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The *cis-trans* Energy Difference in Bi-1-cyclopropen-1-yl and Related Compounds

Ramón María Sosa, Oscar Néstor Ventura

Cátedra de Química Cuántica, Facultad de Química, Avda. Gral. Flores 2124, Montevideo, Uruguay

Arno Liberles[*]

Fairleigh Dickinson University, Teaneck, New Jersey 07666, USA.

The *cis-trans* energy difference of bi-1-cyclopropen-1-yl and the fluoro-substituted derivatives are studied by *ab initio* methods in order to establish the stability of the *cis* and *trans* diene isomers.

The results of the *ab initio* method STO-3G points toward the *trans* bi-1-cyclopropen-1-yl as the most stable isomer (0.2 kcal/mol). The energy of the transition state is about 2.5 kcal/mol above that of the *trans* isomer. The electronic transitions of the isomers are also reported.

Key words: Bi-1-cyclopropen-1-yl – Fluoroderivatives, conformational stability.

1. Introduction

The problem of steric interaction and conformational preference is an important one in organic chemistry. The idea that groups, nonbonded in the classical sense, do interact is well known [1, 2, 3]. The possibility that this interaction can be favorable as well as unfavorable is less frequently discussed, yet a number of different results have come to light [4–9]. For example, the ground state of *cis*-2-butene is less stable than that of the *trans* isomer. However in the 60,60-transition states for coupled methyl rotation, the *cis* isomer is the more stable [8, 9, 11, 12]. The lesser stability of the *cis* ground state relative to the *trans* isomer is thought to be due to unfavorable interactions between the in-plane hydrogens of the former. Yet their removal in the *cis* isomer by rotation of the methyl groups is not, by itself, sufficient to cause its energy to

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[*] Senior Fullbright–Hays Scholar to Uruguay.

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move below that of the *trans* one. The absence of unfavorable interactions in the former should cause both isomers to have the same energy unless other factors are present. One must postulate either that the two methyl groups of the *trans* isomer interact unfavorably, which is contrary to current thinking, or that additional favorable interactions are present in the *cis* one.

The 1,3-butadiene molecule represents another system of general interest. Only the *s-trans* form is detected experimentally, and the exclusion of the *s-cis* one is generally thought to be due to unfavorable interactions in the latter between two of the in-plane hydrogens. Thermodynamic methods estimate the energy difference at 2.3 kcal/mol [13]. Theoretical *ab-initio* calculations with flexible geometries yield a value of about 5 kcal/mol [11, 14]. More recently calculated values of 4.3 kcal/mol and 5.7 kcal/mol have also been reported [12]. The barrier separating the isomers has a height of about 5 cal/mol above the *trans* isomer [13].

It was at one time of considerable interest to determine whether substituted 1,3-butadiene, existing in both *s-cis* and *s-trans* geometries, were possible. Lide pointed out that a fluorine properly introduced into the system might stabilize the *s-cis* form [15]. However, both 2-fluoro and 1,1-difluoro-1,3-butadiene exist only in the planar *s-trans* form [15, 16]. Another approach was to attempt to destabilize the *s-trans* isomer rather than stabilize the *s-cis*, and the introduction of several halogens or large alkyl groups did force the dienyl system out of the *s-trans* configuration. However, a nonplanar geometry emerged rather than the *s-cis* [17].

With hydrocarbons, or closely related compounds, it has not been possible to find a 1,3-dienyl system in which the *s-cis* and *s-trans* forms coexist to a measurable degree. Of course, other conjugated systems do behave in this way. Acryloyl fluoride and the acid itself, exist in the two isomeric forms, and in furfural, for example, the *s-cis* isomer is actually preferred over the *s-trans* one [18–22]. Furfural, however, is a special case, reflecting other interactions as well, and it would still be desirable to find a simple hydrocarbon for which the *s-cis* and *s-trans* isomer have comparable energies. Since attempts to destabilize the *s-trans* isomers have led to nonplanar configurations, our approach has been to look for a system in which the *s-cis* form would be able to compete. The instability of the latter is generally thought to be due to the unfavorable hydrogen–hydrogen interactions at the 1- and 4-positions, and for a hydrocarbon to be equally or nearly equally, stable in both isomeric forms, these unfavorable interactions must be absent.

It is possible to devise a system meeting this criterion. For example, the bi-1-cyclopropen-1-yl isomers **A** and **B** should coexist in dynamic equilibrium for in neither are the hydrogens oriented poorly. While the molecule has not yet been synthetized, theoretical calculations can indicate the magnitude of the energy difference, and accordingly, we have calculated the energies of **A** and **B** as well as that of the transition state for their interconversion using the *ab initio* 3G basis set [24].

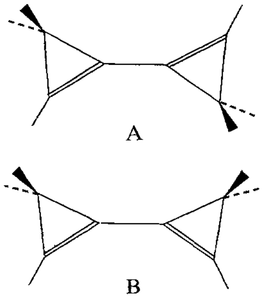

Fig. 1. The two isomers of bi-1-cyclopropen-1-yl

2. Geometry and Calculations

The geometry of the cyclopropenyl rings in A and B cannot differ much from that of cyclopropene, itself. Experimental values for the latter seem firmly established [25, 26]. A 3G optimized geometry has also appeared and differs only slightly from the experimental one [27]. We have used with minor modifications, the experimental values of Stigliani et al. [25]. The bonds external to the cyclopropenyl rings, or their in-plane projections, were allowed to bisect their respective angles. While this represents a minor deviation from the experimental result, it cannot affect the *s-cis*, *s-trans* energy difference in any significant way. The bond length of the bond joining the rings is uncertain, and we calculated the energy of the isomers for several values of this parameter. Experimental and theoretical results support the idea that, in the absence of large groups or many halogens, planar, or nearly planar, conformations of the heavy atoms represent energy minima in systems of this type [11, 18–22]. Furthermore, the calculations are not sufficiently accurate to pick up in any reliable manner slight deviations from planarity. Therefore, planar geometries were employed for the heavy atoms in A and B, and points on the rotational coordinate close to 0° or 180° were not calculated. We did, however, calculate, at the optimal *ab initio* bond length of 1.45 Å the energy of geometries rotated 30° from the planar isomers in order to verify that large deviations from planarity were not present. We present the results of the calculations in Table 1. The rate of interconversion of the isomers depends on the height of the

Table 1. The *s-cis* and *s-trans* energies of bi-1-cyclopropen-1-yl for various values of the inter-ring distances using the 3G basis set [24]. Energy values are in Hartrees, energy differences are in kcal/mol. θ is the rotational parameter

Molecule	Inter-ring distance (Å)			Energy differences (in kcal/mol)
	1.42	1.45	1.48	
A $\theta = 0°$	−227.6796	−227.6801	−227.6792	0.19
B $\theta = 0°$	−227.6799	−227.6804	−227.6795	2.50
$\theta = 90°$		−227.6764		
$\theta = 30°$		−227.6794		
$\theta = 150°$		−227.6792		

barrier, and even small energy differences need not lead to a dynamic mixture if the barrier separating the isomers is large. Since the energy difference between the isomers is small (0.19 kcal/mol), the transition state must lie close to the 90° midpoint along the rotational reaction coordinate. We have calculated its energy without further optimization of geometry, and, therefore, the values given in Table 1 represent the upper limit to the calculated barrier height. The barrier is only 2.5 kcal/mol, and it is evident that interconversion will take place rapidly. An appreciable fraction on these molecules will exist in the *s-cis* form.

3. Fluoro-substituted Bi-1-cyclopropen-1-yls

The previous experiments on fluoro-substituted 1,3-butadienes show only the absence of the *s-cis* isomer; they do not indicate the magnitude of the influence exerted by fluorine [15, 16]. Calculations show, thought, that one or more fluorines in the 2 or 2,3-positions of 1,3-butadiene do decrease slightly the *cis-trans* energy difference [28]. We have calculated the energies for the fluoro-substituted molecules (I)–(IV) using the STO-3G method, and these results are presented in Table 2. The inter-ring distance in these calculations is 1.42 Å. In our systems, the olefinic fluorine affects the *cis-trans* energy difference in a very favorable way, while the aliphatic fluorine influence the equilibrium adversely.

Table 2. The *s-cis* and *s-trans* energies in, fluoro-substituted bi-1-cyclopropenyl-1-yl using the 3G method. The inter-ring distance is 1.45 Å. Energies are in Hartrees. Energy differences are in kcal/mol [32]

Molecule	Energy	Energy difference
I	−325.13853	0.032
II	−325.13858	
III	−325.13710	0.251
IV	−325.13760	

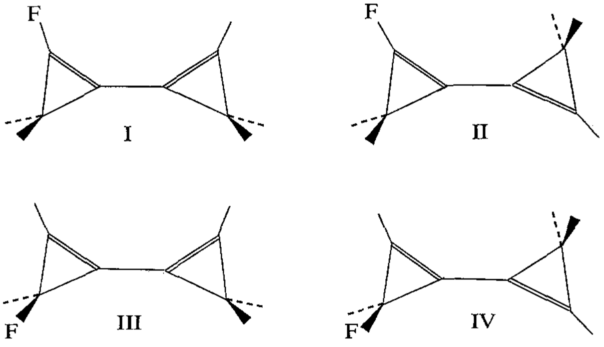

Fig. 2. Isomers of the fluoro-substituted derivatives of bi-1-cyclopropen-1-yl

4. Spectral analysis

Since the bi-1-cyclopropen-1-yl isomers, as well as their fluoro-substituted derivatives, can coexist in dynamic equilibrium, it seems worthwhile to analyse the spectral transitions of the *s-cis* and *s-trans* forms. Sieiro et al. have pointed out that the CNDO method does not give satisfactory results for rotational reaction coordinates when the central bond is a part of a delocalized system [29]. We have found this to be true in the present case. Using the CNDO method with the original parametrization the 90° geometry is predicted to be most stable, followed by the *s-cis* isomer. Inclusion of the most important doubly excited configuration affords some improvement but the reaction coordinate still differs from the *ab initio* results. However, assuming that planar geometries are those actually involved in the equilibrium, we have used the CNDO method with the parametrization of Jaffé [30, 31] to calculate spectral transitions.

The most important transitions, those whose wavelengths are greater than 200 nm, are given in Table 3 together with their oscillator strengths. For the unsubstituted compounds A and B transitions at 218 and 251 nm are sufficiently distinct and strong to permit their spectral identification. The weak band at 217 nm and the intensities of the 223 and 230 nm bands may serve to differentiate between I and II. For III and IV the weak bands at 203 and 225 nm serve to identify the latter while a transitions at 210 nm identifies the former.

Table 3. Wavelengths and oscillator strengths for the spectral transitions involving wavelengths greater than 200 nm for the various bi-1-cyclopropen-1-yls. Oscillator strengths are in parenthesis

Molecule	Electronic transitions						
A	282.4	231.4	218.35				
	(0.41)	(0.003)	(0.066)				
B	283.0	251.1	230.1				
	(0.45)	(0.001)	(0.004)				
I	290.0	245.2	230.2	223.1			
	(0.41)	(0.001)	(0.002)	(0.064)			
II	291.0	233.7	227.7	216.9			
	(0.46)	(2×10^{-4})	(0.008)	(0.002)			
III	275.0	252.9	237.9	217.4	215.8	210.1	201.9
	(0.40)	(0.011)	(0.007)	(0.009)	(0.035)	(0.022)	(0.001)
IV	275.0	251.5	238.5	224.8	215.0	203.5	
	(0.45)	(0.018)	(0.004)	(0.002)	(0.004)	(0.004)	

5. Conclusions

In 1,3-butadiene and related conjugated hydrocarbons the *s-trans* isomer is always much more stable, and even the introduction of olefinic fluorine does not alter the situation in any real way. The introduction of several large halogens or large alkyl groups forces the dienyl system out of the *s-trans* configuration, but a non-planar situation results. In other conjugated dienes involving carbonyl groups, a mixture of planar isomers is found, and furfural is even more stable in the *s-cis* form.

It is desirable to find a hydrocarbon system for which the isomers coexist. A system such as bi-1-cyclopropen-1-yl, in which the unfavorable interactions of *s-cis*-1,3-butadiene are absent, should behave properly, *Ab initio* calculations support this conclusion, favoring the *s-trans* form by only 0.19 kcal/mol.

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