, *101*, 178–186.

(9) Jiang, Q.; Graham, W. R. M. *J. Chem. Phys.* **1993**, *98*, 9251–9255.

(10) Lander, D. R.; Unfried, K. G.; Glass, G. P.; Curl, R. F. *J. Phys. Chem.* **1990**, *94*, 7759–7763.

(11) Tomašić, Z. A.; Scuseria, G. E. *J. Phys. Chem.* **1991**, *95*, 6905–6908.

(12) Cooksy, A. L.; Tao, F.-M.; Klemperer, W.; Thaddeus, P., in preparation.

(13) $HC_3O$, $HC_3S$, and the molecules in the present study are all subject to a ground-state Renner–Teller effect. The doubly degenerate $^2\Pi$ state of the linear geometry splits into nondegenerate $^2A'$ and $^2A''$ electronic states when the molecule becomes nonlinear. This causes additional complications at higher energies, but need not be included in an introductory examination of the $^2A'$ potential surface.

(14) McCarthy, M. C.; Vrtílek, J. M.; Gottlieb, E. W.; Tao, F.-M.; Gottlieb, C. A.; Thaddeus, P. *Astrophys. J.* **1994**, *431*, L127–L130.

(15) Hinchliffe, A. *J. Mol. Struct.* **1977**, *39*, 123–126.

Experimental observation of a secondary isomer would require it to have a lifetime longer than the timescale of the measurement. Those lifetimes are extremely sensitive to the isomerization barrier height, and the accuracy of the present calculations is insufficient to yield meaningful lifetimes. Regardless of the lifetime, there are states at suitably high vibrational excitation for which the equilibrium and secondary structures contribute comparably, and, therefore, the thermochemistry and vibrational spectroscopy at high temperature may be strongly affected by the existence of the secondary structure. The molecules discussed in the present work, which are characterized by potential curves of the sort sketched in Figure 2, b and c, lie very close to the boundary between isomers and resonance structures.

## 2. Methods

*Ab initio* calculations were performed on the ground electronic state potential energy surfaces of the $X^2A'$ free radicals $NC_2O$, $FC_3O$, $ClC_3O$, $HC_3NH$, $HC_4H_2$, $HC_2N_2$, and $FC_4H_2$, all isovalent with $HC_3O$ (treating hydrogen and halogens as isovalent). These molecules were selected for the following characteristics: (1) computational simplicity; (2) likelihood of application to combustion or interstellar processes; and (3) existing thermodynamic data on closed-shell molecular analogues. $FC_4H_2$ was chosen to test application of group additivity to the computational results, based on the results for $FC_3O$ and $HC_4H_2$.

The calculations were carried out using the GAUSSIAN 92 package for molecular structure calculations.[16] The 6-311G** basis set, which is found to converge well for $HC_3O$[12], was used in all optimizations and calculations of the stable structure properties. Initial geometry optimizations were carried out under the unrestricted Hartree–Fock self-consistent field (SCF) approximation. Geometry optimizations were carried out at least three times, with initial geometries corresponding to canonical structures I, II, and III. If more than one stable geometry was identified at the SCF level, configuration interaction with single and double excitations (CISD) was included, and the geometries were optimized using initial parameters from the SCF minima. If any of the three canonical structures did not correspond to a CISD local minimum, the stabilization energy was evaluated at the lowest energy point with the $sp^2$ bond angles fixed to 135° (for structures I or II) or with the heavy atom bond angles fixed to 180° (for structure III). All calculations assumed the molecules to be planar; this is supported by *ab initio* frequency analysis of the SCF structures and by the near-zero inertial defect measured for $HC_3O$.[8]

Activation barriers for isomerization between the two most stable structures were evaluated at the SCF level by direct optimization to the transition state structure. At the CISD level, the geometries were optimized at 5° increments along the "reaction coordinate," which was chosen as one of the two bond angles centered on a changing MO hybridization (*e.g.*, either the FCC or CCO bond angles in $FC_3O$). The maximum energy structure along this path was chosen as the transition state.

Permanent dipole moments were determined from the CISD electron densities as a guide for future rotational spectroscopy. These are expected to be reliable to roughly 0.1 D, based on comparison to experimental results for other open-shell species.[17] Because of the highly fluxional localization of the unpaired electron, these dipole moments will probably have a strong vibrational state dependence. Harmonic vibrational frequencies were determined for the stable structures at the SCF level, but these are not reliable for bending modes coupled to the very anharmonic isomerization coordinate. These frequencies are available as supplementary material.

Limited testing of these methods is possible for $HC_3O$.[8,12] The greatest discrepancies are for the HCC and CCC bond angles, predicted to lie at 179° and 175°, respectively, whereas the experimental bond angles are 168(7)° and 163(2)°. This difference has been tentatively ascribed to the large expected contribution of vibrational averaging in the experimental geometry, due to the flat and asymmetric potential in the isomerization coordinate.[12] In the present work, as for $HC_3O$ previously, CISD was chosen as the most rigorous method for calculating the isomer energies in the available computer time.

**Table 1.** Selected *ab Initio* Parameters of $FC_4H_2$, as Functions of Basis Set and Computational Method[a]

| method<br>basis | SCF<br>6-31G** [a] | SCF<br>6-311G** | MP2<br>6-31G** | CISD<br>6-31G** | CISD<br>6-311G** |
|---|---|---|---|---|---|
| | | Structure I | | | |
| $\Delta E$ ($cm^{-1}$) | [2560] | 2170 | 0 | 0 | 0 |
| $\theta_{C_bC_cC_d}$ | [135.0] | 144.9 | 140.6 | 143.8 | 144.0 |
| $\mu_a$ (D) | [0.61] | 0.68 | 0.24 | 0.41 | 0.38 |
| $\alpha_{C_c}$ (MHz) | [575] | 474 | 222 | 320 | 293 |
| | | Structure II | | | |
| $\Delta E$ ($cm^{-1}$) | 0 | 0 | 150 | 1220 | 280 |
| $\theta_{FC_aC_b}$ | 133.6 | 134.1 | 140.6 | 137.4 | 138.6 |
| $\mu_a$ (D) | 2.01 | 2.07 | 1.37 | 1.64 | 1.60 |
| $a_{C_a}$ (MHz) | 808 | 775 | 413 | 568 | 516 |
| | | Structure III | | | |
| $\Delta E$ ($cm^{-1}$) | [3350] | 2970 | 1120 | 780 | 550 |
| $r_{C_bC_c}$ (Å) | [1.326] | 1.325 | 1.363 | 1.345 | 1.344 |
| $\mu_a$ (D) | [0.81] | 0.83 | 0.15 | 0.44 | 0.42 |
| $a_{C_c}$ (MHz) | [384] | 290 | −3 | 135 | 90 |

[a] The carbons are labeled in the order $FC_aC_bC_cC_dH_2$, and $\Delta E$ is the energy relative to the global minimum. Structures I and II are not stable at the SCF/6-31G** level, and values are reported for the optimized structure with $\theta_{C_bC_cC_d}$ fixed to 135° (I) or with the FCCC chain fixed to linear (III).

It must be emphasized that accurate *quantitative* predictions of the dynamical properties of these molecules will require considerably greater effort, and there is presently little experimental data with which to test them. Table 1 demonstrates for the case of $FC_4H_2$ that, for differing basis sets and methods, the relative isomer energies fluctuate on a scale comparable to the relative energies themselves. The geometries of the stationary points are fairly well-converged, however. Based on this dispersion and that observed in previous results for $HC_3O$[12] and $HC_3S$[14], the accuracy of relative energies in the present calculations is estimated at 1000 $cm^{-1}$.

With isomerization barriers comparable to the zero-point vibrational energy, the effective one-dimensional potential surface along the isomerization coordinate should be corrected for the vibrational energy of the other modes,[12] and harmonic vibrational frequencies may be too inaccurate. Contribution to the stabilization energy by the electronic spin–orbit interaction, which is neglected here, should be less than 100 $cm^{-1}$. Calculations that treat the anharmonic and electron spin effects carefully remain extremely arduous, even for small molecular free radicals. The present work seeks primarily to establish if this class of potential surface is likely to become a topic of experimental and theoretical interest with advancing studies of reactive, conjugated $\pi$-electron carbon chains.

## 3. Results and Discussion

**A. Ab Initio Results.** The principal results are summarized in Table 2, including previous results for $HC_3O$ for comparison.[18] Of the seven molecules tested, $NC_2O$ and $HC_2N_2$ exhibit only one minimum at the SCF level, structure I. Two or three minima were identified at the SCF level for each of the remaining five molecules. Structure III is not the global minimum in any of the systems studied, although it is a local minimum for $HC_4H_2$ and $FC_4H_2$.

The SCF and CISD results give similar geometries for the stationary points. The principal effect of including electron correlation is to change the relative energies of the isomers. The correlation energy (the difference between the SCF and CI stabilization energies) is constant to within 2% among structures

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[16] GAUSSIAN 92, Revision C: Frisch, M. J., *et al.* Gaussian, Inc.: Pittsburgh, PA, 1992.

[17] Hinchliffe, A. *Ab Initio Determination of Molecular Properties*; Adam Hilger: Bristol, 1987; pp 82–90.

[18] In $HC_3O$, a surprisingly large *ab initio* Fermi contact term is found for the center C atom, at which little spin density is expected. That anomaly does not appear in predictions for the present set of molecules.

**Table 2.** Calculated Properties of Selected $X^2$ A′ Free Radicals[a]

| | $HC_3O$[b] | $FC_3O$ | $ClC_3O$ | $HC_3NH$ | $HC_4H_2$ | $FC_4H_2$ |
|---|---|---|---|---|---|---|
| | | | Structure I | | | |
| $\Delta E_{SCF}$ ($cm^{-1}$) | 0 | 3360 | 1610 | 0 | 0 | 2170 |
| $\Delta E_{CI}$ ($cm^{-1}$) | 0 | [2100] | 220 | 0 | 0 | 0 |
| $\mu_{a,CI}$ (D) | −2.56 | | −2.39 | −0.65 | −0.12 | 0.38 |
| $\mu_{b,CI}$ (D) | 0.04 | | 0.29 | 0.92 | −0.49 | −0.46 |
| $a_{Y,CI}$ (MHz)[c] | 73 | | −7 | 19 | −43 | 55 |
| | | | Structure II | | | |
| $\Delta E_{SCF}$ ($cm^{-1}$) | 550 | 0 | 0 | 980 | [650] | 0 |
| $\Delta E_{CI}$ ($cm^{-1}$) | 1990 | 0 | 0 | [2400] | [1800] | 280 |
| $\mu_{a,CI}$ (D) | −1.80 | 0.20 | −0.60 | | | 1.60 |
| $\mu_{b,CI}$ (D) | −0.34 | −0.78 | −0.64 | | | −0.01 |
| $a_{Y,CI}$ (MHz)[c] | 44 | 477 | 42 | | | 383 |
| | | | Structure III | | | |
| $\Delta E_{SCF}$ ($cm^{-1}$) | [1600] | [6800] | 3430 | 1360 | 240 | 2970 |
| $\Delta E_{CI}$ ($cm^{-1}$) | [2400] | [5800] | [2600] | [1900] | 300 | 830 |
| $\mu_{a,CI}$ (D) | | | | | −0.04 | 0.42 |
| $a_{Y,CI}$ (MHz)[c] | | | | | −67 | 102 |
| $E_{a,SCF}$ ($cm^{-1}$) | 720 | 3980 | 1910 | 1280 | | 2180 |
| $E_{a,CI}$ ($cm^{-1}$) | 2130 | | 1710 | | | 800 |

[a] Square brackets denote values for unstable structures obtained by fixing one or more bond angles (see text). $E_a$ is the barrier height for isomerization between structures I and II, measured relative to the global minimum. [b] Reference 12. [c] Fermi contact hyperfine constants for atom Y, with Y equal to $^{19}F$ ($FC_3O$ and $FC_4H_2$), $^{35}Cl$ ($ClC_3O$), $^{14}N$ ($HC_3NH$), and $^1H_a$ ($H_aC_3O$ and $H_aC_4H_2$).

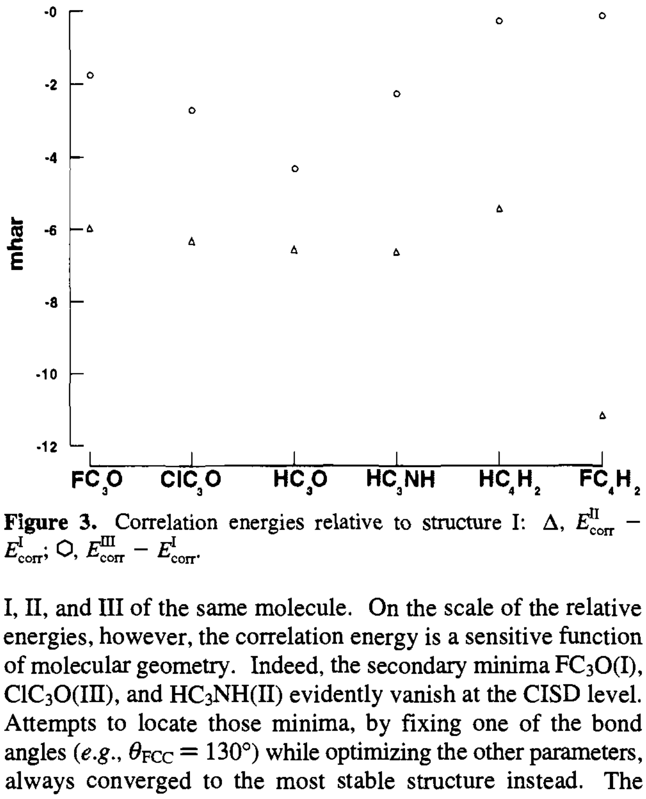

**Figure 3.** Correlation energies relative to structure I: Δ, $E^{II}_{corr} - E^{I}_{corr}$; ○, $E^{III}_{corr} - E^{I}_{corr}$.

I, II, and III of the same molecule. On the scale of the relative energies, however, the correlation energy is a sensitive function of molecular geometry. Indeed, the secondary minima $FC_3O$(I), $ClC_3O$(III), and $HC_3NH$(II) evidently vanish at the CISD level. Attempts to locate those minima, by fixing one of the bond angles (*e.g.*, $\theta_{FCC} = 130°$) while optimizing the other parameters, always converged to the most stable structure instead. The correlation energies of structures II and III relative to I are plotted in Figure 3. Structure I is always stabilized most by electron correlation, and structure II is stabilized least. The large difference in correlation energy between $FC_4H_2$(I) and $FC_4CH_2$(II) yields the only case in which the SCF global minimum (II) is not the same as the CISD minimum (I).

Although $HC_4H_2$(III) and $FC_4H_2$(III) were found to be stable at both SCF and CISD levels, these minima are extremely shallow and narrow. The transition state for $HC_4H_2$, for example, is found to lie within 1° of linearity in the CCC angles. It is improbable, therefore, that these will be observed experimentally as stable isomers.

The stable CISD geometries identified in this study are shown in Figures 4 and 5. Substitution of the electrophilic halogens for hydrogen in $HC_3O$ stabilizes structure II, making it the equilibrium geometry. Derivatives of $HC_3O$ involving substitution of the O atom or CO group are most stable in structure I, but the similarities do not extend to the secondary minima. Further results are summarized below.

**$NC_2O$.** Although structure II is not stable for $NC_2O$, its energy relative to structure I is only 2900 $cm^{-1}$ at the SCF level. The potential surface along the isomerization coordinate in $NC_2O$ is therefore expected to be of the form in Figure 2b.

**$FC_3O$.** The F-atom substitution polarizes the carbon chain so strongly that the $FC_3O$ minimum is characteristic of *trans*-bent $F{-}\ddot{C}_{sp^2}{=}\ddot{C}^{-}{}_{sp^2}{-}C^{+}{}_{sp}{=}O$, having a CCC bond angle of 137° and Mulliken charge densities on the C atoms of 0.31, −0.38, and 0.44, respectively. This is the only molecule of this set for which the $C_aC_bC_c$ angle is less than 160°.

**$ClC_3O$.** The effect of the correlation energy is to make geometries I and II effectively isoenergetic in $ClC_3O$ ($\Delta E^{II,I} = E^{II} - E^{I} = -220$ $cm^{-1}$). The isomerization barrier of 1500 $cm^{-1}$ is the largest in the present set, and the mass of the Cl atom results in the lowest predicted zero-point energy in the isomerization coordinate (58 $cm^{-1}$ based on SCF harmonic frequencies). $ClC_3O$ is therefore the most likely of the cases considered to possess two observable isomers.

**$HC_3NH$.** Structure II is a secondary minimum in the SCF calculations for $HC_3NH$, with a well-depth of about 300 $cm^{-1}$. In the CISD calculations, however, the barrier between I and II has vanished. $HC_3NH$ has the added complication of an isomer, stable at both the SCF and CISD levels, corresponding to the *cis*-CCNH form of structure I and less stable by 1400 $cm^{-1}$ at the CISD level. The *cis* form of $HC_3NH$(II) is not stable.

**$HC_4H_2$.** Although the linear minimum is too shallow to support bound vibrational states, the vibrational spectrum of $HC_4H_2$ should be characteristic of a quasilinear molecule,[19] given the energy gap $\Delta E^{III,I}$ of only 300 $cm^{-1}$.

**$HC_2N_2$.** Unique among the molecules in this study, $HC_2N_2$ substitutes the $C_c$ atom in $HC_3O$, and strongly resists straightening of the heavy atom chain, with $\Delta E^{III,I}$ of 7000 $cm^{-1}$ at the SCF level. Deformation from the equilibrium geometry toward structure II, with the HCC angle fixed to 135°, requires less than 3000 $cm^{-1}$ at the SCF level. Neither the *cis* nor the *trans* form of $HC_2N_2$(II) is stable.

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(19) Winnewisser, B. P. In *Molecular Spectroscopy: Modern Research*; Rao, K. N., Ed.; Academic Press: Orlando, FL, 1985; Vol. III, pp 321–419.

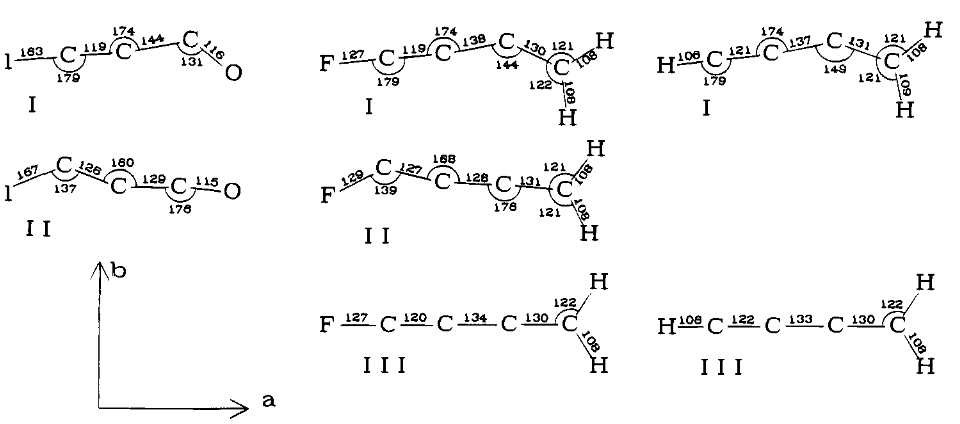

**Figure 4.** Stable geometries identified at the CISD level for molecules found to have multiple minima. Bond lengths are given in picometers, bond angles in degrees. Structure III heavy-atom bond angles are 180°. The molecules are planar, and the coordinate axes indicated are the *a* and *b* principal inertial axes.

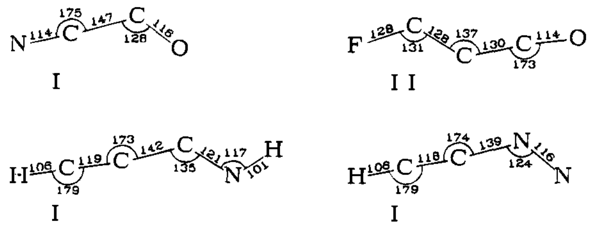

**Figure 5.** Stable geometries identified at the CISD level for molecules found to have single minima.

**$FC_4H_2$.** This molecule, exhibiting minima at all three structures, demonstrates that effects of different functional groups may be additive in this context. Based on the results for $HC_3O$, $FC_3O$, and $HC_4H_2$, the substitution H → F stabilizes structure II relative to I, whereas O → $CH_2$ favors structure I. In $FC_4H_2$, the effects cancel, leaving structures I and II nearly isoenergetic. Structure III, which is stable for $HC_4H_2$ but not for $HC_3O$ or $FC_3O$, becomes stable for $FC_4H_2$. Pronounced polarization of the carbon chain, as found for $FC_3O$, is not observed in $FC_4H_2$. While this may be ascribed to the lack of an analogue to the $F{-}\dot{C}{=}\ddot{C}^{-}{-}C{\equiv}O^{+}$ resonance structure, there is no indication from the $FC_3O$ charge distribution that such a structure is important.

**B. Application of the Resonance Model.** A considerable literature surrounds the problem of estimating relative stabilities of free radical intermediates in organic reactions, much of it centered on improving chemical models that have both intuitive simplicity and predictive power. Principal among these models are the resonance model[20] and the molecular orbital model.[21] Despite admonitions against using one molecular model (such as *ab initio* theory) to estimate properties of another molecular model,[22] we shall for the present treat the *ab initio* results as valid, in order to illustrate that the molecules in the present work provide novel tests of the resonance model.

Application of the resonance model here is ambiguous, because one of the primary requirements of the model is that the resonance structures of a given molecule have nearly identical geometries.[20] This constraint is intended to disallow structural isomers, such as *n*-butane and isobutane, from contributing simultaneously to the molecular stability. While $ClC_3O$(I) and $ClC_3O$(II) are not structural isomers, the ClCC and CCO bond angles in Figure 4 change by 40° and 45°, respectively, between minimum energy positions during the rearrangement. Because these differences are greater than the bond angle shifts typically associated with resonance structures, we may assume that the stability enhancement due to resonance in these radicals is small. This interpretation is supported by the *ab initio* results, since the geometries are sufficiently different that they often correspond to distinct minima on the potential.

If instead we treat structures I, II, and III as distinct isomers, structure III alone should be resonance stabilized, by the same logic that argues the stability of the allyl radical.[20] Resonance structures for I and II that preserve the canonical bond angles are possible only with the introduction of carbene centers or formal charges, and should not greatly influence the stability. Yet structure III is always less stable than structure I and is less stable than II in $HC_3O$, $FC_3O$, $ClC_3O$, and $FC_4H_2$. The resonance structures of III given in Section IA have bond orders identical with those of structures I and II, respectively, differing primarily in that III has more net s character in its $\sigma$-bonds than I or II, and in that the unpaired electron has no s character. Additional s character tends to stabilize chemical bonds; therefore the loss of s character in the unpaired electron distribution appears to be the principal destabilizing influence. This may also explain the resistance of $HC_2N_2$ to straightening of the CNN chain, which requires either formal charge separation or redistribution of *two* electrons into pure p-character orbitals. The resonance stabilization afforded when the R − C − S chain becomes linear, however, may justify the weak, strongly localized minima at structure III for $HC_4H_2$ and $FC_4H_2$.

The existence of multiple minima on the *ab initio* potential energy surfaces of free radicals may not be restricted to the $^2A'$ molecules. For the isomerization I ↔ II, an unpaired electron is donated from an $sp^2$ MO and accepted by an sp MO. In principle, other analogous isomerizations are possible. The propadienyl/propynyl radical, $CH_2CCH$, for example, has two favorable canonical structures, $H_2C_{sp^2}{=}C{=}\dot{C}_{sp^2}H$ and $H_2\dot{C}_{sp^3}{-}C{\equiv}\dot{C}_{sp}H$. However, in the ground state the dominant contribution to the geometry is from a third structure with an unpaired electron delocalized in the $\pi$-system perpendicular to the molecular plane. The competing geometries have been successfully regarded as resonance structures in previous theoretical work on this system.[23] The predicted equilibrium geometry represents a mixture of the canonical structures, and attempts as part of the present work to identify SCF secondary minima on the $CH_2CCH$ potential surface failed.

**C. Group Additivity.** The energy differences between structures of the same molecule are comparable to the roughly

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(20) See: Wheland, G. W. *Resonance in Organic Chemistry*; John Wiley: New York, 1955.

(21) Dewar, M. J. S. *J. Am. Chem. Soc.* **1952**, *74*, 3341–3363.

(22) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 669–682.

(23) Honjou, H.; Yoshime, M.; Pacansky, J. *J. Phys. Chem.* **1987**, *91*, 4455–4459.

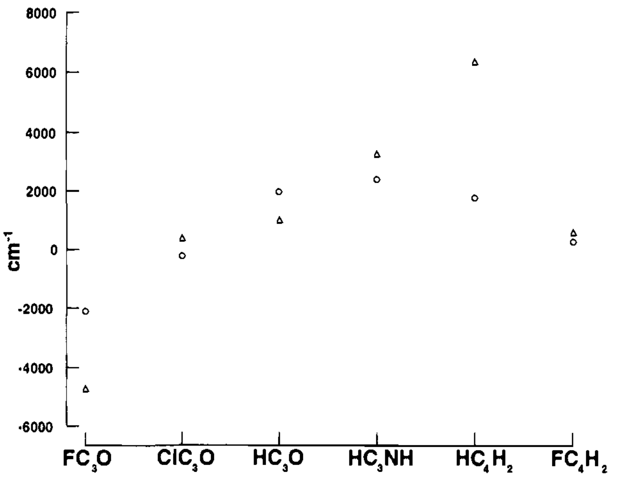

**Figure 6.** $\Delta E^{\mathrm{II,I}}$ values obtained from CISD calculations (○) and from group additivity of closed-shell molecular analogues as described in section 3C (△).

1000 cm$^{-1}$ accuracy estimated for the absolute energies. It may, nonetheless, be possible to estimate the relative stability of molecules in which one group of atoms has been substituted by a functionally similar group. The thermodynamic properties of functional groups have been extensively tabulated for such application.[24] Unfortunately, too little data are yet available on the free radical groups for the relative stabilities of the present set of molecules to be estimated from these tables. We, therefore, resort to a cruder approximation: that the relative stability of the radical may be estimated from the relative stabilities of corresponding closed-shell molecules in which the unpaired electron is replaced by a bond to hydrogen.

The starting point chosen is the relative stability of $HC_3O$(I) and $HC_3O$(II), approximated by the relative stability of the hydrogenated analogues propynal and propadienone. Thermochemical data are not available for most of the closed-shell analogues of the three-carbon radicals, and the effect of substitution is predicted from results for analogous two-carbon molecules. For example, the effect of the substitution $HC_3O\text{(I)} \rightarrow FC_3O\text{(I)}$ is assumed to be the same as that of the substitution $HCCH \rightarrow FCCH$ ($-28.2$ kcal mol$^{-1}$ = $-9900$ cm$^{-1}$),[25] while the effect of the substitution $HC_3O\text{(II)} \rightarrow FC_3O\text{(II)}$ is assumed to be the same as for $H_2CCH_2 \rightarrow FHCCH_2$ ($-45.5$ kcal mol$^{-1}$ = $-16000$ cm$^{-1}$).[25] The effect of the F atom substitution on the relative energy $\Delta E^{\mathrm{II,I}}$ is, therefore, estimated as the difference between these two energies: $\Delta E^{\mathrm{II,I}}(FC_3O)$ (cm$^{-1}$) = $\Delta E^{\mathrm{II,I}}(HC_3O)$ (cm$^{-1}$) $- 9900 - (-16000)$. These results are plotted in Figure 6. Only the qualitative trend of the calculations is successfully predicted; discrepancies of 2000 cm$^{-1}$ appear to be typical. The largest discrepancies, in opposite directions, are for $FC_3O$ and $HC_4H_2$, and these appear to nearly cancel for $FC_4H_2$. The structure III isomers have been omitted from this analysis because closed-shell analogues are lacking.

Additivity may also be checked within the *ab initio* calculations. The *ab initio* values for $\Delta E^{\mathrm{II,I}}$ of $HC_3O$, $FC_3O$, and $HC_4H_2$ from Figure 6 are sufficient for a rough prediction of $\Delta E^{\mathrm{II,I}}$ for $FC_4H_2$. Predicting this energy gap to be $-\Delta E^{\mathrm{II,I}}(HC_3O) + \Delta E^{\mathrm{II,I}}(FC_3O) + \Delta E^{\mathrm{II,I}}(HC_4H_2)$ yields $-3300$ cm$^{-1}$ (SCF) and $-2300$ cm$^{-1}$ (CISD), in good agreement with the direct *ab initio* SCF value of $-2200$ cm$^{-1}$, but not with the CISD value of 300 cm$^{-1}$.

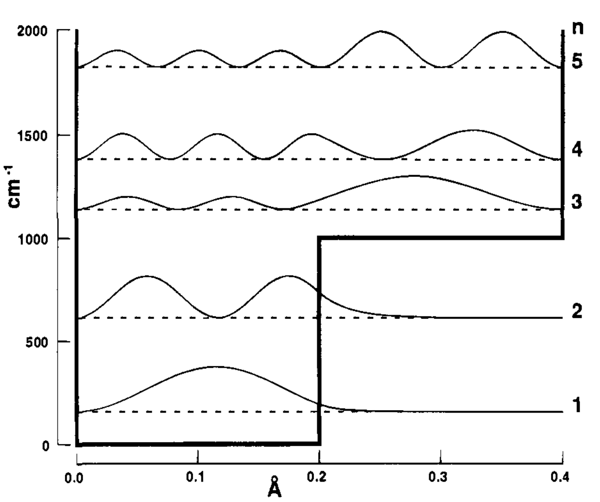

**Figure 7.** Lowest five energy levels and corresponding $|\psi|^2$ plots for a "split-level" one-dimensional particle-in-a-box potential, using a reduced mass of 20 amu.

**D. Experimental Implications.** The present work has focused on multiple *ab initio* minima chiefly for the immediate application to subsequent computational studies. However, the principal result for experimental work does not rest with the existence of secondary minima. Although rigid molecular geometries are invaluable conceptual tools, it is crucial to remember that the molecules are dynamic systems, particularly at the temperatures typical of combustion and pyrolysis. Unlike geometry optimization in an *ab initio* calculation, the properties of a vibrational wave function change continuously with changes in the potential surface, including the disappearance of a secondary minimum.

The results in Table 2 indicate that the potential surfaces of $ClC_3O$ and $FC_4H_2$ have double wells, similar to the potential in Figure 2c. The wells correspond to configurations I and II and have depths much greater than the probable zero-point energy for the isomerization coordinate. The lifetime of the secondary structure may therefore be long enough for it to be experimentally observable, and to influence any subsequent chemistry of the radical.

The other molecules have potential surfaces more similar to the type drawn in Figure 2b, in some cases with small isomerization barriers. The lowest bending frequency for each molecule is predicted to lie below 200 cm$^{-1}$; hence, several vibrational levels will effectively sample only the equilibrium structure. At some energy, on the order of 10 vibrational quanta, the classically allowed parameter space increases greatly. At 3000 cm$^{-1}$, all seven candidates having bending amplitudes in excess of 40°. For $C_3O$, the bending amplitude is predicted by the same methods to be less than 20°.

The qualitative behavior in these cases may be modeled by a "split-level" box potential, illustrated in Figure 7. The secondary structure corresponds to the region where the potential energy is constant at 1000 cm$^{-1}$ above the equilibrium energy. This second floor of the potential loosely divides the vibrational states into low-energy-regime ($<1000$ cm$^{-1}$) and high-energy-regime ($>1000$ cm$^{-1}$) states. The low-energy-regime states sample a limited region of the potential surface, near the equilibrium structure of the molecule ($n = 1$ and 2 in Figure 7). In the lowest state of the high-energy regime ($n = 3$),

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orthogonality conditions require that the wave function disproportionately sample the secondary structure. Measured properties of this primarily reflect the secondary structure, even if there is no minimum in that vicinity. This property has received particular attention in studies of vibrational dynamics in van der Waals clusters.[26] The vibrational energy levels also become much denser at this energy, because the force constant is reduced. Subsequent states ($n \geq 4$) sample the full classically allowed space with less discrimination.

Even for molecules with negligible isomerization barriers, the character of vibrational states near the transition between low- and high-energy regime reflects the secondary structure more than the equilibrium structure. The shift in electron density that accompanies this effect may lead to anomalously large vibrational transition moments between these states and the ground state, but the increased level density will hinder assignment of the vibrational quantum numbers. The transition between the low- and high-energy regimes occurs below 3000 $cm^{-1}$ for every molecule in the present set. Such excitation will be accompanied by a sudden increase in delocalization of the unpaired electron, and the product distributions of subsequent addition reactions may differ from those of the ground state. Previous work on the role of $HC_4H_2$ in acetylene pyrolysis[3] and the preliminary indications of $HC_3O$ in the reaction kinetics of CCH[10] suggest that this isomerization will merit attention in future studies of combustion-related radicals.

If distinct isomers do exist for any of these molecules, the prospects for experimental verification are good. Matrix isolation ESR spectroscopy should be capable of establishing the existence of the multiple isomers, given the distinctive magnetic hyperfine interactions. The magnitude of the N-, F-, or Cl-atom hyperfine constants would depend on which end of the molecule has the greatest unpaired electron density; this in turn depends on whether the isomer is best represented by structure I, II, or III, as indicated in Table 2. Carbon-13 substitution of the $C_a$ or $C_c$ atoms, where the unpaired electron is nominally localized, enlarges this effect by an order of magnitude.

Precise determination of the geometries is feasible by pure rotational spectroscopy, the technique successful in the case of $HC_3O$.[8] Precise measurements are required because all three configurations of each molecule have similar moments of inertia. Even the distinction between linear and nonlinear structures can be blurred by the large-amplitude zero-point bending motions to which these molecules are susceptible.[14] Spectroscopy of the present molecules will in most cases be more difficult than that of $HC_3O$ because there are reduced dipole moments, increased partition functions, and more complicated hyperfine structure. The $b$-axis dipole moments for the nonlinear structures, however, are considerably more favorable for the observation of $\Delta K_a \neq 0$ transitions, compared to $HC_3O$(I).

## 4. Conclusions

The existence of several favorable canonical structures such as those in Figure 1 is not sufficient for the existence of multiple minima in the *ab initio* potential surface. Nonetheless, two or more stable structures are found for five of the seven molecules examined in this study at the SCF level of theory, and for three of the seven at both the SCF and CISD levels. This work and previous results for $HC_3O$[12] and $HC_3S$[14] constitute a persuasive case that the $^2A'$ carbon chain free radicals are highly prone to multiple minima.

For future *ab initio* studies, this has an important consequence: geometry optimizations for these molecules should be carried out from at least three initial geometries—approximating structures I, II, and III in Figure 1—to avoid missing the global minimum. Whether or not the higher energy structures correspond to minima on the potential energy surface is less relevant to gross features of experimental work. All of these compounds are subject to large amplitude motion between at least two canonical forms at energies less than 3000 $cm^{-1}$. $ClC_3O$ and $FC_4H_2$ are the most likely members of this set to have distinct observable isomers.

In summary, $^2A'$ carbon chain free radicals clearly pose a danger of multiple local minima to *ab initio* calculations, but this may be circumvented by employing several initial geometries corresponding to structures I, II, and III. More difficult will be experimental or theoretical vibrational analysis, given the flat, highly anharmonic vibrational potential surface and the possibility of distinct isomers.

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**Supplementary Material Available:** Tables of the SCF harmonic vibrational frequencies and infrared intensities, CISD Mulliken spin densities, and CISD charge densities for the stable, nonlinear structures (2 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.

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(26) Hutson, J. M. *J. Phys. Chem.* **1992**, *96*, 4237–4247 and references therein.