

AB-INITIO STUDIES OF STRUCTURAL FEATURES NOT EASILY AMENABLE TO EXPERIMENT : 10.  
CORRELATION BETWEEN THERMAL REACTIVITY AND EQUILIBRIUM STRUCTURE OF TRICYCLO  
[3.1.0.0<sup>2,4</sup>]HEXANE.

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ABSTRACT

The equilibrium structure of tricyclo [3.1.0.0<sup>2,4</sup>]hexane is computed by ab-initio methods in the 4-21G basis set with complete geometry relaxation. A correlation with thermal reactivity and with effects found in <sup>13</sup>C-nmr is discussed.

The thermal reactions of alicyclic hydrocarbons have in the past found considerable interest (see e.g. ref. 1). We have now started a series of structure determinations by ab-initio or joint ab-initio and experimental procedures in order to detect potentially existing correlations between details of equilibrium structure of such compounds and their reactivity. As a first example we like to present our results for tricyclo [3.1.0.0<sup>2,4</sup>]hexane (TCH).

The equilibrium structure of TCH is shown in Fig. 1. The parameters presented here are the result of an ab-initio geometry optimization which was executed by using Pulay's force method<sup>2</sup>, the 4-21G basis set<sup>2</sup> and our normal coordinate force relaxation procedure<sup>3</sup>. The geometry shown, which has an inversion center, was refined in seven cycles until the largest residual force on any atom was 0.002 mdyne. Geometry refinements on this level usually generate structures for organic molecules which are consistently close to experiment (see e.g. refs. 2-4) and allow determining accurate structural trends within one molecule.

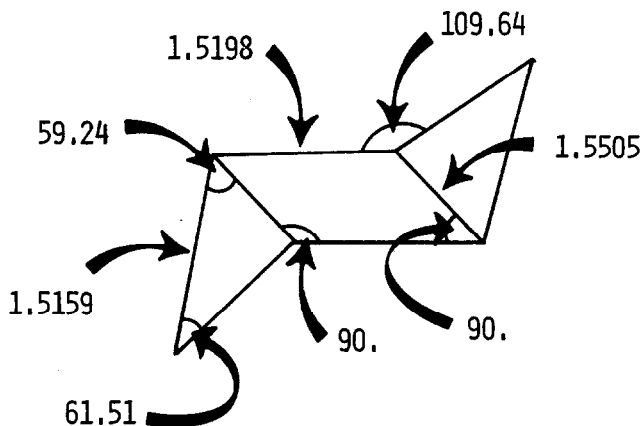
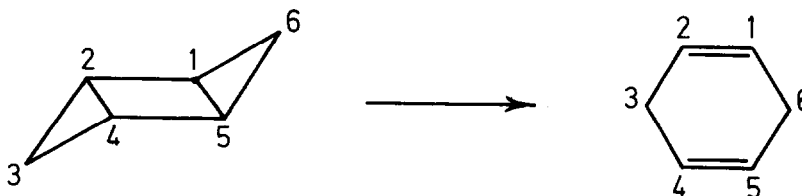


Figure 1 : Equilibrium geometry calculated for tricyclo [3.1.0.0<sup>2,4</sup>]hexane.

Since the experimental structure determination of TCH is not unequivocal<sup>5</sup>, Fig. 1 represents the best now available estimate of its equilibrium structure. In addition, the values given show an interesting correlation between the thermal reactivity of the compound and the relative extension of the C-C bonds.

Thermal reactions of tricyclohexane-systems are well known<sup>6</sup>, to yield cyclohexadiene or its derivatives.



If one postulates that, in a thermal reaction of TCH, the weakest C-C bond should dissociate with preference, then C<sub>1</sub> - C<sub>5</sub> (atom numbering above) should be longer than C<sub>1</sub> - C<sub>2</sub> or C<sub>1</sub> - C<sub>6</sub>. This expectation is in perfect agreement with the structure calculated (fig. 1).

The exo-, endo-, and in-plane (four-membered ring) C-H bond lengths in this compound also turned out to be different in our calculations (1.0732, 1.0719 and 1.0688 Å, respectively). These values are in excellent agreement with the trend postulated for the C-H bonds of TCH by Figeys et al.<sup>7</sup> on the basis of <sup>13</sup>C-NMR spectroscopic measurements. The trend established for the C-C bonds of TCH by our calculations is also in good agreement with the same trend established for bicyclo [2.1.0]pentane by microwave spectroscopy<sup>8</sup>.

Similar studies, including combinations of ab-initio and gas electron diffraction techniques, are currently under way in our laboratories.

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