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PREVIEW

Bicyclo(5.1.0)Octa-2,4-Diene Derivatives

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Bicyclo(5.1.0)Octa-2,4-Diene Derivatives

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TO MY BELOVED PARENTS AND MY WIFE

PREVIEW

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Introduction

The conformations of conjugated cycloalkadienes containing five and six carbons in the ring have been the subject of many studies by organic chemists. They have been examined by ultraviolet (UV) and microwave spectroscopy, electron diffraction, and molecular mechanics. There is general agreement between these studies that 1,3-cyclopentadiene has C_{2v} symmetry with a dihedral angle of 0° . The evidence is good that 1,3-cyclohexadiene has C_2 symmetry with a dihedral angle of 18° .

For seven or more membered 1,3-cycloalkadienes, because these larger ring systems are more conformationally mobile and therefore more complex than the small ring compounds, the conclusions about the most stable conformations are not so clear.

Conformational effects in conjugated dienes that have large dihedral angles are not well established since cases where the conformations are known are rare. The purpose of this study is to prepare a bicyclic 1,3-diene which may have a large dihedral angle and which would be more rigid than the corresponding monocyclic diene, and to obtain its NMR and UV spectra for comparison with other compounds of similar structure.

Coplanarity is required for the most effective overlap of the π -orbitals. When the dihedral angle between two carbons is not 0° or 180° the overlap is reduced so that the UV absorption maximum is expected to shift to shorter wavelength.

(A) UV Studies of 1,3-Cycloalkadienes

In conjugated dienes such as 1,3-butadiene, there is an effective overlap of the π -orbitals across the essential single bond of the conjugated system (1) (Fig. 1).

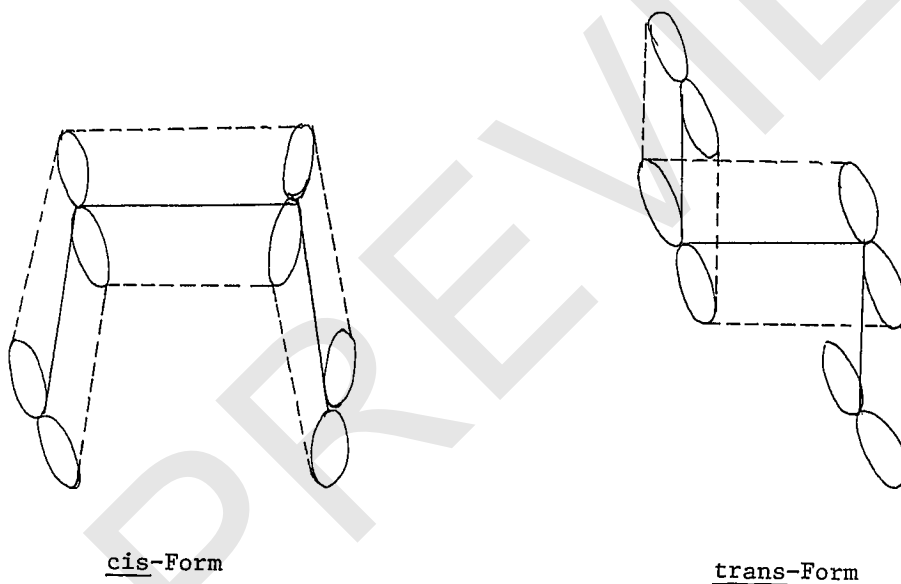


Fig. 1 Conjugated system of cis- and trans-1,3-butadiene

The earliest attempts to correlate ring size and conformation in the 1,3-cycloalkadiene series depended mainly upon molecular models^{2,3} and UV spectra^{2,3,4}. Braude², using an early molecular model set and an approach based on the UV epsilon (ϵ) value seemed more successful than Allinger³ who used Dreiding models⁵ and the more sophisticated Pariser-Parr-Pople^{6,7} method. Allinger and Miller³ attempted to correlate the spectra of the 1,3-cycloalkadiene series with the $N \rightarrow V_1$ transition wavelengths calculated using dihedral angles predicted from Dreiding models (Table 1).

Table 1. $N \rightarrow V_1$ Transition Wavelengths of Conjugated Dienes
as a Function of the Dihedral Angle³

<u>Compound</u>	<u>Dihedral angle</u>	<u>$\lambda, m\mu(\text{calc})$</u>	<u>$\lambda, m\mu(\text{exp})$</u>
δ - <u>trans</u> Butadiene	180°	212	209.4
1,3-Cyclopentadiene	0°	250	242
1,3-Cyclohexadiene	17°	245	256.4
1,3-Cycloheptadiene	52°	230	248
1,3-Cyclooctadiene	64°	216	229

The results based on the Pariser-Parr-Pople (PPP) method seem to suffer from several deficiencies.

- 1) The deformation of the bond angles from the optimum 120° expected for a sp^2 hybridized carbon atom was ignored. Chou⁸ postulated that the deviation of the observed wavelengths from the predicted values may increase as the deformation of the bond angle increases.
- 2) The predicted dihedral angles of 1,3-cycloalkadienes were based on Dreiding models, which give a dihedral angle of 52° and C_2 symmetry for 1,3-cycloheptadiene. The dihedral angle predicted by Allinger and Miller for this compound is apparently too large since the electron diffraction results reported by Chiang and Bauer⁹ and Hagen and Traetteberg¹⁰, as well as the microwave spectral data of Avirah¹¹ suggest that the molecule has C_s symmetry with a dihedral angle of 0° . The C_2 and C_s forms are shown in (Fig. 2).
- 3) They ignored the fact that the longest wavelength absorption peak of this compound is quite broad. This fact makes it difficult to rely on an exact wavelength for the correlation. This observation can also be interpreted as indicating that there is an equilibrium mixture of several conformers each of which contributes at a different wavelength.

Lloyd¹² has suggested the following approach to improve on Allinger and Miller's³ results presented in Table 1. Because 1,3-cyclohexadiene has