

1. Microwave spectrum and DFT calculations of 4,4-dimethyl-1,3-dioxane

By Mamleev, A. Kh.; Galeev, R. V.; Faizullin, M. G.

From *Journal of Structural Chemistry* (2011), 52(2), 432-435. Language: English, Database: CAPLUS, DOI:10.1134/S0022476611020272

In the microwave spectrum of 4,4-dimethyl-1,3-dioxane, the rotational transitions of a, b, and c types with $J \leq 54$ are identified in the ground vibrational state of the mol. in the frequency range of 12 GHz to 37 GHz. Rotational consts., quartic centrifugal distortion consts., and the dipole moment of the mol. are detd. The revealed transitions belong to the chair conformer. The B3PW91/aug-cc-pVDZ method is used to calc. the geometric parameters of 1,3-dioxane, 4-methyl-1,3-dioxane, and 4,4-dimethyl-1,3-dioxane. Alkyl substitution is shown to cause changes in the geometry of the 1,3-dioxane core.

~1 Citing

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2. Freshness characterisation of whiting (*Merlangius merlangus*) using an SPME/GC/MS method and a statistical multivariate approach

By Duflos, Guillaume; Leduc, Francois; N'Guessan, Assi; Krzewinski, Frederic; Kol, Ossarath; Malle, Pierre

From *Journal of the Science of Food and Agriculture* (2010), 90(15), 2568-2575. Language: English, Database: CAPLUS, DOI:10.1002/jsfa.4122

BACKGROUND: The freshness of whiting was studied at five stages of ice storage by comparing the anal. of volatile compds. obtained through solid phase microextrn./gas chromatog./mass spectrometry (SPME/GC/MS) with two sensory methods. RESULTS: Of the volatile compds. identified, 38 were analyzed using a statistical multivariate approach and classified according to their role in the estn. of freshness during storage as markers of freshness or spoilage. Regarding the evolution of the presence or absence of individual compds., three categories were defined. For example, the volatile compds. propanal, hexanal, 1-penten-3-ol, pentanal, 2,3-pentanedione, 1-penten-3-one, heptanal, (E)-2-pentenal, 2,3-octanedione, (Z)-2-penten-1-ol, 1-pentanol, butanal, octanal, 3,5,5-trimethyl-2-hexene, 1-hexanol and 4,4-dimethyl-1,3-dioxane appeared highly relevant, because they are found throughout storage and can be divided into several categories that are directly related to the quality of fish. CONCLUSION: SPME/GC/MS combined with a statistical multivariate approach may be a useful method to identify volatile compds. and characterize fish freshness during storage. Copyright © 2010 Society of Chem. Industry.

~13 Citings

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3. 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 superconjugated σ_{C-C} band substituents with N_e^- and N_a^+ orbitals.

~0 Citings

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4. Effect of the composition of the reagent T-66 on the flotation of coals

By Vlasova, N. S.; Chizhevskii, V. B.; Savinchuk, L. G.

From *Koks i Khimiya* (1981), (1), 5-8. Language: Russian, Database: CAPLUS

Eight fractions were obtained in the distn. of a reagent T 66 [39393-21-0]. From IR spectra the following moieties could be identified: dioxanic, arom., and naphthenic rings, gem-di-Me, CH_3 , CH_2 , and CH groups, and C:O and C:C bonds. In the chromatograms 47 different components were seen and 16 were identified. The most abundant were pyranic and dioxanic alcs., 4,4-dimethyl-1,3-dioxane [766-15-4] and triols. Fractions 131.3-156.3° and <75.9° had the highest flotation activity.

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5. 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 ^{13}C 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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6. 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

^{17}O 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 ^{13}C parameters for methyloxanes (E., 1979). This linear relation allows ^{17}O shifts of O-contg. 6-membered satd. heterocycles to be used conveniently in conformational and configurational assignments.

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7. Identification of substances in isoprene preparation products

By Druzhinina, E. A.; Gagina, E. A.; Silkina, A. G.; Lopatina, I. V.; Rapoport, E. L.
From *Promyshlennost Sinteticheskogo Kauchuka* (1978), (11), 18-20. Language: Russian, Database: CAPLUS

The manuf. of isoprene [78-79-5] by catalytic decompn. of 4,4-dimethyl-1,3-dioxane [766-15-4] is accompanied by deformation of 13 by-products (as identified by IR spectroscopy and b.p. detn.), e.g., CO-contg. compds., unsatd. C_5 alc., and unsatd. C_{6-8} hydrocarbons. The identification characteristics of the byproducts are discussed.

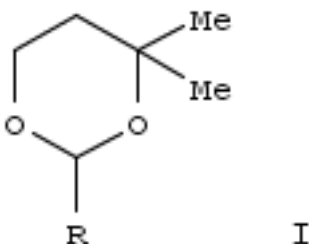
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8. Synthesis and proton and carbon-13 NMR spectra of 2-alkyl-4,4-dimethyl-1,3-dioxanes

By Samitov, Yu. Yu.; Musavirov, R. S.; Karataeva, F. Kh.; Kantor, E. A.; Rakhmankulov, D. L.; Nikiforova, N. A.
From *Zhurnal Organicheskoi Khimii* (1978), 14(12), 2483-7. Language: Russian, Database: CAPLUS

The NMR spectra of **I** ($\text{R} = \text{H}, \text{C}_1\text{-C}_6 \text{ n-alkyl}, \text{Me}_2\text{CH}, \text{Me}_2\text{CHCH}_2, \text{C}_8\text{H}_{17}$) corresponded to a chair conformation. Two torsional angles were calcd. by different methods. One indicated a slight compression of the C portion of the ring, compared to 1,3-dioxane itself, but the other indicated a normal chair conformation.



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9. Analysis of by-products of isoprene synthesis using combined instrumental analytical methods

By Belafi-Rethy, Katalin; Iglewski, Stanislaw; Kerenyi, Ervin

From *Sbornik Vysoke Skoly Chemicko-Technologicke v Praze, D: Technologie Paliv* (1976), D33, 111-21. Language: Russian, Database: CAPLUS

By-products from cracking of 4,4-dimethyl-1,3-dioxane [766-15-4] (prepd. from isobutene and HCHO) are sepd. by distn. and by liq. and preparative gas chromatog., and are identified by structure type using IR, UV, proton NMR, anal. gas chromatog., mass spectrometry, and elemental anal. The structure of 3-methyl-2-buten-1-ol [556-82-1] was detd.

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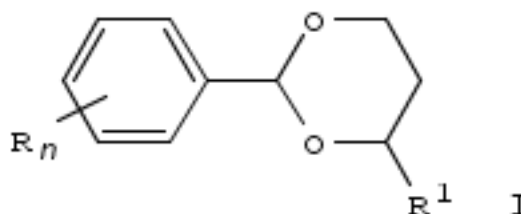
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10. Proton and carbon-13 NMR spectroscopic study of six-membered cyclic acetals of substituted benzaldehydes

By Lezina, V. P.; Stepanyants, A. U.; Alimirzoev, F. A.; Zlotskii, S. S.; Rakhmankulov, D. L.

From *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya* (1976), (4), 792-8. Language: Russian, Database: CAPLUS

The ^1H and ^{13}C NMR spectra of **I** [$R_n = \text{H}$; 2-, 3-, 4- NO_2 ; 2-, 4-MeO; 2-F; 2-, 4-OH; 4-Me 2N ; 3-Br; 2,4-(MeO) $_2$; $R_1 = \text{H}$, Me] were examd. R_n exerted its largest effect on C-2 and H-2 of the dioxane ring.



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11. New collectors for coal flotation

By Petukhov, V. N.; Avdeenko, V. P.

From *Sbornik Nauchnykh Trudov - Magnitogorskii Gorno-Metallurgicheskii Institut imeni G. I. Nosova* (1974), 142, 3-7. Language: Russian, Database: CAPLUS

An exptl. flotation app. was used to study the effectiveness of different classes of pure org. compds. as collectors for coal flotation. Arom. and unsatd. hydrocarbons are more efficient and effective at lower concns. than satd. and naphthenic ones. The performance depended on the structure and length of the hydrocarbon chain. The 4,4-dimethyl-1,3-dioxane [766-15-4], 2-butenyl-4-methyl-1,3-dioxane [56631-53-9], and 2-octyl-1,3-dioxane [17357-15-2] are particularly effective and can be used without the addn. of surfactants. Studies by EPR and ir methods indicated significant differences in the nature of the adsorbed hydrocarbon layer on the coal surface. Satd. and naphthenic hydrocarbons were retained by van der Waals forces, whereas the π electrons of the conjugated double bonds in arom. and olefinic hydrocarbons combined with the free surface radicals to form a surface film of increased thickness and strength with enhanced flotation properties.

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12. Ring inversion barrier in 5,5-difluoro-1,3-dioxane

By Binsch, Gerhard; Eliel, Ernest L.; Mager, Sorin

From *Journal of Organic Chemistry* (1973), 38(23), 4079-81. Language: English, Database: CAPLUS, DOI:10.1021/jo00987a033

The ring inversion barrier in 5,5-difluoro-1,3-dioxane (**I**) was detd. by low-temp. ^1H and ^{19}F NMR spectroscopy to be 8.5 ± 0.3 kcal/mole; it was distinctly lower than the barriers in 1,3-dioxane and 5,5-dimethyl-1,3-dioxane. Possible reasons are discussed.

~3 Citings

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13. 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.

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14. N

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R. spectra of conformational isomers of 1,3-dioxane

By Delmau, J.

From [Compt. Rend. Congr. Natl. Soc. Savantes, Sect. Sci. \(1965\), 90\(Pt. 1\), 123-5](#). Language: French, Database: CAPLUS

The diequatorial trans-4,5-dimethyl-1,3-dioxane shows 2 distinct resonances characteristic of the equatorial and axial H's sepd. by 23 cps. Each resonance is a doublet (J = 6 cps.). 5,5-Dimethyl-1,3-dioxane and 4,4-dimethyl-1,3-dioxane show only one resonance signal as a result of rapid equilibration of **I**; each species has a lifetime of <1/1000 sec. 4-Methyl-4-ethyl-1,3-dioxane is restricted to one conformation, as shown by the existence of 2 resonances sepd. by 3 cps.

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15. Hydrolysis of linear and cyclic acetals in an acid medium. IV. Substituted 1,3-dioxanes

By Aftalion, Florin; Lumbroso, Daniel; Hellin, Michel; Coussement, Fernand

From [Bulletin de la Societe Chimique de France \(1965\), \(7\), 1958-75](#). Language: French, Database: CAPLUS

The influence of substituents in positions 4, 4,6, or 5 on the rate of hydrolysis of cyclic 1,3-acetals in H₂O and H₂O-paradioxane (40-60 vol.-%) has been investigated. H₂SO₄ served as catalyst. The course of the reaction was followed by measurement of methylene glycol formed by hydrolysis. Side reactions are without influence on the kinetics. Two series of measurements were carried out: at const. temp and various acidities; at const. acidity and various temps. The rate constants were correlated by application of the Hammett acidity function H₀. Hydrolysis of known mixts. of 4,6-dimethyl-1,3-dioxanes [CH₃-equatorial-axial (ea) and diequatorial (ee)] showed that the compd. with the ea position of the substituents was hydrolyzed 6 times faster. The influence of the substituents consists mainly in a steric interaction between substituent and ring. For the hydrolysis of cyclic formaldehyde acetals substituted in position 4 in H₂O-paradioxane mixts., a chelation effect has to be considered. Application of the Hammett-Taft relation under consideration of the chelate effect resulted in good agreement of the exptl. determined and calcd. values of the rate constants. Most of the 1,3-dioxanes (see table) were prepd. by Prins reactions with formol (30 %-wt. aq. soln.) or paraformaldehyde (previously depolymerized to formal in the presence of aq. H₂SO₄) and the appropriate olefins in aq. H₂SO₄. The aq. and org. phases are vigorously stirred (reaction temp. and time tabulated), and at the end of the reaction, the 1,3-dioxanes, little sol. in the aq. phase, form with unreacted olefin and org. phase which is decanted, neutralized with Na₂CO₃, dried over CaCl₂, and distd. to recover the 1,3-dioxanes. 2-Methyl-1-buten-3-one led to a disubstituted dioxane in position 5. 5-Methyl-1,3-dioxane, 5-ethyl-1,3-dioxane, 4,6-dimethyl-1,3-dioxane (ee or ea) have been prepd. by boiling a mixt. of 1 mole of the corresponding 1,3-diol, 35-40 g. paraformaldehyde, 20-30 g. H₂SO₄, and 70-80 g. H₂O. A heteroazeotropic mixt. of 1,3-dioxane and H₂O is obtained by fractional distn., the phases are sepd., and the org. phase redist. after drying over CaCl₂. For prepn. of 5,5-dimethyl-1,3-dioxane, a mixt. of 2,2-dimethyl-1,3-propanediol, 60 g. paraformaldehyde, 100 g. H₂SO₄, and 240 g. H₂O is heated under stirring for 2 hrs. at 50°. Substituent, b.p. or m.p., n_D²⁰, d₄²⁰: 4-tert-butyl-4-methyl, b₂₅ 84°, 1.448₀, 0.952; 4,4-diethyl, b. 177°, 1.442₇, 0.949; 4-ethyl-4-methyl, b₁₅ 49°, 1.433₄, 0.958; 4-isopropyl, b₂₀ 50°, 1.430₀, 0.949; 4-ethyl, b₇₅₀ 138°, 1.424₂, 0.957; 4-vinyl-4-methyl, b. 154°, 1.444₉, 0.988; 4-vinyl, b. 142°, 1.445₈, 0.993; 4-phenyl-4-methyl, b₂ 90-7°, 1.526₀, --, m.PhCH₂CO₂OCMe₃, 40°, --, --; 4-phenyl, b_{0,6} 68-71°, 1.531₀, 0.904; 4-chloromethyl-4-methyl, b₁₀ 71°, 1.465₃, 1.173; 4-chloromethyl, b₃ 50°, 1.469₁, 1.2107; 4-cyanomethyl-4-methyl, b₁ 80-5°, 1.462₂, --; 5-methyl, b. 120°, 1.418₃, 0.985; 5-ethyl, b. 149°, 1.425₇, 0.965; 5,5-dimethyl, b. 126°, 1.420₅, 0.953; 5,5-diethyl, b₂₀ 76°, 1.439₉, 0.955; 5-hydroxymethyl-5-methyl, b₁ 87°, 1.459₈, 1.120; 5-acetyl-5-methyl, b₃ 79°, 1.461₀, 1.092; 5-nitro-5-methyl, m. 71°, --, --; 4e,6e-dimethyl, b. 125°, 1.413₅, 0.930; 4,4,5-trimethyl, b₃₀ 64°, 1.431₃, 0.958; 4,4,6-trimethyl, b. 139°, 1.420₉, 0.926; 5,5-Diethyl-1,3-dioxane has been prepd. analogously from 2,2-diethyl-1,3-propanediol, with only 70 g. H₂O and heating for 1 hr. at 80°. A mixt. of meso- and dl-2,4-pentanediol was made as follows: 400 g. redist. acetylacetone and 15 g. Raney Ni was placed into a stirring autoclave at 25°. H at 120 atm. was pressed in until absorption ceased. The catalyst was filtered off, and the diol recovered by distn. By acetalization, it yielded a mixt. of 4,6-dimethyl-1,3-dioxane (ee) and 4,6-dimethyl-1,3-dioxane (ea), contg. 50% of each according to gas chromatographic and N.M.R. analysis. 4,4,6-Trimethyl-1,3-dioxane was prepd. as follows: A mixt. of 2,4,4,6-tetramethyl-1,3-dioxane (75 g.), 30 g. paraformaldehyde, 50 g. paradioxane, and 10 g. concd. HCl was kept at boiling temp. A first-running mixt. of paradioxane and acetaldehyde was discharged. The transformation of the tetramethyl into the trimethyl deriv. was followed by gas chromatographic detn. after the samples taken had been neutralized. After all the tetramethyl deriv. had reacted, the mixt. was cooled, neutralized with Na₂CO₃, 5, dried over CaCl₂, and distd. Ir absorption bands of the 1,3-dioxanes are discussed extensively and tabulated.

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16. Hydrolysis of linear and cyclic acetals in an acid medium. III. Hydrolysis of 4-methyl-1,3-dioxane and 1,3-dioxane in water. Isotopic effect of the solvent in heavy water

By Aftalion, Florin; Lumbroso, Daniel; Hellin, Michel; Coussemant, Fernand

From *Bulletin de la Societe Chimique de France* (1965), (7), 1950-7. Language: French, Database: CAPLUS

cf. CA 63, 8142e. The kinetics of the hydrolysis of 4-methyl-1,3-dioxane (I), 4,4-dimethyl-1,3-dioxane (II), and 1,3-dioxane (III) were investigated. For the detn. of an eventual isotopic effect, hydrolysis was also carried out in deuterized H₂SO₄ as hydrolysis catalyst. The kinetic measurements were performed as described previously (loc. cit.). The single rate constants of hydrolysis and acetal formation were measured using solns. of either pure acetals or the products of hydrolysis only in known concns.; methylene glycol was charged as sodium bisulfite complex. Concns. were about 0.4M, the H₂SO₄ concn. varied between 0.5-2.4 moles/l. Equilibrium constants were calcd. using the relation $K_c = [\text{diol}][\text{formol}]/[\text{dioxane}][\text{H}_2\text{O}]^2$. Measurements of the rate constants verified that hydrolysis follows first order and acetal formation second order kinetics. The energy of activation of each partial reaction and ΔH of the reactions in equilibrium were calcd. The influence of various H₂SO₄ concns. on the rate constants was determined. The interpretation of the results of the measurements leads to the conclusion that the mechanism for the hydrolysis of cyclic acetals is identical with that for the hydrolysis of linear acetals.

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17. The Prins reactions. IV. The isobutene-formaldehyde system: application of nuclear magnetic resonance to the identification of products

By Delmau, Jean; Davidson, Mircea; Parc, Guy; Hellin, Michel

From [Bulletin de la Societe Chimique de France \(1964\), \(2\), 241-4](#). Language: Unavailable, Database: CAPLUS

cf. CA 60, 14378c, 15861h. The nuclear magnetic resonance spectra of a series of previously obtained (loc. cit.) 1,3-dioxanes indicated for -OCH₂O a single peak at 4.70-4.75 p.p.m. when there were two conformations in equil., and a doublet at ~4.6 or 4.9 p.p.m. if onecon former predominated. For -OCH₂C-, -CCH₂C- and -Me (as substituents) peaks appeared at ~3.8, 1.5, and 1.2 p.p.m., resp.

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