Internal Rotation in Dicyclopropylacetylene

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In organic chemistry, the interactions between groups are generally separated into two broad categories—electronic and steric.[1] This separation, although artificial, works quite well. It is well known that electronic effects can be transmitted through double and triple bonds while steric effects, in the classic sense, are generally assumed not to be. Thus the absence of a rotational barrier in 2-butyne[2] is not surprising despite the fact that the Hamiltonian and the resulting molecular orbitals encompass the entire system, including the two methyl groups. In diarylacetylenes, on the other hand, one might expect a rotational barrier, and the experimental evidence does seem to indicate that certain conformations are preferred.[3] Semiempirical calculations predict, though, that the barrier is small.

Dicyclopropylacetylene has recently been synthesized and some of its reactions studied.[4–7] This system is of interest in the same sense and is sufficiently small to allow ab initio calculations on the rotamers.

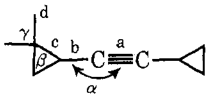
Quantum mechanically, interactions of the cyclopropyl rings with each other and with the alkyne linkage certainly take place, and even a more classic examination would predict some interaction of the cyclopropyl electrons with the triple bond. Consequently, it is of interest to determine whether a rotational barrier actually exists and whether such a barrier, if found, is large or small.

Discussion

The quantum mechanical calculations were all single-determinantal SCF calculations using the 3G basis set of Pople and co-workers.[8]

Table I gives the bond lengths and bond angles. All of the internal cyclopropyl angles β were set equal to 60°, and all external angles γ were set equal to 115°. The cyclopropyl geometries were obtained from the experimental values of cyclopropane and its derivatives,[9–11] the triple bond distance from acetylene and various substituted alkynes.[12–14] The 1.46-Å carbon–carbon value for a number of substituted alkynes has been discussed by Costain and Stoicheff[12] and by Dewar.[15] Geometries 1–7 corresponding to dihedral rotations of 0, 34.39389, 68.78778, 90°, 107.196945, 145.60611, and 180° were used (Table II).

Table I. Bond Lengths (Angstroms) and Bond Angles (Degrees) for Dicyclopropylacetylene



a	b	c	d	α	β	γ
1.205	1.460	1.515	1.085	180°	60°	115°

Table II. Geometries Used for Dicyclopropylacetylene

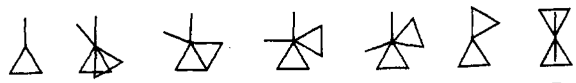
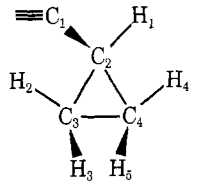


Table III. Calculated Energies and Dipole Moments of Geometries 1–7 of Dicyclopropylacetylene

	E	μ
1	−304.92488	0.28
2	−304.92495	0.28
3	−304.92508	0.25
4	−304.92512	0.22
5	−304.92512	0.18
6	−304.92502	0.08
7	−304.92495	0.00

Table IV. The Electronic Density ρ at Each Position in Dicyclopropylacetylene



	C_1	C_2	C_3	C_4	H_1	H_2	H_3	H_4	H_5
ρ	6.06	6.07	6.13	6.13	0.92	0.93	0.92	0.93	0.92

Results

The data in Table III give the calculated energies and dipole moments μ of each rotamer. The energy units are hartrees; one hartree equals 627.5 kcal/mol.

In Table IV we present the electronic densities, calculated by a population analysis, at each position in the molecule. The electronic density underwent very little change during the rotation, and we choose geometry **5**. Furthermore, the symmetry of the system requires that only half the molecule be given.

Conclusion

The barrier to internal rotation in dicyclopropylacetylene has been calculated using the 3G basis set. A larger basis set would certainly give a better description of the cyclopropyl rings,[16,17] and in some cases can alter the shape of the reaction coordinate.[18,19] However, in the present case, the 3G result appears reasonable, and although a small barrier is present, for all practical purposes the cyclopropyl rings can be considered as free rotors. The cyclopropyl rings destroy the cylindrical symmetry of the alkyne linkage, yet the interactions do not give rise to a significant barrier to rotation.

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Registry No.—Dicyclopropylacetylene, 27998-49-8.

References and Notes

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