

effect on the interaction energies in the anilinium cations (eq 12) is significantly greater than found in the isolated molecules. This result means that either (or both) the substituent-induced polarization of the ring π -electrons or the change in s hybridization of the ring carbon atoms is of importance here and accounts for almost one-third of the total inductive effect.

Further work is continuing on the use of the isolated molecule approach.

Acknowledgment. I am grateful to Dr. J. Bromilow, D. Craik, and the La Trobe University Computer Center for help with the computations.

3,3'-Bicyclopropenyl: Evidence for Novel Long-Range Conjugation of π Orbitals

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Abstract: Ab initio calculations employing the STO-3G and 4-31G basis sets indicate that 3,3'-bicyclopropenyl is the highest energy accessible (CH)₆. The calculations indicate the presence of long-range interactions between the two π systems of this molecule, and the predictions are supported by photoelectron spectroscopy data. Calculational studies of model compounds are included, and the origin of the electronic effect of 3,3'-bicyclopropenyl is discussed in light of the electronic distribution in cyclopropene.

The dipole moment of cyclopropene is unusual in its direction and magnitude. Its "reversed polarity" is the result of net electron donation from the π_{CC} to $\sigma^*_{CH_2}$ "component orbitals" imposed by the molecule's symmetry.² The magnitude of the dipole moment (0.455 debye³) originates in the extensive mixing between these "component orbitals". (A qualitative appreciation of this factor may be gained upon comparison of computer drawings of the π orbitals of cyclopropene and propene;⁴ furthermore, the presence of an appreciable diamagnetic ring current in cyclopropene has been suggested following magnetic susceptibility anisotropy studies.)^{5,6}

The appreciable π -electron density at C3 of cyclopropene raises the interesting question of the interaction between two such rings joined at these positions. The resulting molecule, 3,3'-bicyclopropenyl (**1**), is the only accessible benzene valence isomer, (CH)₆, to elude synthesis, although simple derivatives have been reported.⁷⁻⁹

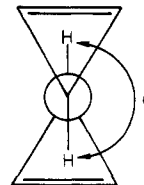


In the present study, ab initio molecular orbital calculations have been applied to a study of the structure and energy of 3,3'-bicyclopropenyl. This allows its comparison with the other four (CH)₆. The electronic interactions between cyclopropene rings have been studied as a function of conformation and com-

pared with those present in model cyclic and acyclic molecules.

Methods

Ab initio molecular orbital calculations used in this work employ the GAUSSIAN 70 program series¹⁰ at the STO-3G¹¹ and 4-31G¹² levels. The geometry of the rings in **1** (and simple derivatives) is assumed to be the same as calculated for cyclopropene.¹³ The C3-C3' bond is found to be 1.51 Å and the H3-C3-C3' angle equal to 114.7° (assumed to be bisected by the ring plane containing C3) following a limited geometry search (STO-3G) on the anti conformer. Bicyclopropyl was employed as a partial model for **1**. It is known to exist as a mixture containing almost equal fractions of an anti conformer (torsional angle $\theta = 180^\circ$) having rotational amplitude $\pm 80^\circ$ and a gauche conformer ($\theta = 49^\circ$) having rotational amplitude $\pm 18^\circ$.¹⁴⁻¹⁶ In the present study, analogous anti ($\theta = 180^\circ$, **1a**) and gauche ($\theta = 45^\circ$, **1b**) as well as syn ($\theta = 0^\circ$, **1c**) conformers of 3,3'-bicyclopropenyl have been investigated at the 4-31G level. These conformers, as well as others ($\theta = 30, 60, 90, 120, 135, 150^\circ$), have also been investigated by using the STO-3G basis set.



1a, $\theta = 180^\circ$
1b, $\theta = 45^\circ$
1c, $\theta = 0^\circ$

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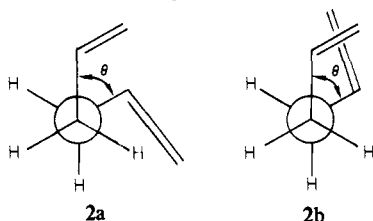
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Table I. Calculated Total Energies (hartree) and Relative Energies (kcal/mol) for Conformers of 3,3'-Bicyclopropenyl and the Planar Trans Conformer of 1,1'-Bicyclopropenyl

θ , deg	STO-3G		4-31G ^a	
	total <i>E</i>	rel <i>E</i>	total <i>E</i>	rel <i>E</i>
0	-227.66093	1.56	-230.1281	1.9
30	-227.66208	0.82		
45	-227.66251	0.56	-230.1310	0.1
60	-227.66226	0.69		
90	-227.66053	1.82		
120	-227.66025	1.98		
135	-227.66107	1.47		
150	-227.66218	0.77		
180	-227.66341	0.00	-230.1312	0.0
1,1'-bicyclopropenyl	-227.68190	-11.6	-230.1445	-8.3

^a 4-31G calculations employ STO-3G partially optimized geometries.

Conformers of bicyclopropyl have also been examined at the STO-3G level. The ring geometry is taken to be that calculated for cyclopropane,¹³ and the C1-C1' distance is assumed to be 1.51 Å, while the H1-C1-C1' angle is assumed to be 113.8°. The angle between each ring bisector and the C1-C1' axis was found to be 129.1° following an operation in which this angle was enlarged starting from an idealized structure in order to reduce steric repulsion. Idealized structures for 1,5-hexadiene [related to *C_s* structure **2a** ($\theta = 0^\circ$) or *C₂* structure **2b** ($\theta = 0$)] have also been calculated with the STO-3G basis set. Bond lengths are typical of those in propene. All angles were assumed to be 109.5 or 120° except for the C3-C4-C5 angle for which a value of 115.5° substantially reduces steric repulsion.



Energies of 3,3'-Bicyclopropenyl and Related Molecules

Table I lists calculated total energies obtained with the STO-3G and 4-31G basis sets for conformers of 3,3'-bicyclopropenyl as well as for the hypothetical planar *anti*-1,1'-bicyclopropenyl, which is not a benzene valence isomer. 3,3'-Bicyclopropenyl is predicted to have a small rotational barrier and, like bicyclopropyl,¹⁴⁻¹⁶ two low-energy structures: the *gauche* ($\theta = 45^\circ$) and *anti* conformers. Both basis sets predict that 3,3'-bicyclopropenyl is the highest in energy of the five (CH)₆ in line with the predictions of bond-additivity calculations.¹⁷ Relative energies obtained at the STO-3G level for benzene, Dewar benzene, benzvalene, prismane, and 3,3'-bicyclopropenyl (0, 78.7, 68.2, 92.5, 142.9 kcal/mol) are in better quantitative agreement with experimental values¹⁷ than are those obtained with the 4-31G basis set (0, 102.2, 104.5, 149.9, 154.4 kcal/mol).^{18,19} However, the larger basis set predicts the correct order of isomer stabilities while the smaller basis set reverses the ordering of Dewar benzene and benzvalene energies. 1,1'-Bicyclopropenyl is calculated to be 8.3-11.6 kcal/mol more stable than *anti*-3,3'-bicyclopropenyl, and this value is probably underestimated.

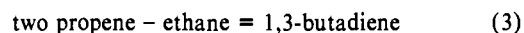
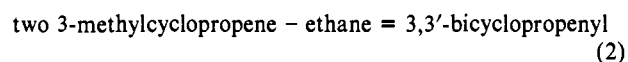
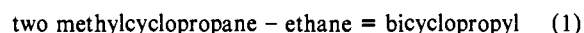
Table II lists STO-3G calculated energies for conformers of bicyclopropyl. In agreement with experiment,¹⁴⁻¹⁶ *anti* and *gauche* conformers are found to be most stable. The total energy curve as a function of torsional angle is similar to that of 3,3'-bi-

Table II. STO-3G Total Energies (hartree) and Relative Energies (kcal/mol) for Conformers of Bicyclopropyl

θ , deg	total <i>E</i>	rel <i>E</i>
0	-230.18593	3.49
30	-230.18934	1.35
45	-230.19062	0.55
60	-230.19048	0.64
90	-230.18926	1.40
120	-230.18870	1.76
150	-230.19011	0.87
180	-230.19150	0.00

cyclopropenyl, although the energy maxima are greater for the former.

There is rather good agreement between calculated enthalpies of formation and experimental data for 1,3-butadiene and bicyclopropyl. The calculated value for 3,3'-bicyclopropenyl, presumably *anti*, also looks reasonable. This is apparent through comparison of isodesmic eq 1-3. (Total calculated energies for the C4 species in eq 1-3 are from the literature;²⁰ standard gas phase enthalpies of formation are obtained from a compendium.²¹)



For 1,3-butadiene, the experimental standard enthalpy for isodesmic eq 3 (-3.5 kcal/mol) is quite close to the theoretical values calculated at both STO-3G (-3.7 kcal/mol) and 4-31G (-3.6 kcal/mol) levels. For bicyclopropyl (eq 1) the STO-3G value (-0.4 kcal/mol) is in reasonable agreement with the experimental value (-2.3 to -3.3 kcal/mol²²). While no experimental data are available for 3,3'-bicyclopropenyl, the STO-3G (-1.2 kcal/mol) and 4-31G (-1.6 kcal/mol) values for isodesmic eq 2 are reasonable. Specifically, one would expect the energy change for eq 2 to be less than that for eq 3.

The rotational energy (STO-3G) curves for 3,3'-bicyclopropenyl and bicyclopropyl have been fitted by Fourier expansions. This procedure has been found to provide some insights into the components of torsional barriers.²³ Following the published procedure,²³ relative energies (kcal/mol) at torsional angles of 0, 60, 120, and 180° have been employed for Fourier decompositions. The Fourier expansion for the relative energy of 3,3'-bicyclopropenyl is given in eq 4 and that for bicyclopropyl is presented in eq 5. Both indicate a preference for the *anti* conformer over the *syn* and preference for staggered conformations. However, the V_2 term for 3,3'-bicyclopropenyl indicates a mild preference for the *syn* (or *anti*) conformer over the perpendicular conformer. The negative V_2 term for bicyclopropyl indicates a mild preference for the perpendicular conformer.

$$V(\theta) = 1.56 - 0.18/2(1 - \cos \theta) + 0.74/2(1 - \cos 2\theta) - 1.38/2(1 - \cos 3\theta) \quad (4)$$

$$V(\theta) = 3.49 - 1.58/2(1 - \cos \theta) - 0.73/2(1 - \cos 2\theta) - 1.91/2(1 - \cos 3\theta) \quad (5)$$

With the assumption that further structural optimization will not markedly change these expansion coefficients, it is still not obvious what the source of the qualitative difference in V_2 is. The

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Table III. STO-3G Total Energies (hartree) and Relative Energies (kcal/mol) for **2a** and **2b** Conformers of 1,5-Hexadiene^a

θ , deg	total E	rel E
1,5-Hexadiene (2a)		
0	-230.14525	5.64
30	-230.14946	3.00
45	-230.15227	1.24
60	-230.15368	0.36
90	-230.15116	1.94
120	-230.14810	3.86
150	-230.15115	1.94
180	-230.15420	0.03
1,5-Hexadiene (2b)		
0	-230.14612	5.10
180	-230.15425	0.00

^a The structures calculated are idealized and are about 8 kcal/mol above the minimum.

total energy of the 4 electrons occupying classical olefinic π orbitals in 3,3'-bicyclopropenyl is at a minimum at about 50°, and the maximum occurs at 180° (Fourier expansion coefficients of total π energy (kcal/mol): V_0 , 1.84; V_1 , 1.54 (preference for syn over anti); V_2 , 2.15 (preference for perpendicular over parallel); V_3 , -0.61 (preference for staggered over eclipsed)). The energy of the 8 electrons occupying "peripheral" Walsh-type orbitals²⁴ in 3,3'-bicyclopropyl is at a minimum at 180° and a maximum near 45° (Fourier coefficients: V_0 , 26.29; V_1 , -25.52; V_2 , 10.15; V_3 , -0.77). The total π plus "peripheral" Walsh energy (12 electrons) is at a minimum at 180° and a maximum near 30° (Fourier coefficients: V_0 , 25.37; V_1 , -23.99; V_2 , 7.99; V_3 , -1.38). The total energy of the 8 electrons occupying "peripheral" Walsh-type orbitals in bicyclopropyl is minimized at 180° and maximized at 90° (Fourier coefficients: V_0 , 13.84; V_1 , -8.30; V_2 , 19.37; V_3 , -5.54).

The rotational barrier for 1,5-hexadiene (**2a**) is qualitatively similar between 0° and 180° to those of 3,3'-bicyclopropenyl and bicyclopropyl. The present, comparatively limited, geometry optimization of 1,5-hexadiene found the anti rotamer of **2b** to be most stable. Table III lists STO-3G energies for rotamers of **2a** and **2b**. Optimization of 1,5-hexadiene is not crucial to this study, and the values in Table III are about 8 kcal/mol too high (conclusion based on comparison of experimental and calculated isodesmic data).

Long-Range π Interactions in 3,3'-Bicyclopropenyl

A most interesting feature in the present study is that the two classical π bonds in 3,3'-bicyclopropenyl interact strongly. The STO-3G basis set predicts a splitting of 1.24 eV for the gauche (45°) conformer and 1.40 eV for the anti conformer. In both conformers, a "peripheral" Walsh-type orbital (W_{as})²⁵ is predicted to occur between the two π combinations. Figure 1B depicts this situation, and Figure 1A is a plot of the relative energy vs. torsional angle included for reference. The 4-31G basis set obtains lower energies (higher ionization energies) for the higher lying orbitals than does the STO-3G basis set. If one assumes Koopmans' theorem,²⁶ then the vertical ionization energies for π_+ , W_{as} , and π_- orbitals are (in eV): *anti*-3,3'-bicyclopropenyl (9.05, 9.82, 10.19); *syn*-3,3'-bicyclopropenyl (9.34, 9.77, 9.87); *gauche*-3,3'-bicyclopropenyl (45°) (9.16, 10.10, 10.06). (A π_+ orbital is symmetric with respect to the plane of symmetry in *syn*-1 or the axis of symmetry in *anti*-1.) The anti conformer is predicted to have a orbital splitting of 1.14 eV an interceding Walsh-type orbital. For comparison's sake, the anti conformer of 3-cyclopropylcyclopropene (**3**) is predicted to have an ionization potential of 9.55 eV—about midway between π_+ and π_- (the W_{as} orbital

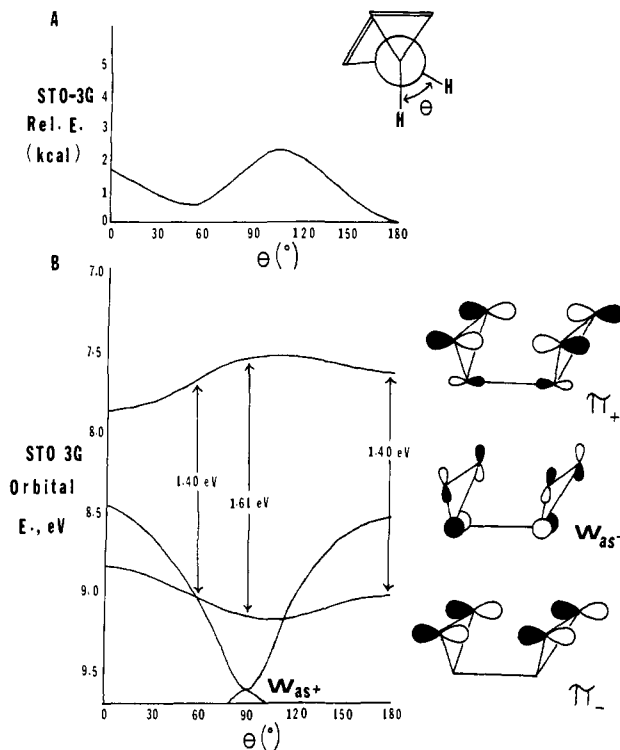
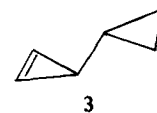
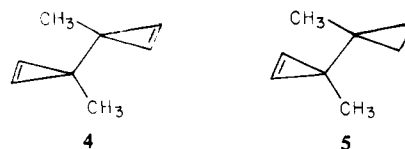


Figure 1. (A) STO-3G relative energies (kcal/mol) for 3,3'-bicyclopropenyl as a function of torsional angle. (B) STO-3G orbital energies for π and highest energy Walsh-type orbitals of 3,3'-bicyclopropenyl as a function of torsional angle (values in eV; note that 4-31G basis set provides values in better agreement with experiment: see text).

is calculated at 9.85 eV, about the same as in *syn*- or *anti*-3,3'-bicyclopropenyl).



The predicted orbital splitting has been experimentally confirmed for the dimethyl derivative (**4**). Schweig and co-workers²⁷ find a first ionization energy for **4** of 8.76 eV and further indicate that the highest three orbitals are π , σ (Walsh), π . They also find a first ionization energy for model compound **5** of 9.10 eV. If the single π (olefinic) orbital in **5** is about midway between π_+ and π_- , as the calculations on **3** and 3,3'-bicyclopropenyl predict, then the splitting between π combinations in **4** is ca. 0.68 eV. This is a very striking interaction between double bonds separated by three formal single bonds and having no "through-space" interaction²⁸ (this assumes that the anti conformer is most stable, a tendency which should be strengthened by the methyl substituents in **4**).



Substitution of methyl for hydrogen at an allylic carbon lowers the π ionization energy by an average of 0.10 eV.²⁹ The first ionization energy calculated for **4** at the STO-3G level is 0.23 eV lower than that for *anti*-3,3'-bicyclopropenyl (the STO-3G splitting in **4** is calculated at 1.67 eV). Thus, one would expect a 4-31G

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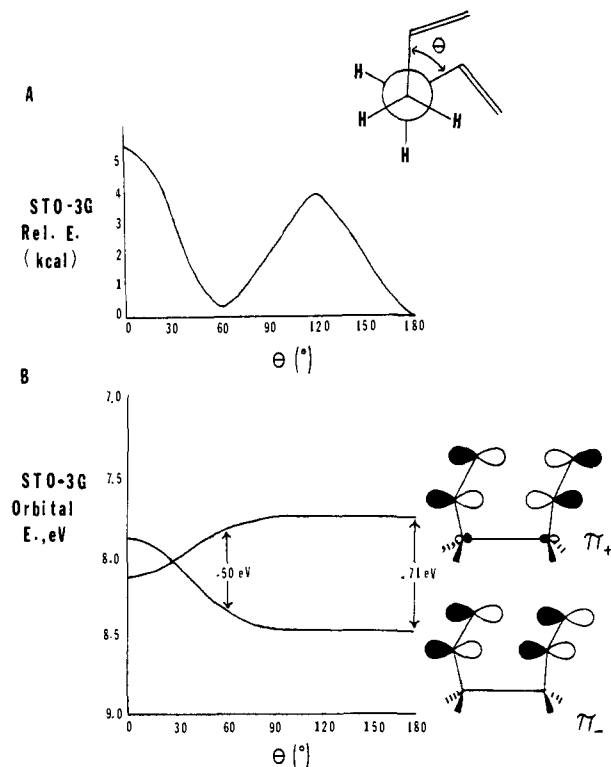


Figure 2. (A) STO-3G relative energies (kcal/mol) for 1,5-hexadiene (**2a**) as a function of torsional angle. (B) STO-3G orbital energies for π orbitals of 1,5-hexadiene as a function of torsional angle (values in eV; note that the 4-31G basis set provides values in better agreement with experiment: see text).

first ionization energy for *anti*-3,3'-dimethyl-3,3'-bicyclopropenyl (**4**) equal to 8.82–8.95 eV (subtract 0.23 to 0.10 eV from the calculated value of 9.05 eV) in good agreement with the experimental value.

The novel long-range π interaction in **4** (or the parent compound) is apparent when comparison is made with 1,5-hexadiene. In Figure 2B the π_+ and π_- orbital energies for this molecule (**2a**) are plotted for torsional angles between 0° and 180°. Figure 2a is a plot of relative energy vs. torsional angle. The maximum splitting in 1,5-hexadiene is calculated to be less than half that in 3,3'-bicyclopropenyl. An interesting feature in 1,5-hexadiene is the calculated change in the energy ordering of the π_+ and π_- combinations that causes their virtual degeneracy at 30°. At 0°, the "through-space" interaction is about one-third the magnitude of the "through-bond" interaction. Experimentally, the splitting between π_+ and π_- in 1,5-hexadiene is found to be 0.31–0.46 eV (range due to uncertainty in assigning a vertical IP),³⁰ a value approximately half that in **4**. (Both experimental values are equal to roughly half of the respective calculated values.) Another illustration is achieved by noting that the adiabatic ionization energy of 1,5-hexadiene (ca. 9.30 eV) is only 0.15 eV less than that in 1-hexene.³¹ However, the "addition" of a similarly remote double bond in **4** lowers its ionization energy by 0.34 eV relative to that in **5**. This again indicates twice as much splitting between the remote π bonds in 3,3'-bicyclopropenyl as in 1,5-hexadiene.

It is important to examine how well 4-31G level calculations predict ionization energies of π electrons (assuming Koopmans' approximation) and how well STO-3G and 4-31G basis sets predict splittings between interacting orbitals. The 4-31G basis set predicts first ionization energies that are usually 8–10% too low.^{19,32} For example, the calculated ionization energy of ethylene is 10.28 eV

while the adiabatic ionization energy is 10.51 eV.²⁹ The calculated first ionization energy of 1,3-butadiene is 8.75 eV while the adiabatic ionization energy is 9.03 eV.²⁹ However, the agreement between the theoretical value (9.64 eV) and the observed adiabatic ionization energy of cyclopropene (9.67–9.70 eV)^{29,32,33} is, probably fortuitously, better. The calculated splitting in 1,3-butadiene (3.62 eV, STO-3G; 3.41 eV, 4-31G) is almost 50% greater than the experimental value (2.43 eV).²⁹ Similarly, as stated earlier, the experimental π splitting in 1,5-hexadiene appears to be about half the calculated value. The splitting between π_+ and π_- orbitals in Dewar benzene is found to be 0.30 eV,³⁴ a value again smaller than that calculated by STO-3G (0.39 eV) or 4-31G (0.54 eV) basis sets.³⁵ Finally, while the splittings between the two highest Walsh-type orbital combinations in *gauche*- and *anti*-bicyclopropyl are greater than those experimentally observed, the two sets of four orbitals arising from these two low-energy conformers are in the same order as assigned by Klessinger and Rademacher²⁵ and the quantitative agreements are good.

In summary, the 4-31G basis set tends to calculate π ionization energies which are too low, but this discrepancy is fairly small for cyclopropene. Both STO-3G and 4-31G basis sets significantly overestimate the splitting between π as well as the higher energy Walsh orbital combinations.

Discussion of Results

The significant interaction between π orbitals in 3,3'-bicyclopropenyl is the result of strong "through-bond" interactions which dominate "through-space" interactions in all conformations. The π splitting in this molecule is calculated to be more than double that in 1,5-hexadiene as well as in the hypothetical 3,3'-bicyclobutenyl (*C_i* structure with geometry chosen to mimic that of *anti*-**1**). It is interesting that the π orbital splitting in 3,3'-bicyclopropenyl appears to be more than twice that in its valence isomer Dewar benzene. The latter molecule has much more proximate double bonds which are connected by only two single bonds. Apparently, sizable "through-bond" and "through-space" interactions are opposed in Dewar benzene and a small net split occurs.³⁴ An interesting analogue of 3,3'-bicyclopropenyl is tricyclo[4.2.0.0^{2,5}]octa-3,7-diene. Experimental and theoretical data indicate a large interaction between its double bonds which are also separated by three single bonds.³⁶ STO-3G calculations predict a splitting of 1.44 eV between π combinations in the *anti* isomer (**6**) and only 1.21 eV in the *syn* isomer (**7**). One should note that STO-3G calculations underestimate stabilities of π orbitals and other calculations indicate that Walsh-type orbitals are intermediate in energy between π combinations.³⁶ The large split between π combinations in **6** and **7** is explicable in terms of "through-bond" interactions through relatively high p-character cyclobutane bonds.³⁶



The origin of significant "through-bond" interactions in 3,3'-bicyclopropenyl appears to be in the delocalization of π -electron density onto the C3 and C3' positions as discussed in the introduction. Part of this may have to do with a small amount of "cyclopropenium" character present in each ring. Another point worth noting is that the interaction between cyclopropenium radicals combining to form a model 3,3'-bicyclopropenyl is greater than that between two allyl radicals combining to form a model 1,5-hexadiene. Thus, the C3 coefficient in the HOMO of cy-

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clopropenium radical ($2/6^{1/2}$)³⁷ is greater than the C1(C3) coefficient in the HOMO of allyl radical ($1/2^{1/2}$). Therefore, the overlap in "model 3,3'-bicyclopropenyl" is over one-third greater than that in "model 1,5-hexadiene".

The long-range interaction between double bonds may be significant in the chemistry of 3,3'-bicyclopropenyl and its simple derivatives. Thus, while the interaction does not significantly

(37) The degeneracy in cyclopropenium radical is lost when two such "molecular fragments" interact to form "model 3,3'-bicyclopropenyl".

stabilize or destabilize the molecule thermodynamically, increased susceptibility to oxidation as well as effects on reactions such as the Cope rearrangement are to be expected.

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Interligand Steric Effects in Metal Complexes in Solution Studied through the Residual Circular Dichroism of the d-d Transitions: Application to Tetraaminecobalt(III)-Amino Acid Complexes

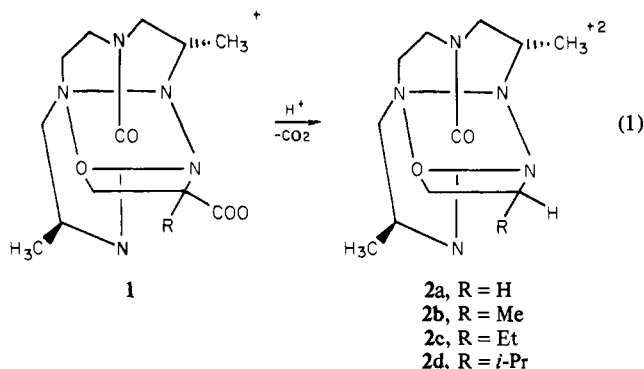
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Abstract: Although additivity of d-d circular dichroism (CD) of chiral metal complexes has been demonstrated widely, the deviations from additivity (referred to as the residual CD) may prove paradoxically to be of greater chemical interest. In this paper, the origin of the residual CD is established in its simplest form so that its use in a practical way may be developed. The residual CD is shown to be a sensitive probe for interligand steric effects and the effect of ligand substitution on the metal-ligand bonding. The method is applied to a study of interligand steric effects in a series of tetraaminecobalt(III)-amino acid complexes, leading to a new method for predicting the outcome of asymmetric syntheses carried out on substrates bound to dissymmetric transition-metal moieties.

Introduction

It has been shown previously that decarboxylation of the Λ - β_2 complex **1** in 1 M HCl, to produce bound alanine, leads to a predominance of (*S*)-alanine (eq 1).² Examination of molecular



models based on an X-ray crystal structure determination does not reveal any clear difference between (*R*)- and (*S*)-alanine in their steric interactions with the tetraaminecobalt moiety.³ Furthermore, even if steric interactions could be discerned in the crystal, solvent effects would preclude any positive conclusions as to the steric environment which may exist in solution. We seek

a technique which will lead to the elucidation of in-solution steric interactions.

The circular dichroism (CD) of the d-d transitions of the central metal ion constitutes a sensitive probe of the ligand environment. The most common practical use of d-d CD for monitoring stereochemistry has been through empirical sector rules.⁴⁻⁶ There are extant theoretical works on the subject; however, as discussed in the literature, these rules are generally of limited practical application.⁷ There is another set of empirical rules, however, that both is of general applicability and, furthermore, has been shown to have a rigorous theoretical foundation.⁸ These are the *additivity rules* which may be illustrated by the following example. Consider a complex, AB₁B₂ (composite complex), with two chiral centers, B₁B₂, and an achiral metal-centered chromophore, A, in which the d-d and charge-transfer transitions are localized. If the complexes AB₁, AB₂ (substituent complexes) have the same achiral chromophore as the composite complex and B₁, B₂ have the same configurational relationship to A in the composite and substituent complexes, then the d-d CD of the composite complex AB₁B₂ is simply the sum of that of the substituent complexes AB₁, AB₂. This is the simplest example of an additivity rule. Additivity has been addressed empirically and addressed in the models of Mason and Richardson.^{9,10}

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