By Carlin, Silvia; Vrhovsek, Urska; Franceschi, Pietro; Lotti, Cesare; Bontempo, Luana; Camin, Federica; Toubiana, David; Zottele, Fabio; Toller, Giambattista; Fait, Aaron; et al From Food Chemistry (2016), 208, 68-80. Language: English, Database: CAPLUS, DOI:10.1016/j.foodchem.2016.03.112

We carried out comprehensive mapping of volatile compds. in 70 wines, from 48 wineries and 6 vintages, representative of the two main prodn. areas for Italian sparkling wines, by HS-SPME-GCxGC-**TOF-MS** and multivariate anal. The final scope was to describe the metabolomics space of these wines, and to verify whether the grape cultivar signature, the pedoclimatic influence of the prodn. area, and the complex technol. were measurable in the final product. The wine chromatograms provided a wealth of information, with 1695 compds. being found. A large no. of putative markers influenced by the cultivation area was obsd. A subset of 196 biomarkers fully discriminated between the two types of sparkling wines investigated. Among the new compds., safranal and α -isophorone were obsd. We showed how correlation-based network anal. could be used as a tool to detect the differences in compd. behavior based on external/environmental influences.

~0 Citings

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2. GC-MS determination of bioactive components of Polycarpaea corymbosa Lams. (Caryophyllaceae)

By Sindhu, S.; Manorama, S. From Hygeia (2013), 5(1), 5-9. Language: English, Database: CAPLUS

Plan: The investigation was carried out to det. the possible chem. components from Polycarpaea corymbosa Lam. root and aerial parts. Methodol.: GC-MS was analyzed using Agilent (Model 5975C) Gas Chromatog.-Mass Spectrometry. Outcome: GC-MS anal. of methanolic ext. of root and aerial part led to identification of 30 and 24 compds. resp. The components were identified by comparing their retention indexes and mass spectra fragmentation patterns with those stored in the National Institute of Stds. and Technol. (NIST) library. The major constituents reported are n-Hexadecanoic acid in methanolic aerial ext. and 5-Hydroxymethyl furfural in methanolic root ext.

~0 Citings

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3. Determination of volatile compounds in cherry wine using headspace-solid-phase micro-extraction coupled with GC-MS

By Zhu, Jian-cai; Xiao, Zuo-bing; Niu, Yun-wei; Wang, Jin; Yu, Hai-yan From Shipin Gongye (Shanghai, China) (2012), 33(11), 169-172. Language: Chinese, Database: CAPLUS

HS-SPME/GC-MS was applied to ext. and accurately quantify aroma components of cherry wine. A total of 84 kinds of aroma substances in 7 com. cherry wines were detected, including 13 alcs., 7 acids, 21 esters, 6 aldehydes and ketones, 16 arom. compds., 9 terpenoids, 7 phenols, 4 furans and 3 misc. compds. In all quant. compds., isoamyl alc., Et acetate and benzaldehyde were the top three substances.

~0 Citings

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4. Microwave spectrum and structure of 2-methyl-1,3-dioxane

By Shapkin, A. A.; Galeev, R. V.; Gunderova, L. N.; Fayzullin, M. G.; Mamleev, A. H. From Proceedings of SPIE (2006), 6580(15th Symposium on High-Resolution Molecular Spectroscopy, 2006), 658005/1-658005/5. Language: English, Database: CAPLUS, DOI:10.1117/12.724780

The microwave rotational spectra of parent and five isotopic species with ¹³C and ¹⁸0 in natural abundance for 2- methyl-1,3-dioxane, $C_5H_{10}O_2$, were obsd. in the 28.0-44.0 GHz frequency region. The a- and c- type transitions with $4 \le J \le 10$ were assigned. The rotational consts. for all isotopomers were detd. The substituted coordinates of the heavy atoms were calcd. from the principal moments of inertia of normal and ${}^{13}C(2){}^{12}C_4H_{10}$ ${}^{16}O_2$, ${}^{13}C(4){}^{12}C_4H_{10}$ ${}^{16}O_2$, ${}^{13}C(5){}^{12}C_4H_{10}$ ${}^{16}O_2$, ${}^{13}C(7){}^{12}C_4H_{10}$ ${}^{16}O_1{}^{8}O_1{}^{8}O_2{}^{8}O_$

~0 Citings

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5. Structure and spectra of 1,3-dioxanes. II. Microwave spectrum, structural parameters, and ab initio calculations of 2-methyl-1,3-dioxane

By Mamleev, A. Kh.; Gunderova, L. N.; Galeev, R. V.; Shapkin, A. A.; Faizullin, M. G.; Nikitina, A. P.; Shornikov, D. V.; Kantor, E. A. From Journal of Structural Chemistry (2007), 48(6), 1030-1035. Language: English, Database: CAPLUS, DOI:10.1007/s10947-007-0167-9

The microwave spectra of five isotopomers with the ¹³C and ¹⁸O natural abundance isotopes of the 2-methyl-1,3-dioxane mol. (22-50 GHz) were studied. Rotational transitions of a and c types with $4 \le J \le 12$ were identified. The rotational consts. and the substitution r_{s} and effective r_{o} structural parameters of the mol. were detd. Ab initio calcns. on 2-methyl-1,3-dioxane were performed with mol. structure optimization. The results of quantum-chem. calcns. at different levels are compared with exptl. data.

~5 Citings

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6. Microwave spectrum, centrifugal distortion, dipole moment and conformation of 2-methyl-1,3-dioxane

By Mamleev, A. Kh.; Galeev, R. V.; Gunderova, L. N.; Faizullin, M. G.; Shapkin, A. A. From Journal of Structural Chemistry (2006), 47(2), 367-370. Language: English, Database: CAPLUS, DOI:10.1007/s10947-006-0308-6

Microwave spectrum of 2-methyl-1,3-dioxane has been investigated in the frequency range 8-40 GHz. Rotational a-type and c-type transitions with J \leq 40 have been identified. Rotational consts. A = 4658.122(2) MHz, B = 2503.221(1) MHz, C = 1783.950(1) MHz and centrifugal distortion consts. for the ground vibrational state have been found. Dipole moment components $\mu_a = 1.43 \pm 0.01$ D, $\mu_c = 1.15 \pm 0.01$ D and overall dipole moment $\mu = 1.84 \pm 0.02$ D have been detd. The data obtained are in accord with the chair conformation of the mol. having equatorial arrangement of the Me group.

~6 Citings

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7. Identification of Trace Volatile Compounds in Freshly Distilled Calvados and Cognac Using Preparative Separations Coupled with Gas Chromatography-Mass Spectrometry

By Ledauphin, Jerome; Saint-Clair, Jean-Francois; Lablanquie, Odile; Guichard, Hugues; Founier, Nicole; Guichard, Elisabeth; Barillier, Daniel From Journal of Agricultural and Food Chemistry (2004), 52(16), 5124-5134. Language: English, Database: CAPLUS,

From Journal of Agricultural and Food Chemistry (2004), 52(16), 5124-5134. Language: English, Database: CAPLUS, DOI:10.1021/jf040052y

GC-MS using both electron impact and chem. ionization detection modes led to the detn. of the volatile compn. of 2 samples of freshly distd. Cognac and 2 samples of freshly distd. Calvados. A total of 169 volatile compds. were directly identified in dichloromethane exts. obtained by liq.-liq. extn. Trace compds. present in both spirits were characterized with the help of preparative sepns. In a 1st step, groups of compds. were sepd. by preparative GC, and the fractions were analyzed on a polar stationary phase by GC-MS. In a 2nd step, silica gel fractionation was used to sep. them by polarity. In 331 compds., of which 162 can be considered as trace compds., were characterized in both freshly distd. Cognac and Calvados. Of these, 39 are common to both spirits; 30 are specific to Cognac with numerous hexenyl esters and norisoprenoidic derivs., whereas 93 are specific to Calvados with compds. such as unsatd. alcs., phenolic derivs., and unsatd. aldehydes.

~64 Citings

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8. Modeling deoxyribose radicals by neutralization-reionization mass spectrometry. Part 1. Preparation, dissociations, and energetics of 2-hydroxyoxolan-2-yl radical, neutral isomers, and cations

By Vivekananda, Shetty; Sadilek, Martin; Chen, Xiaohong; Turecek, Frantisek From Journal of the American Society for Mass Spectrometry (2004), 15(7), 1055-1067. Language: English, Database: CAPLUS, DOI:10.1016/j.jasms.2004.03.017

Collisional neutralization of several isomeric $C_4H_7O_2$ cations is used to generate radicals that share some structural features with transient species that are thought to be produced by radiolysis of 2-deoxyribose. The title 2-hydroxyoxolan-2-yl radical (1) (I) undergoes nearly complete dissocn. when produced by femtosecond electron transfer from thermal org. electron donors di-Me disulfide and N,N-dimethylaniline in the gas phase. Product anal., isotope labeling (²H and ¹⁸O), and potential energy surface mapping by ab initio calcns. at the G2(MP2) and B3-PMP2 levels of theory and in combination with Rice-Ramsperger-Kassel-Marcus (RRKM) kinetic calcns. are used to assign the major and some minor pathways for 1 dissocns. The major (~90%) pathway is initiated by cleavage of the ring C-5-O bond in 1 and proceeds to form ethylene and •CH₂COOH as main products, whereas loss of a hydrogen atom forms 3-butenoic acid as a minor product. Loss of the OH hydrogen atom forming butyrolactone (2, ~9%) and cleavage of the C-3-C-4 bonds (<1%) in 1 are other minor pathways. The major source of excitation in 1 is by Franck-Condon effects that cause substantial differences between the adiabatic and vertical ionization of 1 (5.40 and 6.89 eV, resp.) and vertical recombination in the precursor ion 1+ (4.46 eV). +NR+ mass spectra distinguish radical 1 from isomeric radicals 2-oxo-(1H)oxolanium (3), 1,3-dioxan-2-yl (9), and 1,3-dioxan-4-yl (10) that were generated sep. from their corresponding ion precursors.



~5 Citings

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9. 1H, 13C and 17O NMR spectral studies on monocyclic dioxolanes, dioxanes, dioxepanes and dioxocanes and cycloalkane-fused (5-8-membered) bicyclic 1,3-dioxolanes and 1,3-dioxanes

By Pihlaja, Kalevi; Nummelin, Heli; Klika, Karel D.; Czombos, Jozsef From Magnetic Resonance in Chemistry (2001), 39(11), 657-671. Language: English, Database: CAPLUS, DOI:10.1002/mrc.869

¹H, ¹³C and ¹⁷O NMR data for a set monocyclic dioxolanes, dioxanes, dioxepanes, and dioxocanes and cycloalkanefused (5-8-membered) bicyclic 1,3-dioxolanes and 1,3-dioxanes comprising 81 compds. in all are presented. This systematic configurational and conformational study addresses the deficiency in the available data regarding the conformational behavior and, in particular, the scant ¹⁷O NMR data for 1,3-dioxaalkanes. Many of the compds. are new and together with the known compds. measured under similar conditions they constitute a well documented compilation of spectral data suitable for addn. to databases and assistance in chem. shift calcns.

~17 Citings

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10. Mass spectra of the negative ions of some dioxanes

By Furlei, I. I.; Shmakov, V. S.; Rakhmankulov, D. L.; Zlotskii, S. S. From Russian Chemical Bulletin (Translation of Izvestiya Akademii Nauk, Seriya Khimicheskaya) (1999), 48(11), 2173-2175. Language: English, Database: CAPLUS, DOI:10.1007/BF02494872

It was established by mass spectrometry of neg. ions that fragmentation of some 1,3- and 1,4-dioxanes proceeds through intermediate $[M - H]^-$ ions. The fragmentation pathway depends on the site of neg. charge localization in these ions.

~1 Citing

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11. Proton chemical shifts in NMR. Part 12. Steric, electric field and conformational effects in acyclic and cyclic ethers

By Abraham, Raymond J.; Warne, Mark A.; Griffiths, Lee From Journal of the Chemical Society, Perkin Transactions 2: Physical Organic Chemistry (1998), (8), 1751-1757. Language: English, Database: CAPLUS

The NMR spectra of tetrahydropyran, at room temp. and -85°, where the ring inversion is slow on the NMR timescale, 2methoxy-, 3-methyl- and several 4-substituted tetrahydropyrans, 2-methyl-1,3-dioxolane and the rigid cyclic ethers 7oxabicyclo[2.2.1]heptane and 1,8-cineole were recorded and completely analyzed. These results together with literature data on acyclic and cyclic ethers (1,3- and 1,4-dioxane, dioxolane, 4-oxa-5 α -androstane, etc.) allowed the detn. of the O substituent chem. shifts (SCS) in these systems. This data set consisting of 78 proton chem. shifts in 17 compds. was used to test the application of a previous theor. model of proton chem. shifts to these compds. The model gives a very good account of the proton chem. shifts in these systems. The ether-O SCS are due to both steric and electrostatic terms, the steric term predominating at short distances (e.g., in the 1,3-diaxial interactions in methoxycyclohexanes). Conformational isomerism in these compds. was also studied. Low-temp. NMR gave ΔG (eq-ax) + 1.0 kcal mol⁻¹ for 4hydroxy-THP. Anal. of the couplings in the CHCH₂OH side chain of 2-(hydroxymethyl)-THP has shown that the preferred conformer is gt in both CHCl₃ and Me₂CO solvents.

~15 Citings

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12. Nonempirical calculations of the effect of molecular fragments on proton chemical shifts in heterocycles

By Aminova, R. M.; Aganov, A. V.; Zakirova, G. K. From Teoreticheskaya i Eksperimental'naya Khimiya (1990), 26(2), 149-57. Language: Russian, Database: CAPLUS

A gradient-invariant AO calcn. is reported on the effect of the 1-3 heterocyclic fragment (i.e., -OCH₂O-, -SCH₂S-) on the proton chem. shift in positions 4-6 in 1,3-heterocycles (i.e., 1,3-dioxane, 1,3-dithiane, resp.). The calcns. successfully reproduced the effect of the nature and orientation of alkyl substituents, as well as the effect of variation of the heterocyclic fragment.

~2 Citings

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13. Proton and carbon-13 NMR study of the structure of cyclic ortho esters and their hetero analogs

By Pastushenko, E. V.; Lapuka, L. F.; Khatuntsev, I. I.; Zlotskii, S. S.; Rakhmankulov, D. L. From Zhurnal Obshchei Khimii (1986), 56(1), 59-64. Language: Russian, Database: CAPLUS

The ¹H and ¹³C NMR spectra of title compds. I ($\mathbf{R} = H$, Me, OEt, OPr, NMe₂; $\mathbf{R}^1 = H$, Me), II ($\mathbf{R} = H$, OEt, NMe₂, CHMe₂), and III ($\mathbf{R} = H$, Me, alkoxy, NMe₂, cyclohexyl; $\mathbf{X} = \mathbf{O}$, NPh, \mathbf{S}) were analyzed. A reversal of the screening consts. of the axial and equatorial protons at C-4 and C-6 of 2-alkoxy-1,3-dioxanes was obsd. in their ¹H spectra.



~1 Citing

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14. Photoelectron spectra of oxygen and sulfur containing heterocyclic compounds. Methyl-substituted 1,3dioxanes

By Villem, N. V.

From Tartu Riikliku Ulikooli Toimetised (1985), 707, 158-67. Language: Russian, Database: CAPLUS

The UPS of 2-Me-, 4-Me-, 2,4-diMe-, 5,5-diMe-, 2,5,5-triMe-, 2,2,5,5-tetraMe-, and 2,4,4,6-tetraMe-1,3-dioxane were obtained. The bands of spectra were assigned by the use of the fragment-orbital model. The spacing of 2 highest MO Δ IE, which were characterized as combinations of the n_x (2p)-type O lone pairs, had values of 0.19-0.35 eV. The max. value of splitting was obsd. for 5,5-diMe-1,3-dioxane. Energies of n - and n +-orbitals depend more on the no. of Me groups than their position. The main influence of Me groups on the orbital structure and form of bands took place at 12-15 eV.

~0 Citings

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15. Structural assignments of ethylidene acetals by NMR spectroscopy

By Grindley, T. Bruce; Wickramage, Chandra From Journal of Carbohydrate Chemistry (1985), 4(2), 171-92. Language: English, Database: CAPLUS, DOI:10.1080/07328308508058830

The ¹H and ¹³C NMR spectra of ethylidene derivs. of simple diols, e.g. dioxolanes I (R, R¹ = H, Me), and of carbohydrates e.g. ethylideneglucopyranoside II were measured to det. whether NMR parameters could be found which could be related to structure. The chem. shifts of the acetal proton and carbon, the ${}^{2}J_{C,H}$ value between the acetal proton and Me carbon and the ${}^{1}J_{C,H}$ value of the acetal carbon were considered. The values of these parameters were all somewhat related to ring-size but the ${}^{2}J_{C,H}$ value was most closely related. The sign of ${}^{2}J_{C,H}$ was pos. for 2-methyl-1,3-dioxolane and 2-methyl-1,3-dioxone. Comparison of the ${}^{13}C$ NMR chem. shifts of the acetal with the parent diol gave information about acetal location.



~0 Citings

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16. Carbon-13 NMR study of the composition of aqueous solutions of glyoxylic acid

By Chastrette, Francine; Bracoud, Corinne; Chastrette, Maurice; Mattioda, Georges; Christidis, Yani From Bulletin de la Societe Chimique de France (1985), (1), 66-74. Language: French, Database: CAPLUS

The ¹³C NMR spectra of 20-60% aq. solns. of glyoxylic acid (I) were examd. in order to det. their compn. The 2 wellsepd. regions (acids and esters on 1 side, acetals, hemiacetals and hydrates on the other) display indirectly related intensities, owing to the relaxation times of carbonyl C atoms. The chem. shifts for possible I dimers and trimers were detd. from model compds. The species identified were the dimeric hemiacetal-acids, the erythro and threo isomers, and 4,5-dihydroxy-1,3-dioxolanecarboxylic acid (II). The II concn. increased with that of glyoxal in I, and some of its derivs. were isolated. I acetalization and esterification with EtOH in acidic media, effected with H_2O removal, provided a mixt. of ester-acetals, which was analyzed by coupled gas-liq. chromatog.-mass spectrometry and -chem. ionization (with NH_3). The anal. confirmed the existence of the above monomer and dimers in proportions related to the compn. of the aq. soln.; a small amt. of a cyclic dimer is also obsd. Aq. I exists as 69-88% monomeric hydrate and 2.5-12% dimeric hemiacetal-acids. Higher oligomers never exceed 5% in concd. solns., but glyoxal, if present, combines easily with I to form various compds., the major one accounting for $\leq 12\%$ of the material in some concd. glyoxal-I mixts.

~2 Citings

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17. Photoelectron spectra of methyl-substituted 1,3-dioxanes

By Asfandiarov, N. L.; Zykov, B. G.

From Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya (1983), (10), 2293-5. Language: Russian, Database: CAPLUS

Photoelectron spectra were obtained and identified for 7 Me-substituted 1,3-dioxanes. Empirical parameters were found characterizing the inductive effect and supercongugated σ_{C-C} band substituents with N_e ⁻ and N_a ⁺ orbitals.

~0 Citings

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18. Carbon-13 nuclear magnetic resonance and conformational analysis of 5-chloro-2-oxo-1,3,2-dioxathianes

By Gorrichon, Jean Pierre; Chassaing, Gerard; Cazaux, Louis From Organic Magnetic Resonance (1983), 21(7), 426-8. Language: English, Database: CAPLUS, DOI:10.1002/omr.1270210705

The ¹³C NMR chem. shifts in CDCl₃ for eight cyclic sulfites (e.g., I), chlorinated at C-5, are reported. The α - and β deshielding effects and the γ -shielding effects for the chlorine substituent are compared with similar effects in the 1,3dioxane series and with the effects arising from Me groups in the sulfite series. Conformational equil. studies for II and III shows that it is difficult to use ¹³C NMR spectroscopy for the conformational anal. of cyclic sulfites because of the frequent participation of twist forms, with 1,4- and 2,5-axes, to these equil.



~4 Citings

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19. 13C chemical shifts - sensitive detectors in structure determination. 1. 13C NMR studies of saturated heterocycles. 4. Methyl-substituted 1,3-dioxanes

By Pihlaja, Kalevi; Nurmi, Timo From Israel Journal of Chemistry (1980), 20(1-2), 160-7. Language: English, Database: CAPLUS, DOI:10.1002/ijch.198000066

The ¹³C chem. shifts for 1,3-dioxane and 50 methyl-substituted derivs. are reported. Substituent effects on them are derived and their magnitude shown to be closely related to the exact ring geometry and other conformational aspects. The results confirm the high chair-twist preference and support the view that 1,4-twist is appreciably more stable than 2,5-twist. Only 2,4-diaxially substituted compds. normally attain a twist form whereas 4,6-diaxial substitution alone is not enough but deform the chair form. A combination of the detailed knowledge on the stereochem. of the 1,3-dioxane ring and on the type of significant shift parameters leads inevitably to the conclusion that a proper understanding of their interdependence offers a useful tool for conformational and configuration anal.

~11 Citings

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20. Oxygen-17 NMR spectra of ring compounds. Correlation of oxygen-17 and carbon-13 methyl substitution parameters

By Eliel, Ernest L.; Pietrusiewicz, K. Michal; Jewell, Linda M. From Tetrahedron Letters (1979), (38), 3649-52. Language: English, Database: CAPLUS, DOI:10.1016/S0040-4039(01)95487-5

¹⁷O NMR spectra were obtained for twenty-two 1,3-dioxanes, 4 oxanes, four 4-heterooxanes, 4 tetrahydrofurans, and four 1,3-dioxolanes. Me substitution parameters detd. for the 1,3-dioxanes, including γ_a , correlated linearly with the reported corresponding ¹³C parameters for methyloxanes (E., 1979). This linear relation allows ¹⁷O shifts of O-contg. 6-membered satd. heterocycles to be used conveniently in conformational and configurational assignments.

~4 Citings

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21. NMR experiments on acetals. 41. Empirical study of the effect of alkyl substituents on the chemical shift of the ring hydrogen atoms in 1,3-dioxanes

By Tavernier, D.; Anteunis, M. From Journal of Magnetic Resonance (1969-1992) (1974), 13(2), 181-8. Language: English, Database: CAPLUS, DOI:10.1016/0022-2364(74)90005-5

The chem. shift (solvent CS2) of the ring H atoms of 74 alkyl substituted 1,3-dioxanes is given in tabular form. The effect of alkyl groups (Me, Et, Pr, Me2CH, iso-Bu, neopentyl, and tert-Bu) on chem. shifts is compiled. The spatial orientation of nonaxially sym. alkyl groups greatly influences the shift of the gem-H atom.

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22. Stereochemistry of heterocycles. Vibrational spectra of some substituted 1,3-dioxanes

By Gren, A. I.

From Voprosy Stereokhimii (1972), No. 2, 76-84. Language: Russian, Database: CAPLUS

The ir spectra of the cis and trans isomers of 14 1,3-dioxanes contg. Me, Et, Pr, Bu, and hexyl groups in the 2-, 4-, and 5-positions were reported. A band at 670 \pm 20 cm-1 was characteristic of the trans isomers. The ir spectra of 1,3-dioxane and its 2-, 4-, and 5-methyl and 5,5-diethyl derivs. were also given.

~0 Citings

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23. Carbon-13 magnetic resonance. Conformation in some tert-butyl-1,3-dioxanes

By Jones, Alan J.; Eliel, Ernest L.; Grant, David M.; Knoeber, M. C.; Bailey, William F. From Journal of the American Chemical Society (1971), 93(19), 4772-7. Language: English, Database: CAPLUS, DOI:10.1021/ja00748a018

The natural abundance carbon-13 NMR spectra of 12 tert-butyl-1,3-dioxanes and pertinent supporting data are described. The chem. shifts of the ring and substituent C atoms are affected by the positions and by the conformations of the substituents. Substituent shift correlations can in most instances be transferred from cyclohexane derivs. to their heterocyclic analogs provided one takes into consideration the deshielding effects of the ring oxygens on axial 5-substituents.

~4 Citings

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24. Conformational effects in compounds with six-membered rings. VIII. Preferred orientations of alkyl groups in allenes and in 2-alkyl-1,3-dioxanes and -dioxolanes

By Riddell, F. G.; Robinson, M. J. T. From Tetrahedron (1971), 27(17), 4163-9. Language: English, Database: CAPLUS, DOI:10.1016/S0040-4020(01)98146-3

The preferred orientations of ethyl and isopropyl groups in 1-alkyl-1-3,3-diphenylallenes and in 2-alkyl-1,3-dioxanes and dioxolanes were detd. from the temp. dependence of the spin-spin coupling consts. for appropriate vicinal protons. In the allenes, a Me group rather than a H atom eclipses a double bond but in the cyclic acetals skew interactions between Me groups and O atoms are minimized in the preferred conformations. The conformational preferences in simple ketones and aldehydes depend primarily on the double bonds rather than on the electronegativity of the O atom of the CO-group.

~1 Citing

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25. Carbon-13 nuclear magnetic resonance spectra of 1,3-dioxanes. II. Nonchair conformations

By Riddell, Frank G.; Kellie, G. M.

From Journal of the Chemical Society [Section] B: Physical Organic (1971), (5), 1030-4. Language: English, Database: CAPLUS

13C NMR spectra of 36 1,3-dioxanes were reported. Substituent effects on the chem. shifts of the ring C atoms for compds. known to exist in chair conformations failed to predict chem. shifts in compds. that would have 4,6- and 2,4-syn-diaxial interactions in chair conformations. Thus, these compds. are partially in nonchair conformations.

~0 Citings

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26. Nuclear magnetic resonance studies of asymmetrically substituted 1,3-dioxanes

By Ladd, John A.; Jones, Victor I. P. From Journal of the Chemical Society [Section] B: Physical Organic (1971), (3), 567-70. Language: English, Database: CAPLUS

The temp. dependence of NMR spectra of 2-alkyl-1,3-dioxanes (I, R1 = R2 = R3 = H, \mathbb{R} = Me, Et, Me2CH, and Ph), 2,2-dialkyl-1,3-dioxanes (I, R1 = Me, R2 = R3 = H, \mathbb{R} = Et, Pr, and Ph), 2-alkyl-2,5,5-trimethyl-1,3-dioxanes (I, R1 = R2 = R3 = Me, \mathbb{R} = Et, Pr, Me2CH, Me3C, and Ph) and 5-alkyl-5-methyl-1,3-dioxanes (I, \mathbb{R} = R1 = H, R2 = Me, R3 = Et, Pr, and NO2) provided information on the conformations of the substituents. Thermodynamic parameters for ring inversion were detd. for I (R1 = R2 = R3 = Me, \mathbb{R} = Et, Pr, Me2CH, and Me3C) and I (\mathbb{R} = R1 = H, R2 = Me, R3 = Et and Pr).

~0 Citings

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27. 220 Mc/s NMR spectra and geometry of some 2-substituted 1,3-dioxanes

By Buys, H. R.; Eliel, Ernest L. From Tetrahedron Letters (1970), (32), 2779-82. Language: English, Database: CAPLUS, DOI:10.1016/S0040-4039(01)98339-X

The NMR spectra of 2-methyl-, 2-phenyl-, 2-isopropyl-, and 2-tertbutyl-1,3-dioxane were studied to det. the influence of an equatorial substituent at the C-2 position on the geometry in the C-4-C-5-C-6 part of the 1,3-dioxane ring. NMR data for 2-p-chlorophenyl-1,3-dioxane are included. The individual vicinal coupling consts. did not show significant variation, implying that no significant geometrical differences occur in the C-4-C-5-C-6 region. No trend in the ring torsional angle was evident on change of substituent.

~8 Citings

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28. Conformational analysis. NMR spectra of six-membered cyclic acetals

By Pihlaja, Kalevi; Ayras, Pertti From Acta Chemica Scandinavica (1947-1973) (1970), 24(2), 531-49. Language: English, Database: CAPLUS, DOI:10.3891/acta.chem.scand.24-0531

The NMR spectra of 44 1,3-dioxanes were recorded in C6H6 and CCl4 solns. The chem. shifts and coupling consts. are presented and the structural effects are discussed in the light of these parameters. The C6H6 solvent shifts [$\Delta\delta$ (CCl4-C6H6)] were very suitable for the assignment of some signals.

~4 Citings

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29. Carbon-13 nuclear magnetic resonance spectra of some 1,3-dioxanes

By Riddell, Frank G. From Journal of the Chemical Society [Section] B: Physical Organic (1970), (2), 331-3. Language: English, Database: CAPLUS, DOI:10.1039/j29700000331

13C chem. shifts have been measured for 1,3-dioxane and 8 of its derivs. The chem. shifts of the ring C atoms are affected both by the positions and by the conformations of the substituents. Some correlations of chem. shifts with substitution pattern have been drawn.

~1 Citing

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30. Infrared-spectroscopic investigations of 1,3-dioxanes

By Wunderlich, Heinrich

From Fresenius' Zeitschrift fuer Analytische Chemie (1968), 241(3), 234-40. Language: German, Database: CAPLUS

The ir spectra (5000-670 cm.-1) of 17 2-, 4-, and (or) 5-alkyl-substituted 1,3-dioxanes and of analogously substituted 2,4,7,9-tetraoxaspiro[5.5]undecanes are presented and compared. The frequencies of the C-O-C vibrations are correlated with the substituent types and positions.

~0 Citings

31. Studies in organic mass spectrometry. VI. Influence of alkyl substituents on the fragmentation of 1,3dioxane

By Vandewalle, M.; Schamp, N.; Van Cauwenberghe, K. From Bulletin des Societes Chimiques Belges (1968), 77(1-2), 33-42. Language: English, Database: CAPLUS

Characteristic peaks in the mass spectra of 1,3-dioxane and its 2-, 4-, 5-, and 6-alkyl substituted derivs. are tabulated and the mass spectra are discussed. Two main degradation patterns are observed, resulting from initial elimination of a 2-H atom or alkyl substituent and from the expulsion of a CH2O mol. Subsequent fragmentations are strongly influenced by the presence of substituents. 4,6-Disubstituted 1,3-dioxanes show a distinct and typical fragmentation, starting with the expulsion of a substituent.

~0 Citings

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32. Steric factors and benzene solvent shifts in N .M. B. (nuclear magnetic resonance) spectroscopy

R. (nuclear magnetic resonance) spectroscopy

By Anderson, J. Edgar

From Tetrahedron Letters (1965), (51), 4713-17. Language: English, Database: CAPLUS

The 1,3-dioxanes with preferred chair conformation are well adapted for solvent-effect studies since all the protons are generally identified and a wide range of solvent shifts from -0.25 to 0.6 ppm. is obtained in each mol. Changes brought about by substituents are readily observed and steric factors affecting the size and nature of the interaction can be demonstrated. Spectra were measured on 0.4M solute in CCI_4 and C_6H_6 as the inactive and active solvents. A plot of solvent shift vs. the mole fraction of C_6H_6 in CCl₄ is a straight line, indicating a 1:1 complex. The equil. const. for solvent shift vs. the mole fraction of C_6H_6 in CCI₄ is a straight line, indicating a 1.1 complex. The equil. Const. for complex formation was obtained from a plot of (mole fraction C_6H_6 /fraction of total solvent shift) vs. the mole fraction C_6H_6 (Tyrrell, CA 62, 11459h), but such plots for the series I ($\mathbf{R} = H_2$) (II) and I ($\mathbf{R} = Me_2$) (III) are very nearly horizontal, indicating that the complex is less stable than the dissocd. state of the 2 mols. Thus C_6H_6 and 1,3-dioxanes give very weak complexes. The solvent shifts $\Delta\delta^{CCI4}C_{6H_6}$ (difference in shift of a signal in inactive CCI₄ and interacting C_6H_6) for the series II ($\mathbf{R}' = Me_3C$, Me_2CH , Et, Me) and III ($\mathbf{R}' = Me_3C$, Me_2CH , Et, Me) were measured and tabulated. In both series more than 95% of the conformation is at equil. with the 2-alkyl group equatorial. In the II series, the 4-, 5-, and 6positions are shielded, the 2-axial position is little affected, and the protons at the 2-equatorial position are deshielded. This is compatible with location of the C_6H_6 mol. as in the diagrams (IV, V). If the interaction with C_6H_6 is of the type dipole-induced dipole, the nucleophilic C_6H_6 mol. would be expected to prefer position V. All the protons in the 4-, 5-, and 6-positions in compds. of series III are shielded less by 0.15 to 0.30 ppm. than those in the corresponding compds. of series II. The changes could be explained on the basis of IV with the axial Me group in position 5 topping the end of the C_6H_6 mol. away from the dioxane ring. Axial groups on the other side of the mol. as in compds. VI and VII have similar but less marked effect. Compared with the compds. in series II, the 6-axial proton is much less shielded (0.13) as is the 2-axial proton and, in VII, the 6-equatorial proton. That equatorial substituents have little effect is shown by compds. VIII and IX. In VIII, the protons in the 4,6-positions leave almost identical shifts and, in IX, all the shifts. Thus, although the C_6H_6 -dioxane complex is specific, it is not possible to state on which side of the dioxane ring the C_6H_6 mol. is located, since axial groups on either side of the dioxane mol. change the solvent effect. Steric factors can invalidate a direct comparison of solvent shifts of similarly located protons in different mols.

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33. Nuclear magnetic resonance (N

.M.

R.) spectra and structure of 1,3-dioxanes, 1,3-dioxolanes, and some cyclic esters of [phosphorus,] sulfurous, and carbonic acids. I. 1,3-Dioxanes and 1,3-dioxolanes

By Samitov, Yu. Yu.; Aminova, R. M.

From Zhurnal Strukturnoi Khimii (1964), 5(2), 207-16. Language: Unavailable, Database: CAPLUS

A temp. probe permitting ranges from -80° to 130° is described. The N.M. R. spectra and peak assignments are presented for the following dioxanes: 1,3-dioxane (I), 2-methyl-1,3-dioxane (II), 4-methyl-1,3-dioxane (III), and 2,4-dimethyl-1,3-dioxane (IV). Because of rapid conformational transitions at room temp., I has an A_4X_2 spectrum. In II, the added Me group hinders conformational changes, leading thus to an $A_2B_2X_2$ spectrum. For III, inequivalence of axial and equatorial protons produces an AB portion in the spectrum. From its chem. shift, the 2-Me group in IV is in an equatorial position relative to the ring. The N.M. R. spectra and peak assignments are also given for the following 1,3-dioxane derivs.: 4-methyl-1,3-propanediol carbonate (V), substituted methyl-1,3-butanediol phosphite (VI), 2-ethoxy-4-methyl-1,3-dioxane (VII), and 2-ethoxy-1,3-dioxane (VIII). Comparison with the spectrum of III indicates that in V and in VI the Me group is in the equatorial position. Spectral analysis indicates that VII and VIII each consist of a mixt. of 2 conformational isomers. The spectra and peak assignments are given for 2-methyl-1,3-dioxolane, 2-ethoxy-1,3-dioxolane, and substituted ethyl ethanediol phosphite. These spectra permit some qual. remarks about the equivalence of the cis and trans protons owing to rapid inversion. Some features of the spectra of 1,3-dioxolane itself, 2-phenyl-1,3-dioxolane, and 2,2-spiropentamethylene-1,3-dioxolane are pointed out.

~0 Citings

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34. Oxonium theory in the light of optical study of the hydrogen bond in some monovinyl ethers of glycols and polyglycols

By Shostakovskii, M. F.; Batuev, M. I.; Tyupaev, P. V.; Matveeva, A. D. From Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya (1954), 1103-10. Language: Unavailable, Database: CAPLUS

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