QUANTIFYING DISTORTION IN SUBSTITUTED TETRAHYDROPYRANS

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In recent years, biosynthetically interesting and structurally diverse terpene-derived cytoxotoxic tetrahydropyranos have been isolated from marine organisms. Based on these observations, the synthesis of terpene-derived tetrahydropyranos, such as aplysiapyranoid A have attracted our attention. In the course of our work, however, significant difficulties have been encountered in preparing heterocyclic cores of aplysiapyranoids from $\delta$-unsaturated alkenols. Our data showed, that results from ring closure reactions could not be interpreted in terms of polar effects alone. Therefore, we have focused on an analysis of strain, for instance in heterocycle, as major contribution to the observed experimental difficulties. In principle, strain is caused by distortion. Analysis and quantification of strain therefore should be possible, if strainable. Since tetrahydropyran is the reference choice for our purposes, but its solid state geometry has until today not been reported, we have carried out a combined crystallographic and computational study in order to analyze and quantify strain in substituted tetrahydropyranos. Thus, eight hexasubstituted tetrahydropyranos were synthesized and subjected to X-ray diffraction analysis to provide data which in turn were used to establish a computational method for satisfactory reproduction of results from X-ray diffraction studies. Next, 23 different methylsubstituted tetrahydropyranos were optimized using molecular orbital calculations. A parameter was defined for quantification and analysis of distortions of the heterocyclic core and axially arranged substituents from the reference values in tetrahydropyran itself. Fundamentals, scope and limitations of this analysis and its implications on the total synthesis of the aplysiapyranoids are discussed in detail in the present contribution.

Keywords: TETRAHYDROPYRAN, HETEROCYCLIC

STRUCTURE CONFORMATION OF 4-(4-METHOXY PHENYL)-5-PHENYL ISOXAZOLE

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Isoxazole derivatives display interesting biological and medicinal applications. Some derivatives are used as semiconductors and corrosion inhibitors in fuels and lubricants. In agriculture applications herbicidal activity has been identified.

As a part of the study of series of isoaxozoles, with different substituents the title compound was undertook to study the conformation of five membered ring. C$_{60}$H$_{13}$NO$_{2}$, rhombohedral P2$_1$/2$_1$/2$_1$, with a = 6.986(5), b = 12.728(6) and c = 13.961(7) Å, V = 1243.3(12), Z = 4 p = 1.342 Mg/m$^3$, F(000) = 528, $\lambda$ = 0.17013 Å, R = 0.0385 and Rw = 0.0410 for 2056 observed reflections. The structure was solved by direct methods and refined by full matrix least-squares method using SHELXTL.

Isoxazole ring is planar. The phenyl ring and methoxy phenyl rings are oriented at 26.6˚ and 40.3˚ to the isoxazole ring and are at 51.5˚ to each other. At the point of linkage of substituents to the isoxazole ring enlargement in bond lengths and angles and the torsion of the substituted moieties with respect to isoxazole ring are observed.

Keywords: ISOXAZOLES

Keywords: FULLERENES, QUATARONS, HIDDEN PHASE

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