Conformational flexibility of longifolene*

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Abstract. The flexibility of the bicyclo[2.2.1]heptane-based tricyclic bridged system in longifolene is analysed based on x-ray structural data. In this context, the molecular structure of three differently substituted longifolenes has been analysed. The highly substituent-dependent conformation provides scope for the synthesis of a variety of commercially oriented products.

Keywords. X-ray structure analysis; longifolene derivatives; norbornane conformation; cycloheptane conformation.

1. Introduction

Longifolene (C\textsubscript{15}H\textsubscript{24}) has been a molecule of interest to structural chemists because of the flexibility of its bicyclo[2.2.1]heptane-based tricyclic bridged system, and to natural product chemists because of the variety of commercially-oriented products (for example, perfumes) that the molecule can generate owing to this flexibility. From the time this compound was isolated (Simonsen 1920) substantial chemical research has resulted, the highlights of which are reported in recent reviews (Jadhav and Nayak 1980; Sukh Dev 1981a, b). Longifolene has such built-in stereoelectronic features in its rather complex tricyclic moiety that more often than not chemical transformation reactions have led to unexpected results. These abnormal products, more appropriately, sterically-diverted products (Sukh Dev 1981b) lead to newer and exciting chemistry and because of the complexity, x-ray crystallography would be the most appropriate tool for establishing the structures for such compounds. One such example is the structure of alloisologifolene (Shitole \textit{et al} 1983). The bicyclo[2.2.1]heptane moiety is by far the most important of bridged systems because of its frequent occurrence in many mono-, di- and sesquiterpenes. Indeed, this moiety (also called norbornane) has been subject to extensive physical and chemical studies by itself. Detailed empirical force field calculations at various levels of sophistication (Allinger \textit{et al} 1968; Altona and Sundaralingam 1970; Engler \textit{et al} 1973) have been performed to obtain reliable information regarding the geometry of this moiety. Besides norbornane, the longifolene has another flexible moiety, the seven-membered cycloheptane ring. Several strain energy calculations (Hendrickson 1961; Bixon and Lifson 1967; McPhail

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and Sim 1973) have been performed on this moiety and several energetically stable conformational states are realised.

We report here the structure determination of three derivatives of longifolene (figure 1) which demonstrate the nature of flexibility in the system:

(a) 4-hydroxy-12-acetoxy cyclopent-[3-1'-ene-2'-oxo]-longiborane, hereafter referred to as HACPLB.
(b) 8,11-dibromo longiborane, hereafter referred to as DIBRLB.
(c) Alloisolongifolol-p-nitrobenzoate, hereafter referred to as AILFNB.

We have also analysed the overall conformation of the longifolene molecule in terms of these crystal data along with the already available crystal structure data from literature. This analysis is done mainly in two steps (i) the norbornane moiety in terms of the twist induced due to substitution from the expected C2v symmetry and (ii) the cycloheptane moiety in terms of the deviation from C2 or C3 symmetry.

2. Structure determination of HACPLB, DIBRLB and AILFNB

The data were collected on a diffractometer (Enraf-Nonius CAD4-11M) using the ω/2θ scan technique up to 2θ = 48°. Three standard reflections were monitored after every 2000 seconds of exposure time to check for crystal decay, if any. The experimental details are listed in table 1. All the structures were refined using full matrix least squares technique (Gantzel et al 1961) with anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms were fixed based on stereochemical considerations and their positions verified by difference Fourier synthesis.

2.1 HACPLB

Attempts to solve the structure in the automatic mode of MULTAN-78 (Main et al 1978) failed. By a careful examination of the convergence map it was decided to change the origin fixing reflections. Four other reflections were chosen for multi solution to yield overall 64 sets. The set with the best combined figure of merit did not yield the structure. However, the set with the lowest psi zero gave a five-atom fragment which eventually led to the structure solution after a Karle recycling followed by a Fourier synthesis. The