

QUANTIFYING DISTORTION IN SUBSTITUTED TETRAHYDROPYRANS

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In recent years, biosynthetically interesting and structurally diverse terpene-derived cytotoxic tetrahydropyrans have been isolated from marine organisms. Based on these observations, the synthesis of terpene-derived tetrahydropyrans, 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 δ -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 feasible, if strained. Since tetrahydropyran is the reference of 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 tetrahydropyrans. Thus, eight hexasubstituted tetrahydropyrans 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 tetrahydropyrans 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

A NEW MECHANISM OF FULLERENE FORMATION

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Quite a number of years has elapsed since the time when stable carbon cluster made up of 60 atoms, with a typical icosahedral symmetry, named fullerene C₆₀ was discovered [1]. However, how C₆₀ and other carbon clusters from the fullerene family form still remains to be understood. The numerous models describing fullerene assembly from separate atoms or fragments of graphite layers [2-4] do not stand up. Here we propose a radically different mechanism: fullerenes forming from the so-called 'hidden' phase clusters, quatarons, which existence has been recently substantiated [6]. Quatarons arise in supersaturated media, have a typical quasi-spherical shape and, what is important, occur as empty features in a certain size range [7]. It is these empty 'quasi-liquid' quatarons that are fullerene predecessors. The fullerene scaffolding is built on the spherical surface of an empty quataron which radius is dictated by supersaturation. Thus, quatarons generated in supersaturations from zero to the limiting one give rise to the entire spectrum of experimentally observed fullerene clusters with certain predominance of C₆₀. The work was supported by RFFI (grant 02-05-64688) and INTAS (project 99-0247).

References

1. Kroto H.W. et al. // Nature. 313 (1985)162.
2. Robertson D.H., Brenner D.W., White C.T. J. Amer. Chem. Soc., 113(1991)9394.
3. Chang T.M. et al. // J. Chem. Phys. Lett. 114(1992)7603.
4. Wakabayashi T., Achiba J. // J. Chem. Phys. Lett. 190(1992)465.
5. Lozovik Ju.E., Popov A.M. // Progress in Physical Sciences. 167(1997)751.
6. Askhabov A.M., Ryazanov M.A. // Doklady of Russian Acad. Sci. 362(1998)630.
7. Askhabov A.M. // Doklady of Russian Acad. Sci., 374(2000)359.

Keywords: FULLERENES, QUATARONS, HIDDEN PHASE

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 isoxazoles, with different substituents the title compound was undertaken to study the conformation of five membered ring. C₁₆H₁₃NO₂, rhombohedral P2₁2₁2₁ with $a = 6.986(5)$, $b = 12.728(6)$ and $c = 13.981(7)$ Å, $V = 1243.3(12)$, $Z = 4$ $\rho = 1.342$ Mg/m³, $F(000) = 528$, $\lambda = 0.71073$ Å. $R = 0.0385$ and $R_w = 0.0410$ 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

INCLUSION OF C₆₀ AND C₇₀ IN CHANNELS OF 2,4,6-TRIS-4-BROMOPHENOXY)-1,3,5-TRIAZINE (TBPT)

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Fullerenes undergo many kind of inclusions, either by taking up entities into holes of their cubic structure or being included into host lattices of other compounds.¹ In view of tuning physicochemical properties it is of interest to arrange C₆₀ or C₇₀ into planes or chains. In the inclusion complex of triptycene and C₆₀, fullerenes are packed into sheets.² In channels of mesoporous niobium oxide, C₆₀ and potassium were co-included to investigate the electrical properties in one dimension.³ By the present work we report on a first attempt to include C₆₀ and C₇₀ in channels of an organic inclusion compound for obtaining 1-D arrangement of the fullerenes. 2,4,6-tris-(4-bromophenoxy)-1,3,5-triazine (TBPT) showed inclusion of solvent molecules into parallel channels featuring a diameter of about 12 Å.⁴ Co-crystallization of TBPT and C₆₀ or C₇₀ from toluene by temperature lowering or isothermal evaporation techniques yielded needle shaped single crystals showing inclusion of C₆₀ and C₇₀ in channels. Conoscopic investigations showed that these crystals belong to an uniaxial point group. The fullerene molecules are translationally disordered within the hexagonal host structure of TBPT and co-inclusion of toluene was found. A composition of TBPT(C₆₀)_{0.2}(toluene)_{0.6} was determined by NMR and UV/VIS and confirmed by the electron density found inside the channels.

References

- [1] Prassides K., NATO ASI Ser., Ser. C (1994): 443.
- [2] Postma P.M., Jonkman H.T., Spek A.L., Feringa B.L., Chem. Comm. (1999): 1709.
- [3] Ye B., Trudeau M., Antonelli D., Adv. Mater. (2001), 13: 29.
- [4] Jetli R.K.R., Nangia A., Xue F., Mak T.C.W., Chem. Comm. (2001): 919.

Keywords: FULLERENES, INCLUSION CRYSTALS, TRIAZINES