1. Solid-state vibrational circular dichroism studies on the conformation of an amino acid molecule in crystalline state

By Sato, Hisako; Kawamura, Izuru
From Biochimica et Biophysica Acta, Proteins and Proteomics (2020), 1868(8), 140439. Language: English, Database: CAPLUS, DOI:10.1016/j.bbapap.2020.140439

The present article reviews the results of solid-state vibrational CD (SD-VCD) measurements on the crystals of amino acids. The investigated series were Ala, Ile, Leu, Phe, Ser, Val, and Thr. Spectra were recorded for the samples contg. both D- and L-enantiomers. The mol. conformation in a cryst. state was compared among the series. Mol. optimization of their conformation under intermol. interactions in cryst. states was revealed. One noteworthy aspect was that some VCD peaks were remarkably enhanced in comparison with the soln. states. This fact was rationalized in terms of vibrationally coupled delocalization in a closely stacked pair. In addn., for a mol. with two asym. carbons, the signs of the VCD peaks were detd. by the interplay between the two chiral centers. Lastly, the roles of the theor. approach based on d. functional theory calcns. were described.

2. Testing the vibrational exciton and the local mode models on the instructive cases of dicarvone, dipinocarvone, and dimenthol vibrational circular dichroism spectra

By Mazzeo, Giuseppe; Santoro, Ernesto; Abbate, Sergio; Zonta, Cristiano; Fabris, Fabrizio; Longhi, Giovanna
From Chirality (2020), 32(7), 907-921. Language: English, Database: CAPLUS, DOI:10.1002/chir.23232

The vibrational CD (VCD) spectra of dicarvone (1), dipinocarvone (2), and dimenthol (3) have been recorded in the range 900-3200 cm^{-1}, encompassing the mid-IR (mid-IR), the C[n.63742]O stretching, and the CH-stretching regions. For compd. 3 also, the fundamental and the first overtone OH stretching regions have been investigated by IR/NIR absorption and VCD. D. functional theory (DFT) calcns. allow one to interpret the IR and VCD spectra and to confirm the configuration/conformational studies previously conducted by X-ray diffraction. The most intense VCD signals are assocd. with the vibrational normal modes involving symmetry-related groups close to the CC bond connecting covalently the two mol. units. The vibrational exciton (VCDEC) model is fruitfully tested on the VCD data of compds. 1 and 2 for the spectroscopic regions at ~1700 cm^{-1}, and the local mode model is tested on compd. 3 at ~3500 and ~6500 cm^{-1}. For compds. 1 and 2 also, ECD spectra are reported, and the exciton mechanism is tested also there, and connections to the VCDEC model are examd.

3. TRAVIS - A free analyzer for trajectories from molecular simulation

By Brehm, M.; Thomas, M.; Gehrke, S.; Kirchner, B.
From Journal of Chemical Physics (2020), 152(16), 164105/1-164105/20. Language: English, Database: CAPLUS, DOI:10.1063/5.0005078

TRAVIS ("Trajectory Analyzer and Visualizer") is a program package for post-processing and analyzing trajectories from mol. dynamics and Monte Carlo simulations, mostly focused on mol. condensed phase systems. It is an open source free software licensed under the GNU GPL, is platform independent, and does not require any external libraries. Nine years after the original publication of TRAVIS, we highlight some of the recent new functions and features in this article. At the same time, we shortly present some of the underlying algorithms in TRAVIS, which contribute to make trajectory anal. more efficient. Some modern visualization techniques such as Sankey diagrams are also demonstrated. Many anal. functions are implemented, covering structural analyses, dynamical analyses, and functions for predicting vibrational spectra from mol. dynamics simulations. While some of the analyses are known since several decades, others are very recent. For example, TRAVIS has been used to compute the first ab initio predictions in the literature of bulk phase vibrational CD spectra, bulk phase Raman optical activity spectra, and bulk phase resonance Raman spectra within the last few years. (c) 2020 American Institute of Physics.

4. Exploring the gel phase of cationic glycylalanylglycine in ethanol/water. II. Spectroscopic, kinetic and thermodynamic studies

By Di Guiseppi, David M.; Thursch, Lavenia; Alvarez, Nicolas J.; Schweitzer-Stenner, Reinhard
From Journal of Colloid and Interface Science (2020), 573, 123-134. Language: English, Database: CAPLUS, DOI:10.1016/j.jcis.2020.03.108

Recently, we reported a three-dimensional phase diagram for the gelation of cationic tripeptide glycylalanylglycine (GAG) in water-ethanol mixts. We showed that the gel strength reaches an optimum for a peptide concn. of 200 mM and ethanol/water mixts. with ca. 55-60 mol% ethanol. An increase of the ethanol fraction causes a substantial upshift of the gel's softening temp. which is indicative of a reduced peptide soly. We expect the formation of long cryst. fibrils which form the sample spanning network of the gel phase to precede the gelation process and that the fibril microstructure depends on the rate and concn. of peptide. We used UV CD (UVCD) spectroscopy to probe the kinetics of GAG fibril formation as a function of peptide concn. and ethanol fraction. We provide exptl. evidence for the notion that the utilized CD signal reflects the three-dimensional assembly of peptides rather than a two-dimensional sheet structure. UVCD was also used to probe the melting of GAG fibrils with increasing temp. FTIR and vibrational CD (VCD) spectroscopy were employed to characterize the structure of sheets with which the obsd. fibrils were formed. Fibrilization and gelation kinetics occur on a very similar time scale for very short gelation times (< 7 min) obsd. at high peptide concns. and/or ethanol fractions. Otherwise, gelation proceeds significantly slower than fibrilization. The trends in the UVCD spectral response parallel the trends in the storage modulus as a function of peptide concn. and ethanol fraction. IR and VCD profiles of amide I' reveal that fibril structure and the resp. chirality are both affected by peptide concn. and solvent compn. At high ethanol fractions, the VCD changes its sign suggesting a conversion from phase II to phase I. Generally, the latter is obtained only at temps. below 15°C. Altogether, our results reveal how GAG fibrilization and gelation are interrelated and how the gel properties can be tuned by changing the compn. of the ternary GAG/water/ethanol mixt.

5. Theoretical Studies into the Spectral Characteristics, Biological Activity, and Photovoltaic Cell Efficiency of Four New Polycyclic Aromatic Chalcones

By Al-Otaibi, Jamelah S.; Mary, Y. Sheena; Thomas, Renjith; Narayana, B.
From Polycyclic Aromatic Compounds (2020), Ahead of Print. Language: English, Database: CAPLUS, DOI:10.1080/10406638.2020.1747097

In the present work, the mols., (E)-1-(4,4''-difluoro-5'-methoxy-1,1':3',1''-terphenyl-4'-yl)-3-phenylprop-2-en-1-one (DFTP), (2E)-1-(4,4''-difluoro-5'-methoxy-1,1':3',1''-terphenyl-4'-yl)-3-(4-fluorophenyl)prop-2-en-1-one (TFTP), (2E)-3-(4-bromophenyl)-1-(4,4''-difluoro-5'-methoxy-1,1':3',1''-terphenyl-4'-yl)-prop-2-en-1-one (BFTP), and (E)-1-1(4,4''-difluoro-5'-methoxy-1,1':3'-1''-terphenyl-4'-yl)-3-(4-methylphenyl)prop-2-en-1-one (FMTP) have been synthesized and vibrational wavenumbers and electronic properties have also been performed. The compd. series shows good light harvesting properties and photovoltaic modeling shows that they can be used successfully in DSSCs as photo sensitizers. The NLO activity of the title compds. have been investigated and β and γ values varies in the order BFTP > FMTP > TFTP > DFTP. The consequences which were made by electron donor acceptor due to charge transfer mechanism have been scrutinized by the natural bond investigation. Mol. docking has been performed to understand the binding interactions of the analyzed ligands with tyrosine-protein kinase JAK2 and these compds. can be developed as anticancer agent.

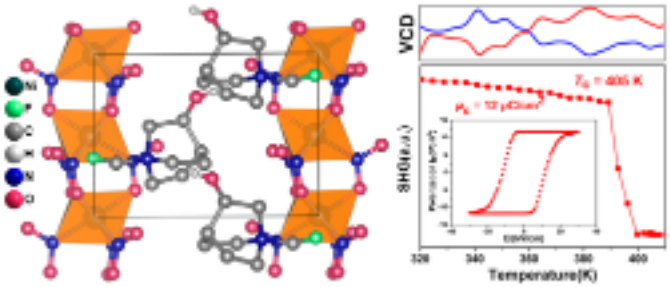
6. A new horizon for vibrational circular dichroism spectroscopy: a challenge for supramolecular chirality

By Sato, Hisako
From Physical Chemistry Chemical Physics (2020), 22(15), 7671-7679. Language: English, Database: CAPLUS, DOI:10.1039/d0cp00713g

A review. Vibrational CD (VCD) spectroscopy is an extension of CD spectroscopy into the IR and near-IR regions where vibrational transitions occur in the ground electronic state of a mol. The method offers the advantage of studying the chiroptical properties of a wide range of mols. in non-cryst. states. However, because of the smallness of the signals, one measurement requires several hours to yield reliable results. Accordingly, its targets were limited to a stable mol. in a soln. To overcome this difficulty, our group applied the VCD method to supramol. systems. The work was launched based on the finding that the VCD signal remarkably enhances when low-mol. mass gelators form gels. By analyzing a no. of well-resolved VCD peaks, the detailed conformation of a component mol. was deduced. This provided a clue to elucidating the mol. organization in supramol. architectures. Our final goal was to clarify the route from microscopic mol. chirality to supramol. chirality. For this purpose, a time-step VCD measurement method was developed for the in situ monitoring of the progress of chirality amplification.

7. Homochiral Nickel Nitrite ABX3 (X = NO2-) Perovskite Ferroelectrics

By Deng, Bin-Bin; Xu, Chu-Chu; Cheng, Ting-Ting; Yang, Yi-Ting; Hu, Yan-Ting; Wang, Pan; He, Wen-Hui; Yang, Meng-Juan; Liao, Wei-Qiang
From Journal of the American Chemical Society (2020), 142(15), 6946-6950. Language: English, Database: CAPLUS, DOI:10.1021/jacs.0c02580



Chiral org.-inorg. perovskites (COIPs) have recently attracted increasing interest due to their unique inherent chirality and potential applications in next-generation optoelectronic and spintronic devices. However, COIP ferroelecs. are very sparse. In this work, for the first time, we present the nickel-nitrite ABX_3 COIP ferroelecs., [(R and S)-N-fluoromethyl-3-quinuclidinol]$Ni(NO_2)_3$ ([(R and S)-FMQ]$Ni(NO_2)_3$), where the X-site is the rarely seen NO_2^- bridging ligand. [(R and S)-FMQ]$Ni(NO_2)_3$ display mirror-relationship in the crystal structure and vibrational CD signal. It is emphasized that [(R and S)-FMQ]$Ni(NO_2)_3$ show splendid ferroelectricity with both an extremely high phase-transition point of 405 K and a spontaneous polarization of 12 μC/cm^2. To our knowledge, [(R and S)-FMQ]$Ni(NO_2)_3$ are the first examples of nickel-nitrite based COIP ferroelecs. This finding expands the COIP family and throws light on exploration of high-performance COIP ferroelecs.

8. Computational prediction of chiroptical properties in structure elucidation of natural products

By Grauso, Laura; Teta, Roberta; Esposito, Germana; Menna, Marialuisa; Mangoni, Alfonso
From Natural Product Reports (2020), Ahead of Print. Language: English, Database: CAPLUS, DOI:10.1039/c9np00018f

A review. This review covers the current status of the quantum mech. prediction of chiroptical properties, such as electronic CD and optical rotation, as needed for stereochem. assignments in new natural products. The reliability of the prediction of chiroptical properties is steadily increasing, with a parallel decrease in the required computational resources. Now, quantum mech. calcns. for a medium-sized natural product can be reliably performed by natural product chemists on a mainstream PC. This review is aimed to guide natural product chemists through the numerous steps involved in such calcns. Through a concise, but comprehensive, discussion of the current computational practice, enriched by a few illustrative examples, this review provides readers with the theor. background and practical knowledge needed to select the most appropriate parameters for performing the calcns., to anticipate possible problems, and to critically evaluate the reliability of their computational results. Common reasons for mistakes are also discussed; in particular, the importance of the correct evaluation of conformational ensembles of flexible mols. (an aspect often overlooked in current research) is stressed.

9. Recent Trends in Chiroptical Spectroscopy: Theory and Applications of Vibrational Circular Dichroism and Raman Optical Activity

By Krupova, Monika; Kessler, Jiri; Bour, Petr
From ChemPlusChem (2020), 85(3), 561-575. Language: English, Database: CAPLUS, DOI:10.1002/cplu.202000014

Chiroptical spectroscopy exploring the interaction of matter with polarized light provides many tools for mol. structure and interaction studies. Here, some recent discoveries are reviewed, primarily in the field of vibrational optical activity. Technol. advances results in the development of more sensitive vibrational CD (VCD), Raman optical activity (ROA) or circular polarized luminescence (CPL) spectrometers. Significant contributions to the field also come from the light scattering and electronic structure theories, and their implementation in computer systems. Finally, new chiroptical phenomena have been obsd., such as enhanced CD of biopolymers (protein fibrils, nucleic acids), plasmonic and resonance chirality-transfer ROA expts. Some of them are not yet understood or attributed to instrumental artifacts so far. Nevertheless, these unknown territories also indicate the vast potential of the chiroptical spectroscopy, and their investigation is even more challenging.

10. Resolution, structures, and vibrational circular dichroism of helicoidal trinickel and tricobalt paddlewheel complexes

By Cortijo, Miguel; Valentin-Perez, Angela; Rosa, Patrick; Daugey, Nicolas; Buffeteau, Thierry; Hillard, Elizabeth A.
From Chirality (2020), 32(6), 753-764. Language: English, Database: CAPLUS, DOI:10.1002/chir.23211

It has been recently shown that enantiomers of the helicoidal paddlewheel complex $[Co_3(dpa)_4(CH_3CN)_2]^{2+}$ (dpa = the anion of 2,2'-dipyridylamine) can be resolved using the chiral $[As_2(tartrate)_2]^{2-}$ anion (AsT) and that these complexes demonstrate a strong chiroptical response in the UV-visible and X-ray energy regions. Here we report that the nickel congener, $[Ni_3(dpa)_4(CH_3CN)_2]^{2+}$, can likewise be resolved using AsT. Depending on the stereochem. of the enantiopure AsT anion, one or the other of the trinickel enantiomers crystallize from CH_3CN and di-Et ether in space group $P42_12$ as the $(NBu_4)_2[Ni_3(dpa)_4(CH_3CN)_2](AsT)_2$·[solvent] salt. After resoln., the AsT salts were converted into the PF_6^- salts by anion exchange, with retention of the chirality of the trinickel complex. The enantiopure $[Ni_3(dpa)_4(CH_3CN)_2](PF_6)_2·2CH_3CN$ and $[Co_3(dpa)_4(CH_3CN)_2](PF_6)_2·CH_3CN·C_4H_{10}O$ compds. crystallize in space groups C2 and $P2_1$, resp. Both the Ni(II) and Co(II) complex cations are stable towards racemization in CH_3CN. Vibrational CD (VCD) data obtained in CD_3CN demonstrate the expected mirror image spectra for the enantiomers, the obsd. peaks arising from the dpa ligand. The VCD response is significant, with $\Delta\varepsilon$ values up to 6 $Lmol^{-1}$ cm^{-1} and vibrational dissymmetry factors on the order of 10^{-3}. D. functional theory calcns. well reproduce the exptl. spectra, showing little difference between the peak position, sign, and intensity in the VCD for the cobalt and nickel complexes. These results suggest that VCD enhancement of these peaks is unlikely, and their remarkable intensity may be due to their rigid helicoidal structure.

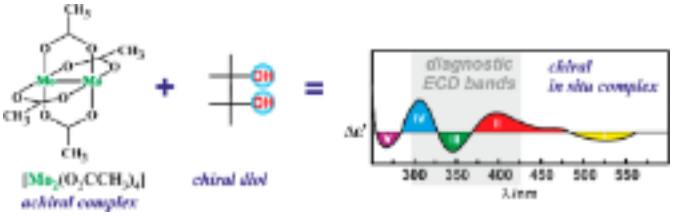
11. Pressure dependence of vibrational optical activity of model biomolecules. A computational study

By Plamitzer, Lubos; Bour, Petr
From Chirality (2020), 32(5), 710-721. Language: English, Database: CAPLUS, DOI:10.1002/chir.23216

Change of mol. properties with pressure is an attracting means to regulate mol. reactivity or biol. activity. However, the effect is usually small and so far explored rather scarcely. To obtain a deeper insight and est. the sensitivity of vibrational optical activity spectra to pressure-induced conformational changes, we investigate small model mols. The Ala-Ala dipeptide, isomaltose disaccharide and adenine-uracil dinucleotide were chosen to represent three different biomol. classes. The pressure effects were modeled by mol. dynamics and d. functional theory simulations. The dinucleotide was found to be the most sensitive to the pressure, whereas for the disaccharide the smallest changes are predicted. Pressure-induced relative intensity changes in vibrational CD and Raman optical activity spectra are predicted to be 2-3-times larger than for non-polarized IR and Raman techniques.

12. A Critical Appraisal of Dimolybdenum Tetraacetate Application in Stereochemical Studies of vic-Diols by Circular Dichroism

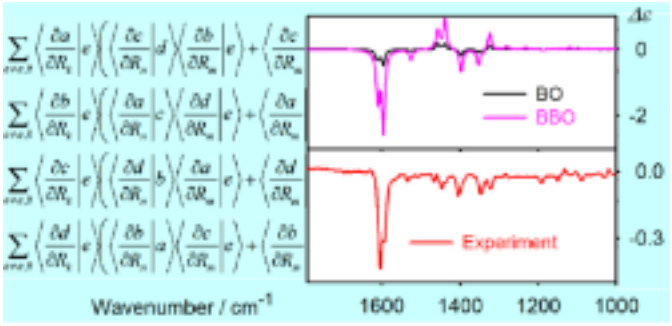
By Gorecki, Marcin; Frelek, Jadwiga
From Journal of Natural Products (2020), 83(4), 955-964. Language: English, Database: CAPLUS, DOI:10.1021/acs.jnatprod.9b00800



This crit. appraisal is intended for users of the dimolybdenum method, well-established in electronic CD (ECD) to det. the abs. configuration of vic-diols and, in particular, for exptl. researchers not being experts in chiroptical methods. The main goal is to demonstrate how to avoid misleading and ambiguous conclusions resulting from the rigorous application of the helicity rule by limiting the anal. to the vic-diol unit alone. We particularly focused on multichromophoric systems, esp. those that may interfere with the absorption of an in situ formed dimolybdenum tetraacetate-diol complex. In this context, examples are presented of vic-diols for which stereochem. assignment based solely on the helicity rule is ambiguous and does not necessarily lead to correct results. The motivation for choosing these examples was to demonstrate the impact of the structure of the substrate on the complexation process with the metal core and its selectivity. For each selected case, results obtained are analyzed in detail together with a discussion of existing restrictions and choice of a support method to increase the credibility of the conclusion. Based on seven both educational and challenging examples, it was shown that the dimolybdenum methodol. can also be effectively applied to complex chromophoric systems, provided that other chiroptical methods and/or computational support verify obtained results.

13. Density Functional Computations of Vibrational Circular Dichroism Spectra beyond the Born-Oppenheimer Approximation

By Tomecek, Josef; Bour, Petr
From Journal of Chemical Theory and Computation (2020), 16(4), 2627-2634. Language: English, Database: CAPLUS, DOI:10.1021/acs.jctc.0c00081



Transition-metal complexes provide rich features in vibrational CD (VCD) spectra, including significant intensity enhancements, and become thus useful in structural and functional studies of mols. Quite often, however, the vibrational spectral bands are mixed with the electronic ones, and interpretation of such expts. is difficult. In the present study, we elaborate on the theory needed to calc. the VCD intensities beyond the Born-Oppenheimer (BO) approxn. Within a perturbation approach, the coupling between the electronic and vibrational states is estd. using the harmonic approxn. and simplified wave functions obtainable from common d. functional theory (DFT) computations. Explicit expressions, including Slater determinants and derivs. of MOs, are given. On a model diamine complex, the implementation is tested and factors affecting spectral intensities and frequencies are investigated. For two larger mols., the results are in a qual. agreement with previous exptl. data. Typically, the electronic-vibrational interaction Hamiltonian coupling elements are rather small (~ 0 to 10 cm^{-1}), which provides negligible contributions to vibrational frequencies and absorption intensities. However, significant changes in VCD spectra are induced due to the large transition magnetic dipole moment assocd. with the d-d metal transitions. The possibility to model the spectra beyond the BO limit opens the way to further applications of chiral spectroscopy and transition-metal complexes.

14. Glucose in dry and moist ionic liquid: vibrational circular dichroism, IR, and possible mechanisms

By Blasius, Jan; Elfgen, Roman; Holloczki, Oldamur; Kirchner, Barbara
From Physical Chemistry Chemical Physics (2020), 22(19), 10726-10737. Language: English, Database: CAPLUS, DOI:10.1039/c9cp06798a

Ionic liqs. and their mixts. with water show remarkable features in cellulose processing. For this reason, understanding the behavior of carbohydrates in ionic liqs. is important. In the present study, we investigated three D-glucose isomers (α, β and open-chain) in 1-ethyl-3-methylimidazolium acetate in the presence and absence of water, through ab initio mol. dynamics simulations. In the complex hydrogen bonding network of these mixts., the most interesting observation is that upon water addn. every hydrogen bond elongates, except the glucose-glucose hydrogen bond for the open-chain and the α-form which shortens, clearly showing the beginning of the crystn. process. The ring glucose rearranges from on-top to in-plane and the open form changes from a coiled to a more linear arrangement when adding water which explains the contradiction that the center of mass distances of the glucose mols. with other glucose mols. grow while the hydrogen bonds shorten. The appearance of coiled open forms indicates that the previously suggested isomerization between these forms is possible and might play a role in the soly. of the related carbohydrates. The calcd. IR and VCD spectra reveal insight into the intermol. interactions, with good to excellent agreements with exptl. spectra. Investigating the role of the cation, distances between the acidic carbon atom of the cation and the glucose carbon atom where ring closure and opening occurs are found, which are way shorter than dispersion-like interactions between aliph. hydrocarbons.

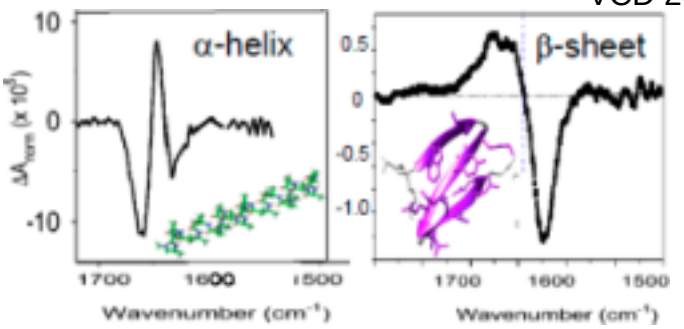
15. Enhancement of the chiroptical response of α-amino acids via N-substitution for molecular structure determination using vibrational circular dichroism

By Polavarapu, Prasad L.; Santoro, Ernesto; Covington, Cody L.; Raghavan, Vijay
From Chirality (2020), 32(5), 564-578. Language: English, Database: CAPLUS, DOI:10.1002/chir.23205

The chiroptical response in the form of vibrational CD (VCD) in the midinfrared region is found to be enhanced when a hydrogen of amino group of L-tryptophan is substituted with acetyl, acryloyl, or maleyl group. The order of preference for VCD enhancement is found to be acryloyl > acetyl > maleyl group. The resulting exptl. VCD spectra are also found to be satisfactorily reproduced by the quantum mech. (QM) predicted spectra. The QM predicted spectra were simulated using the conformer populations, (a) predicted by Gibbs energies and (b) optimized to maximize the similarity between exptl. and predicted VCD spectra. It is found that the conformer populations predicted by Gibbs energies do not yield the max. possible similarity between exptl. and the QM predicted spectra. This work identifies the N-substitution of α-amino acids and detg. the conformer populations that best reproduce the exptl. spectra as two new approaches for mol. structure detn.

16. Structure of Condensed Phase Peptides: Insights from Vibrational Circular Dichroism and Raman Optical Activity Techniques

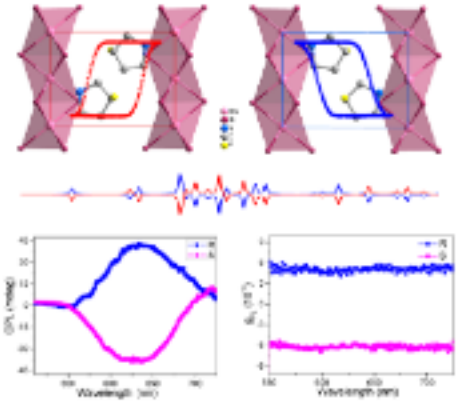
By Keiderling, Timothy A.
From Chemical Reviews (Washington, DC, United States) (2020), 120(7), 3381-3419. Language: English, Database: CAPLUS, DOI:10.1021/acs.chemrev.9b00636



A review. Peptides and proteins are naturally chiral mol. systems so that sensing their structure and conformation with chirality-based spectral methods is an obvious and long-used diagnostic application. Extending chiroptical techniques to measurement of vibrational transitions, as vibrational CD (VCD) and Raman optical activity (ROA), expands the no. and types of excitations available that might provide structural insight and can provide an alternate and, in some cases, a more distinctive conformational probe. Since the dominant repeating structural element in peptides is the locally achiral amide group, VCD senses the polymeric structure through amide coupling, which is directly dependent on secondary structure. Detn. of the type and relative contribution of these structural components through empirical correlation with spectral character has been the main application of VCD for peptides and proteins, although this is now reinforced by extensive theor. modeling. Monitoring structural and conformational change induced by environmental perturbations provides another important application. More recently, VCD has been used to detect morphol. variations in fibril states of aggregated peptides and proteins. ROA has parallel secondary structural sensitivities, with more applications for proteins than peptides, and has more sensitivity to local configuration and side chains. This review covers the range of peptide studies done with VCD and extends them to compare with example protein and ROA applications.

17. Enantiomorphic Perovskite Ferroelectrics with Circularly Polarized Luminescence

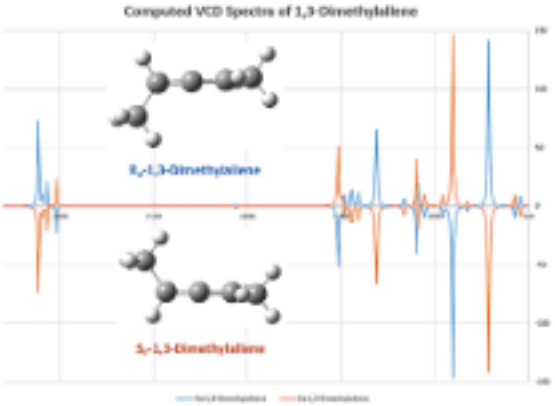
By Gao, Ji-Xing; Zhang, Wan-Ying; Wu, Zheng-Guang; Zheng, You-Xuan; Fu, Da-Wei
From Journal of the American Chemical Society (2020), 142(10), 4756-4761. Language: English, Database: CAPLUS, DOI:10.1021/jacs.9b13291



Materials with circularly polarized luminescence (CPL) activity have immense potential applications in mol. switches, optical sensors, information storage, asym. photosynthesis, 3D optical displays, biol. probe, and spintronic devices. However, the achiral architectures of most of the luminophores severely limit their practical needs. Within this context, mol. ferroelecs. with striking chem. variability and structure-property flexibility bring light to the assembly of CPL-active ferroelec. materials. Herein, we report org.-inorg. perovskite enantiomorphic ferroelecs., (R)- and (S)-3-(fluoropyrrolidinium)$MnBr_3$, undergoing a 222F2-type ferroelec. phase transition at 273 K. Their mirror relationships are verified by both single-crystal X-ray diffraction and vibrational CD (VCD). Furthermore, the corresponding Cotton effect for two chiral crystals was captured by mirror CPL activity. This may be assigned to the inducing interaction between the achiral luminescent perovskite framework and chiral org. components. As far as we know, this is the first mol. ferroelec. with CPL activity. Accordingly, this will inspire intriguing research in mol. ferroelecs. with CPL activity and holds great potential for the development of new optoelectronic devices.

18. Computational Activity to Visualize Stereoisomers in Molecules with an Axis of Chirality

By Pelter, Michael W.; Howell, Mitchell T.; Anderson, Cassandra; Sayeed, Aryana
From Journal of Chemical Education (2020), 97(3), 754-759. Language: English, Database: CAPLUS, DOI:10.1021/acs.jchemed.9b00934



The topic of chirality is often a difficult concept to grasp for the typical undergraduate chem. student. Often, the chirality of mols. is taught by using the concept of an asym. carbon center that generates mols. with nonsuperimposable mirror images. When students encounter a chiral mol. lacking a stereogenic center such as an asym. carbon, the confusion is amplified. In order to study this distinction, this computational study was designed to help students visualize mols. contg. an axis of chirality but no stereogenic center. The mols. chosen for this activity are allenes, binaphthyls, and spiranes. Students first perform a visual inspection by drawing the possible enantiomers side-by-side in a 3D structure drawing program. They then compute vibrational CD (VCD) spectra for the enantiomers. Chiral mols. uniquely interact with circularly polarized light due to the dissymmetry in their MOs. Therefore, detg. if a mol. is chiral may be achieved by computing its VCD spectrum: where chiral mols. produce a peaked spectrum and achiral mols. feature a zero-intensity flat-lined spectrum. For a given enantiomer, the VCD spectrum shows both pos. and neg. peaks. Just as enantiomers are mirror images, VCD spectra are mirror images of each other, meaning a pos. peak from one enantiomer will be a neg. peak from the other enantiomer.

19. Structure of heroin in a solution revealed by chiroptical spectroscopy

By Kralik, Frantisek; Fagan, Patrik; Kuchar, Martin; Setnicka, Vladimir
From Chirality (2020), 32(6), 854-865. Language: English, Database: CAPLUS, DOI:10.1002/chir.23196

In this work, the 3-D structure of the well-known opioid drug heroin in a soln. was investigated. The goal was to provide a complete and detailed description of the stable conformers with their relative abundances. This knowledge is very important from the pharmaceutical and forensic point of view as it could help significantly with deeper understanding of heroin's metab. and the development of antagonist medicines for the case of an overdose. As heroin is a chiral compd. with five stereogenic centers, the methods of chiroptical spectroscopy supplemented by d. functional theory (DFT) calcns. were applied to study its conformations in chloroform soln. The selected chiroptical methods, namely, electronic CD (ECD) and vibrational CD (VCD), are inherently sensitive to the 3-D structure of small- to medium-sized chiral org. mols. A thorough conformational anal. revealed four stable conformers of heroin in chloroform soln., where the conductor-like polarizable continuum model of the solvent was used for all the calcns. The simulated UV, IR (IR), ECD, and VCD spectra were compared with the exptl. ones and very good agreement was found, which enabled a detailed structure description and interpretation of the spectra. Chiroptical spectroscopy in combination with DFT calcns. proved to be a very sensitive tool for the anal. of the 3-D structure of heroin in a soln. in contrast with conventional spectroscopic methods. Esp., the application of VCD seems to be a promising approach for monitoring structural changes, for instance, those caused by solvents or interactions with other agents.

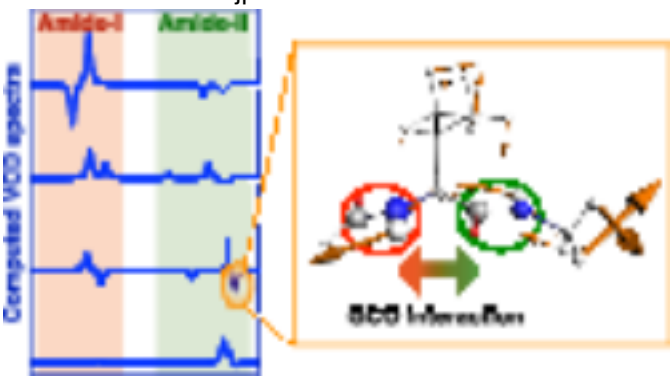
20. Protocol for the analysis of vibrational circular dichroism spectra of small molecules using Gaussian and MOE

By Ajamian, Alain
From Abstracts of Papers, 259th ACS National Meeting & Exposition, Philadelphia, PA, United States, March 22-26, 2020 (2020), COMP-0254. Language: English, Database: CAPLUS

Chirality has important fundamental influences on pharmacol. activity and biorecognition phenomena. Vibrational CD (VCD) spectroscopy is particularly well-suited to the study of stereochem. in biol. relevant chem. systems. Consequently, it has become the method of choice for monitoring and characterizing mol. recognition phenomena in soln. and for studying the stereochem. of chiral drugs and peptides. When combined with computational studies, such exptl. techniques provide invaluable insights for medicinal and biol. chem. researchers. We present a new Spectral Anal. tool that supports computational studies of NMR and VCD spectra for small mols. and peptide systems. The tool provides for quantum chem. calcns. (via third-party quantum chem. software) of both types of spectra and the comparison of results with exptl. data.

21. Analysis of Vibrational Circular Dichroism Spectra of Peptides: A Generalized Coupled Oscillator Approach of a Small Peptide Model Using VCDtools

By Koenis, Mark A. J.; Visscher, Lucas; Buma, Wybren J.; Nicu, Valentin P.
From Journal of Physical Chemistry B (2020), 124(9), 1665-1677. Language: English, Database: CAPLUS, DOI:10.1021/acs.jpcb.9b11261



Vibrational CD (VCD) is one of the major spectroscopic tools to study peptides. Nevertheless, a full understanding of what dets. the signs and intensities of VCD bands of these compds. in the amide I and amide II spectral regions is still far from complete. In the present work, the authors study the origin of these VCD signals using the general coupled oscillator (GCO) anal., a novel approach that has recently been developed. The authors apply this approach to the ForValNHMe model peptide in both α-helix and β-sheet configurations. The authors show that the intense VCD signals obsd. in the amide I and amide II spectral regions essentially have the same underlying mechanism, namely, the through-space coupling of elec. dipoles. The crucial role played by intramol. hydrogen bonds in detg. VCD intensities is also illustrated. Moreover, the authors find that the contributions to the rotational strengths, considered to be insignificant in std. VCD models, may have sizable magnitudes and can thus not always be neglected. In addn., the VCD robustness of the amide I and II modes has been investigated by monitoring the variation of the rotational strength and its contributing terms during linear transit scans and by performing calcns. with different computational parameters. From these studies-and in particular, the decompn. of the rotational strength made possible by the GCO anal.-it becomes clear that one should be cautious when employing measures of robustness as proposed previously.

22. Stereochemistry of the Reaction Intermediates of Prolinol Ether Catalyzed Reactions Characterized by Vibrational Circular Dichroism Spectroscopy

By Golub, Tino P.; Merten, Christian
From Chemistry - A European Journal (2020), 26(11), 2349-2353. Language: English, Database: CAPLUS, DOI:10.1002/chem.201905614

Spectroscopic characterizations of key reaction intermediates are often considered the final confirmation of a reaction mechanism. This proof-of-principle study showcases the application of vibrational CD (VCD) spectroscopy for the characterization of in situ generated reaction intermediates using the key intermediates of enamine catalysis of Jorgensen-Hayashi-type prolinol ether catalysts as model system. By comparison of exptl. and computed spectra, the enamines are shown to preferentially adopt an anti-conformation with E-configured C=C bond. For the parent prolinol catalyst, the structure and stereochem. of the oxazolidine side product is detd. as well. This study thus demonstrates that VCD spectra can provide insights into structural preferences of organocatalysts that utilize a covalent activation mechanism. Thereby it outlines new fields of applications for VCD spectroscopy and finally adds the technique to the toolbox of phys. org. chem. for in-depth mechanistic studies.

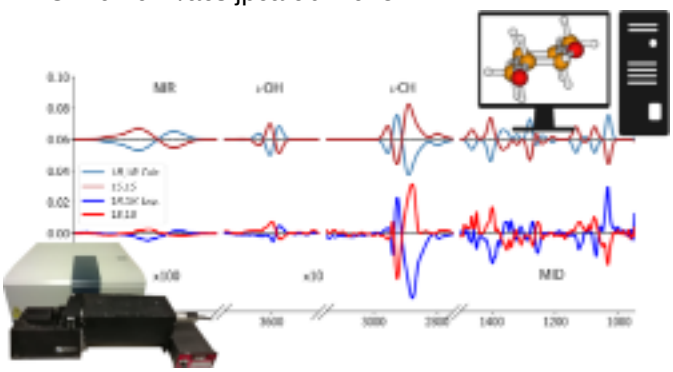
23. Endohedral isomerism in model achiral and chiral La@C58N2 systems

By Ostrowski, Slawomir; Garnuszek, Piotr; Dobrowolski, Jan Cz.
From Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy (2020), 231, 117791. Language: English, Database: CAPLUS, DOI:10.1016/j.saa.2019.117791

Endohedral structures with La^0 or La^{3+} encapsulated in chiral (1,16)$C_{58}N_2$ or achiral (1,4)$C_{58}N_2$ diazafullerenes were studied at the B3LYP/G-31G*/SDD level. Two stable locations of La^0 and La^{3+} are possible in each cage but only with La^0@(1,16)$C_{58}N_2$ can the two isomers coexist. We found that an AIM detd. hapticity of the endohedral species selectively differentiates the systems. We predict that there will always exist IR and Raman bands which allow for them to be identified in the presence of the parent cage. For the La^0@(1,16)$C_{58}N_2$ mols. and the parent diazafullerene, the Raman spectra are likely to reveal a pre-resonance effect even at 785 nm and it seems possible to selectively excite only one isomer. The calcd. electronic spectra suggested a chance to det. the less populated diazafullerene in the presence of the more populated one, be it chiral or achiral. For the chiral endohedral isomers, the calcd. VCD spectra are quite dissimilar and the two endohedral isomers and the parent heterofullerene seem to be easily detected. Eventually, we defined the endohedral isomerism as follows: The endohedral isomerism is the phenomenon whereby an internal individuum captured in a cage can occupy more than one stable position without changing the cage connectivity.

24. Toward Fully Unsupervised Anharmonic Computations Complementing Experiment for Robust and Reliable Assignment and Interpretation of IR and VCD Spectra from Mid-IR to NIR: The Case of 2,3-Butanediol and trans-1,2-Cyclohexanediol

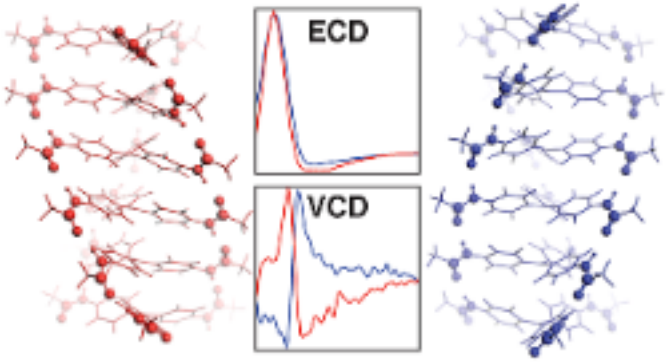
By Paoloni, Lorenzo; Mazzeo, Giuseppe; Longhi, Giovanna; Abbate, Sergio; Fuse, Marco; Bloino, Julien; Barone, Vincenzo
From Journal of Physical Chemistry A (2020), 124(5), 1011-1024. Language: English, Database: CAPLUS, DOI:10.1021/acs.jpca.9b11025



The IR and vibrational CD (VCD) spectra of 2,3-butanediol and trans-1,2-cyclohexanediol from 900 to 7500 cm^{-1} (including mid-IR, fundamental CH and OH stretchings, and near-IR regions) have been investigated by a combined exptl. and computational strategy. The computational approach is rooted in d. functional theory (DFT) computations of harmonic and leading anharmonic mech., elec., and magnetic contributions, followed by a generalized second-order perturbative (GVPT2) evaluation of frequencies and intensities for all the above regions without introducing any ad hoc scaling factor. After proper characterization of large-amplitude motions, all resonances plaguing frequencies and intensities are taken into proper account. Comparison of exptl. and simulated spectra allows unbiased assignment and interpretation of the most interesting features. The reliability of the GVPT2 approach for OH stretching fundamentals and overtones is confirmed by the remarkable agreement with a local mode model purposely tailored for the latter two regions. Together with the specific interest of the studied mols., our results confirm that an unbiased assignment and interpretation of vibrational spectra for flexible medium-size mols. can be achieved by means of a nearly unsupervised reliable, robust, and user-friendly DFT/GVPT2 model.

25. Self-Assembly of Supramolecular Polymers of N-Centered Triarylamine Trisamides in the Light of Circular Dichroism: Reaching Consensus between Electrons and Nuclei

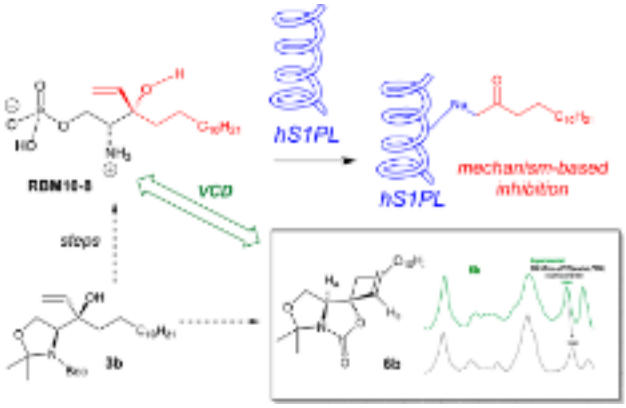
By Koenis, Mark A. J.; Osypenko, Artem; Fuks, Gad; Giuseppone, Nicolas; Nicu, Valentin P.; Visscher, Lucas; Buma, Wybren J.
From Journal of the American Chemical Society (2020), 142(2), 1020-1028. Language: English, Database: CAPLUS, DOI:10.1021/jacs.9b11306



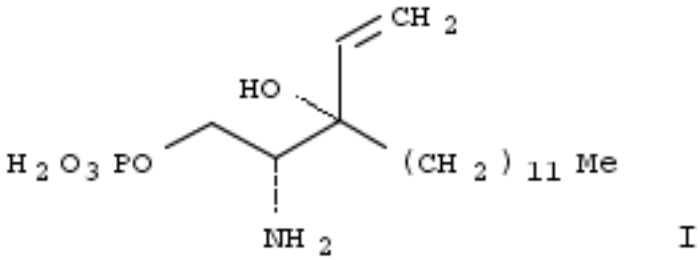
The self-assembly of chiral supramol. polymers is an intricate process that spans a wide range of length scales. CD techniques are ideal to study this process as they provide information on the mol. scale but are at the same time also sensitive probes of the long-range interactions that control the growth and morphol. of these polymers. As yet, Electronic CD that uses electronic transitions as a probe has by far been the method of choice while Vibrational CD, which uses vibrational transitions to probe structure, is much less employed. Here, we report exptl. and theor. studies of the self-assembly of helical supramol. polymers of (S)-triarylamine tris-amides ((S)-TATA) in which both techniques are applied in concert. Theor. studies based on quantum chem. calcns. and on simplified models that allow for extrapolation to "infinitely" long polymers provide a solid basis for interpreting results from each of the two techniques that on their own would appear to be contradictory. In the particular case of (S)-TATA it is shown that upon equilibration the initially formed fibers undergo a conformational transition that becomes only "visible" by the combination of the two techniques. Our studies thus show that combining electronic and vibrational domains offers a unique and complementary means to probe these polymers, precisely because they are sensitive to different aspects of mol. and polymeric structure.

26. A Mechanism-Based Sphingosine-1-phosphate Lyase Inhibitor

By Pons, Guillem; Riba, Daniel; Casasampere, Mireia; Izquierdo, Eduardo; Abad, Jose-Luis; Fabrias, Gemma; Rodriguez Ortega, Pilar G.; Lopez-Gonzalez, Juan J.; Montejo, Manuel; Casas, Josefina; et al
From Journal of Organic Chemistry (2020), 85(2), 419-429. Language: English, Database: CAPLUS, DOI:10.1021/acs.joc.9b02420



The synthesis of a series of vinylated analogs of sphingosine-1-phosphate together with their unambiguous configurational assignment by VCD methods is reported. Among them, compd. RBM10-8 (I) can irreversibly inhibit human sphingosine-1-phosphate lyase (hS1PL) while behaving also as an enzyme substrate. These findings, together with the postulated mechanism for S1PL activity, reinforce the role of RBM10-8 as a new mechanism-based hS1PL inhibitor.



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27. Error bounds on goodness of fit indicators in vibrational circular dichroism spectroscopy

By Monaco, Guglielmo; Procida, Giovanni; Di Mola, Antonia; Herrebout, Wouter; Massa, Antonio
From Chemical Physics Letters (2020), 739, 137000. Language: English, Database: CAPLUS, DOI:10.1016/j.cplett.2019.137000

The bootstrap method has been applied to est. error bounds on five goodness-of-fit indicators in vibrational spectroscopy. The use of these indicators has been first tested on the known vibrational CD spectrum of 3-chloro-1-butyne, and then it has been adopted for the assignment of the abs. configuration of 3-methyl-3-nitromethyl-isoindolinone. The (+) stereoisomer turns out to have the (S) configuration.

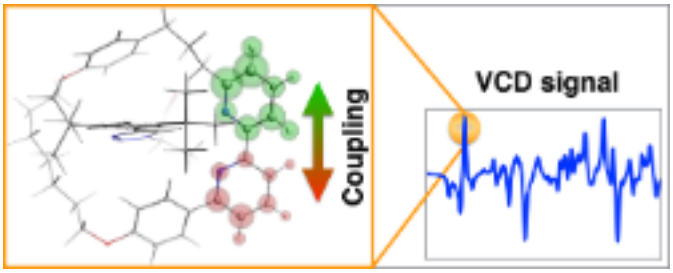
28. How many solvent molecules are required to solvate chiral 1,2-diols with hydrogen bonding solvents? A VCD spectroscopic study

By Weirich, Luisa; Magalhaes de Oliveira, Juliana; Merten, Christian
From Physical Chemistry Chemical Physics (2020), 22(3), 1525-1533. Language: English, Database: CAPLUS, DOI:10.1039/c9cp06030h

Strong solute-solvent interactions have been shown to have a significant influence on the vibrational CD (VCD) spectral signatures of chiral solutes. In order to use VCD spectroscopy to det. abs. configurations, these intermol. interactions thus need to be accounted for in spectra simulations. For hydrogen bond donating functional groups such as carboxylic acids or hydroxy groups, it has been shown that microsolvation with a single solvent mol. is usually sufficient to model the effect of the solvent on the vibrational spectra. In the case of diols, however, solvent mols. are competing against the intramol. hydrogen bond. Therefore, this study investigates the influence of solute-solvent interactions on the conformational preferences and VCD spectroscopic features of chiral 1,2-diols with the aim to answer the title question. We show that both mono- and twofold solvation lead to unique spectral features that can be distinguished exptl. Furthermore, in the context of abs. configuration detns., the results of the study suggest that it will not be possible to derive a general rule that is able to tell whether one or two solvent mols. need to be considered explicitly in the simulation of VCD spectra.

29. GUI Implementation of VCDtools, A Program to Analyze Computed Vibrational Circular Dichroism Spectra

By Koenis, Mark A. J.; Visser, Olivier; Visscher, Lucas; Buma, Wybren J.; Nicu, Valentin P.
From Journal of Chemical Information and Modeling (2020), 60(1), 259-267. Language: English, Database: CAPLUS, DOI:10.1021/acs.jcim.9b00956



As computing power increases, vibrational CD (VCD) calcns. on mols. of larger sizes and complexities become possible. At the same time, the spectra resulting from these computations become increasingly more cumbersome to analyze. Here, we describe the GUI implementation into the Amsterdam D. Functional (ADF) software package of VCDtools, a toolbox that provides a user-friendly means to analyze VCD spectra. Key features are the use of the generalized coupled oscillator anal. methods, as well as an easy visualization of the at. elec. and magnetic transition dipole moments which together provide detailed insight in the origin of the VCD intensity. Using several prototypical examples we demonstrate the functionalities of the program. In particular, we show how the spectra can be analyzed to detect differences between theory and expt. arising from large-amplitude motions or incorrect mol. structures and, most importantly, how the program can be used to prevent incorrect enantiomeric assignments.

30. Experimental and theoretical investigation on optoelectronic properties of organic NLO crystal; S-(4,6-dimethyl-2-pyrimidinyl) O-(p-methoxybenzyl) thiocarbonate

By Vidhya, D.; Ramalingam, S.; Periandy, S.; Aarthi, R.
From Journal of Molecular Structure (2020), 1204, 127527. Language: English, Database: CAPLUS, DOI:10.1016/j.molstruc.2019.127527

Semiorg. S-(4,6-dimethyl-2-pyrimidinyl) O-(p-methoxybenzyl) thiocarbonate single crystal was grown by slow evapn. method with high-quality non linear optical response. The crystal was characterized optically, spectroscopically and theor. The XRD parameters were evaluated and related crystal lattice (orthorhombic) and space group ($P2_12_12_1$) of mol. was validated. The least attractive dispersion forces of efficient Birefringence of crystal emphasized the 2nd and 3rd order optical harmonic frequency conversion. The optimized mol. setup in crystal array was viewed from the parametric calcns. performed by B3LYP method. The charge orientation assignment in the mol. site driven by chem. potential was measured and the cause of polar scattering process was validated. The SHG and parametric oscillation coeffs. were measured from which NLO activity performance (efficiency = $I^{2\omega}$ = 15 X $I^{2\omega}$) was evaluated. The biaxial crystal characteristics were interpreted by dipole-dipole interactive dispersion process induced by mol. electrostatic potential field. The arrangement of electron path was identified and kinetics in the path by driving potential mechanism in the pyridine ring was studied. The modification of charge atm. in and around the mols. is monitored and the mol. kinematics was studied. The dipole moment and polarization activity of polar and non polar bonds in the material were confirmed by performing vibrational studies in various regions of IR and Raman spectra. The chem. energy restoring mechanism in various chemi-potential zones were detd. and chem. reaction path in core and allied C of the mol. Crystallog. data are given.

31. Spectral characterization, thermochemical studies, periodic SAPT calculations and detailed quantum mechanical profiling various physico-chemical properties of 3,4-dichlorodiuron

By Haruna, K.; Kumar, Veena S.; Armakovic, Sanja J.; Armakovic, Stevan; Mary, Y. Sheena; Thomas, Renjith; Popoola, Saheed A.; Almohammedi, A. R.; Roxy, M. S.; Al-Saadi, A. A.
From Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy (2020), 228, 117580. Language: English, Database: CAPLUS, DOI:10.1016/j.saa.2019.117580

A set of exptl. and computational techniques have been applied for the understanding of fundamental spectroscopic and reactive properties of 3-(3,4-dichlorophenyl)-1,1-dimethylurea (diuron) compd. Exptl. techniques employed in this study encompassed spectroscopic characterization via IR and Raman approaches, while optical properties were studied by measurements of UV/Vis spectra. The thermogravimetric anal. was also studied in order to analyze the stability of diuron. Aside from the detn. of reactive properties, DFT calcns. on isolated mols. were also used to thoroughly visualize and analyze spectroscopic properties such as IR and UV/Vis. MD simulations were used in order to understand interactions with water, while periodic DFT calcns. were used in order to analyze band structure and d. of states of the diuron crystal structure. Since the crystal structure of diuron is known, it was used in order to ext. the relevant mol. pairs and investigate interactions between them by DFT and symmetry adapted perturbation theory approaches (SAPT).

32. Hybrid and bioactive cocrystals of pyrazinamide with hydroxybenzoic acids: Detailed study of structure, spectroscopic characteristics, other potential applications and noncovalent interactions using SAPT

By Al-Otaibi, Jamelah S.; Mary, Y. Sheena; Armakovic, Stevan; Thomas, Renjith
From Journal of Molecular Structure (2020), 1202, 127316. Language: English, Database: CAPLUS, DOI:10.1016/j.molstruc.2019.127316

Three cocrystals of pyrazinamide (PYZ) with 2,4-dihydroxy benzoic acid (2,4HBA-PYZ), 2,6-dihydroxybenzoic acid (2,6HBA-PYZ) and 3,5-dihydroxybenzoic acid (3,5HBA-PYZ) are investigated by computational simulations. DFT calcns. have been performed in order to understand the reactive properties of mols. that constitute the cocrystals. These calcns. were followed by symmetry-adapted perturbation theory (SAPT) simulations to understand the interactions between mols. of the studied cocrystals. Mol. Dynamics (MD) simulations helped us to identify possible excipient substances. The ring vibrational modes have small variations during the cocrystal formation, while changes were obsd. in the peaks of the assocd. functional groups. Most reactive sites are identified by MEP maps. From the DFT anal., we found that N-H···N intra mol. hydrogen between the N atom of pyrazine and H-N of amide produces conformational rigidity in the pyrazine ring in the co-crystal assembly of 2,4HBA-PYZ and 2,6HBA-PYZ but not for 3,5HBA-PYZ. The polarization nature of the functional groups was predicted by VCD spectra. Mol. docking results imply that the cocrystals might exhibit inhibitory activity against mycobacterium tuberculosis type II and against methylenetetrahydrofolate reductase and can be formulated as new anti-TB drug. The system showed fairly good light harvesting efficiency (LHE); hence, could be used in photovoltaic systems for energy conversion. Among the three cocrystal systems 2,4HBA-PYZ is a better candidate to be used in DSSC's.

33. Is the VCD spectrum a fingerprint of the conformational population? The conformation of perezone in the spotlight

By Rojo-Portillo, Tania; Reyes-Lopez, Elizabeth; Hernandez-Huerta, Eduardo; Quiroz-Garcia, Beatriz; Joseph-Nathan, Pedro; Sanchez-Castellanos, Mariano; Cuetara-Guadarrama, Fabian; Cuevas, Gabriel
From Journal of Molecular Structure (2020), 1202, 127273. Language: English, Database: CAPLUS, DOI:10.1016/j.molstruc.2019.127273

The M06-2X, B3LYP, ωB97XD and B97D functionals with the 6-311++G(2d,2p) and DGDZVP basis sets were used to describe the stationary points of min. energy of the potential energy surface of perezone. The inability of theor. methods to predict a consistent conformational order, including the effects of zero point energy and dielec. const. was highlighted. Perezone was used as a model of study since it is known that weak interactions are involved in its conformation and represent a challenge of study for theor. methods. Each level of theory here employed generated a significantly different conformational population, ranging from 75% participation of folded conformers (where a π/π stabilizing interaction was predicted) to less than 5%, without producing a uniform conformational order. Surprisingly, in every case, the constructed Vibrational CD (VCD) spectrum with each level of theory was able to reproduce the exptl. spectrum with high level of confidence. The correct R configuration of the stereogenic center of perezone was predicted in all cases.

34. Synthesis and chiroptical properties of cylindrical macrocycles comprising two calix[3]aramide moieties

By Saito, Yuuki; Satake, Misa; Mori, Ryuichi; Okayasu, Misaki; Masu, Hyuma; Tominaga, Masahide; Katagiri, Kosuke; Yamaguchi, Kentaro; Kikkawa, Shoko; Hikawa, Hidemasa; et al
From Organic & Biomolecular Chemistry (2020), 18(2), 230-236. Language: English, Database: CAPLUS, DOI:10.1039/c9ob02022e

Calix[3]aramide-based cylindrical macrocycles were synthesized by the one-step amide coupling reaction of a monomer contg. two meta-alkylaminobenzoic acid units linked by para-phenylene bridges. The major products included a meso-form and an enantiomeric pair, with stereochem. derived from the direction of the amide bonds and their fixed conformation. Mirror-image ECD, VCD, and CPL spectra were obsd. in the enantiomeric pair and the abs. structure was detd. by comparing measured and calcd. ECD and VCD spectra.

35. Isolation, Total Synthesis, and Absolute Configuration Determination of Renoprotective Dimeric N-Acetyldopamine-Adenine Hybrids from the Insect Aspongopus chinensis

By Ding Wei-Yi; Qin Hong-Bo; Yan Yong-Ming; Meng Xiao-Hui; Xu Te; Cheng Yong-Xian; Nafie Laurence A; Dukor Rina K
From Organic letters (2020), , Language: English, Database: MEDLINE

Aspongdopamines A and B (1 and 2), unusual adducts composed of N-acetyldopamine and adenine were isolated from the insect Aspongopus chinensis. Compounds 1 and 2 are positional isomers both isolated as racemates. Chiral separation assisted by 14-step total synthesis and computation including vibrational circular dichroism calculations allowed us to unambiguously assign the absolute configurations of eight stereoisomers. Renal fibrosis inhibition of the stereoisomers was evaluated in TGF-β1-induced rat kidney epithelial cells.

36. Chirality induction on non-chiral dye-linked polysilsesquioxane in nanohelical structures

By Ryu Naoya; Kawaguchi Tsutomu; Shirosaki Tomohiro; Nagaoka Shoji; Yanagita Hiroshi; Takafuji Makoto; Ihara Hirotaka; Okazaki Yutaka; Buffeteau Thierry; Yoshida Kyohei; et al
From Chemical communications (Cambridge, England) (2020), , Language: English, Database: MEDLINE

We demonstrate the direct induction of chirally arranged organic dye-linked polysilsesquioxane through a sol-gel transcription using a chiral supramolecular template. The chiral arrangement was confirmed by using electronic and vibrational circular dichroism and circularly polarized luminescence spectroscopies.

37. Eudesmacarbonate, a Eudesmane-Type Sesquiterpene from a Marine Filamentous Cyanobacterial Mat (Oscillatoriales) in the Florida Keys

By Lydon Christina A; Berry John P; Mathivathanan Logesh; Sanchez Juanita; Dos Santos Larissa A H; Sauvage Thomas; Gunasekera Sarath P; Paul Valerie J
From Journal of natural products (2020), , Language: English, Database: MEDLINE

A new, cyclic carbonate eudesmane-type sesquiterpene, eudesmacarbonate (1), was isolated from marine filamentous cyanobacterial mats associated with apparent ingestion-related intoxications of captive bottlenose dolphins in the Florida Keys. Sequencing of 16S rDNA revealed that mats were composed of closely related Oscillatoriacean species including a previously undocumented species of Neolyngbya. The structure of 1 was elucidated by (+)-HRESIMS, 1D and 2D NMR, single-crystal X-ray diffraction, and vibrational circular dichroism data. Toxicity of 1 was assessed in the zebrafish embryo/larval model, and 1 was found to exhibit effects qualitatively similar to those observed for the known neurotoxin brevetoxin-2 and consistent with neurobehavioral impairment.

38. Synthesis of chiral MOF-74 frameworks by post-synthetic modification using an amino acid

By Tanase-Grecea Stefania; Gheorghe Andreea; Dubbeldam David; Benjamin Strudwick Benjamin; Woutersen Sander; Ashbrook Sharon; Dawson Daniel
From Chemistry (Weinheim an der Bergstrasse, Germany) (2020), , Language: English, Database: MEDLINE

The synthesis of chiral metal-organic frameworks (MOFs) is highly relevant for asymmetric heterogenous catalysis, yet very challenging. Chiral MOFs with MOF-74 topology were synthesized using post-synthetic modification with proline. Vibrational circular dichroism studies demonstrate that proline is the source of chirality. The solvents used in the synthesis play a key role in tuning the loading of proline and its interaction with the MOF-74 framework. In N,N'-dimethylformamide, proline coordinates monodentate to the Zn 2+ ions within the MOF-74 framework, whilst it is only weakly bound to the framework when using methanol as solvent. Introducing chirality within the MOF-74 framework also leads to the formation of defects, with both the organic linker and metal ions missing from the framework. The formation of defects combined with the coordination of DMF and proline within the framework leads to a pore blocking effect. This is confirmed by adsorption studies and testing of the chiral MOFs in the asymmetric aldol reaction between acetone and para -nitrobenzaldehyde.

39. Determining the Regiochemistry and Relative Stereochemistry of Small and Druglike Molecules Using an Alignment Algorithm for Infrared Spectra

By Boselt Lennard; Riniker Sereina; Dotzer Reinhard; Steiner Sandra; Stritzinger Michaela; Salzmann Susanne
From Analytical chemistry (2020), , Language: English, Database: MEDLINE

The relative stereochemistry and isomeric substitution pattern of organic molecules is typically determined using nuclear magnetic resonance spectroscopy (NMR). However, NMR spectra are sometimes nonconclusive, e.g., if spectra are extremely crowded, coupling patterns are not resolved, or if symmetry reasons preclude interpretation. Infrared spectroscopy (IR) can provide additional information in such cases, because IR represents a molecule comprehensively by depiction of the complete set of its normal vibrations. The challenge is thereby that diastereomers and substitution isomers often give rise to highly similar IR spectra, and visual distinction is insufficient and may be biased. Here we show the adaptation of an alignment algorithm, originally developed for vibrational circular dichroism (VCD) spectroscopy, to automatically match IR spectra and provide a quantitative measure of the goodness of fit, which can be used to distinguish isomers. The performance of the approach is demonstrated for different use cases: diastereomers of flexible druglike molecules, E/Z-isomers, and substitution isomers of pyrazine and naphthalene. It can be applied to IR spectra measured both in the gas phase (gas chromatography IR) and in solution.

40. Efficient incorporation and protection of lansoprazole in cyclodextrin metal-organic frameworks

By Li Xue; Zehnacker-Rentien Anne; Porcino Marianna; Martineau-Corcos Charlotte; Guo Tao; Xiong Ting; Zhu Weifeng; Patriarche Gilles; Pechoux Christine; Perronne Barbara; et al
From International journal of pharmaceutics (2020), 585119442, Language: English, Database: MEDLINE

Lansoprazole (LPZ) is an acid pump inhibitor, which readily degrades upon acidic or basic conditions and under heating. We investigated here LPZ stability upon incorporation in particles made of cyclodextrin metal-organic frameworks (CD-MOFs). LPZ loaded CD-MOFs were successfully synthesized, reaching high LPZ payloads of 23.2 ± 2.1 wt%, which correspond to a molar ratio of 1:1 between LPZ and γ-CD. The homogeneity of LPZ loaded CD-MOFs in terms of component distribution was confirmed by elemental mapping by STEM-EDX. Both CTAB, the surfactant used in the CD-MOFs synthesis, and LPZ compete for their inclusion in the CD cavities. CTAB allowed obtaining regular cubic particles of around 5 μm with 15 wt% residual CTAB amounts. When LPZ was incorporated, the residual CTAB amount was less than 0.1 wt%, suggesting a higher affinity of LPZ for the CDs than CTAB. These findings were confirmed by molecular simulations. Vibrational circular dichroism studies confirmed the LPZ incorporation inside the CDs. Solid-state NMR showed that LPZ was located in the CDs and that it remained intact even after three years storage. Remarkably, the CD-MOFs matrix protected the drug upon thermal decomposition. This study highlights the interest of CD-MOFs for the incorporation and protection of LPZ.

41. Chiral Phase Transfer Catalysis in the Asymmetric Synthesis of a 3,3-Disubstituted Isoindolinone and Determination of Its Absolute Configuration by VCD Spectroscopy

By Monaco Guglielmo; Mola Antonia Di; Massa Antonio; Tiffner Maximilian; Waser Mario; Herrebout Wouter
From Molecules (Basel, Switzerland) (2020), 25(10), , Language: English, Database: MEDLINE

In this work we report our endeavors toward the development of an asymmetric synthesis of a 3,3-disubstituted isoindolinone, dimethyl 2-(1-methyl-3-oxoisoindolin-1-yl)malonate, via asymmetric cascade reaction of 2-acetylbenzonitrile with dimethylmalonate and the determination of its absolute configuration (AC) by vibrational circular dichroism (VCD). Bifunctional ammonium salts, derived from trans-1,2-cyclohexanediamine in combination with inorganic bases under phase transfer conditions, were the most effective catalytic systems, leading to the target in high yields and moderate enantioselectivity. An efficient process of heterochiral crystallization allowed the increase of the enantiopurity up to 96% ee and in an acceptable overall yield. An important aim of the present work is the comparison of different VCD methodologies for AC determination of the target compound.

42. Solvent Effects and Aggregation Phenomena Studied by Vibrational Optical Activity and Molecular Dynamics: The Case of Pantolactone

By Ghidinelli Simone; Abbate Sergio; Longhi Giovanna; Abbate Sergio; Longhi Giovanna; Koshoubu Jun; Araki Yasuyuki; Wada Takehiko
From The journal of physical chemistry. B (2020), 124(22), 4512-4526, Language: English, Database: MEDLINE

Raman and Raman optical activity (ROA), IR, and vibrational circular dichroism (VCD) spectra of (R)- and (S)-pantolactone have been recorded in three solvents. ROA has been employed on water and DMSO solutions, VCD on DMSO and CCl4 solutions. In the last solvent, monomer-dimer equilibrium is present. Due to the low conformational flexibility of the isolated molecule and to the possibility of aggregation, this compound has been used here to test different protocols for computation of the spectroscopic responses taking into account solvent effects. Molecular dynamics (MD) simulations have been carried out together with statistical clustering methods based on collective variables to extract the structures needed to calculate the spectra. Quantum mechanical DFT calculations based on PCM are compared with approaches based on different representations of the solvent shell (MM or QM level). Appropriate treatment of the solvent permits obtaining of good band-shapes, with the added advantage that the MD analysis allows one to take into account flexibility of dimeric structures justifying the broadness of observed bands and the absence of intense VCD couplets in the carbonyl and OH stretching regions.

43. Absolute Configuration of trans-Perhydroazulene

By Saito Fumito; Gerbig Dennis; Schreiner Peter R; Becker Jonathan
From Organic letters (2020), 22(10), 3895-3899, Language: English, Database: MEDLINE

We present the absolute configuration (AC) determination of an alkane, trans-perhydroazulene (1), that displays the naturally very common trans fused [5,7] ring system. We outline the first synthesis yielding enantiopure 1 and the application of optical rotatory dispersion (ORD) and vibrational circular dichroism (VCD) techniques. The spectroscopic results are in excellent agreement with the computed ORD at B3LYP/6-311++G(2d,2p) and the computed VCD spectrum at B3LYP/6-311++G(d,p), providing an assignment of the AC as (R,R)-(+)-1.

44. A Proposed Method to Obtain Surface Specificity with Pump-Probe and 2D Spectroscopies

By Petti Megan K; Ostrander Joshua S; Birdsall Erin R; Kunz Miriam Bohlmann; Armstrong Zachary T; Alperstein Ariel M; Zanni Martin T
From The journal of physical chemistry. A (2020), 124(17), 3471-3483, Language: English, Database: MEDLINE

Surfaces and interfaces are ubiquitous in nature. From cell membranes, to photovoltaic thin films, surfaces have important function in both biological and materials systems. Spectroscopic techniques have been developed to probe systems like these, such as sum frequency generation (SFG) spectroscopies. The advantage of SFG spectroscopy, a second-order spectroscopy, is that it can distinguish between signals produced from molecules in the bulk versus on the surface. We propose a polarization scheme for third-order spectroscopy experiments, such as pump-probe and 2D spectroscopy, to select for surface signals and not bulk signals. This proposed polarization condition uses one pulse perpendicular compared to the other three to isolate cross-peaks arising from molecules with polar and uniaxial (i.e., biaxial) order at a surface, while removing the signal from bulk isotropic molecules. In this work, we focus on two of these cases: XXXY and YYYX, which differ by the sign of the cross-peak they create. We compare this technique to SFG spectroscopy and vibrational circular dichroism to provide insight to the behavior of the cross-peak signal. We propose that these singularly cross-polarized schemes provide odd-ordered spectroscopies the surface-specificity typically associated with even-ordered techniques.

45. Synthetic-biology-based discovery of a fungal macrolide from Macrophomina phaseolina

By Morishita Yohei; Sonohara Terutaka; Taniguchi Tohru; Adachi Kiyohiro; Fujita Makoto; Asai Teigo
From Organic & biomolecular chemistry (2020), 18(15), 2813-2816, Language: English, Database: MEDLINE

A synthetic biology approach based on genome mining and heterologous biosynthesis is a powerful tool for discovering novel natural products from a tremendous gene resource. We carried out fungal genome mining guided by a polyketide synthase gene using a public database and found a putative macrolide biosynthetic gene cluster with a highly reducing polyketide synthase gene and a thioesterase gene in Macrophomina phaseolina. Reconstitution of the cluster in Aspergillus oryzae, a model heterologous host for fungal natural product biosynthesis, produced a new 12-membered macrolide, phaseolide A. The absolute stereochemistry was elucidated by vibrational circular dichroism spectroscopy and the crystalline sponge method.

46. Renoprotective Mono- and Triterpenoids from the Fruit of Gardenia jasminoides

By Cao Yan-Gang; Zhang Yan-Li; Zeng Meng-Nan; Qi Man; Ren Ying-Jie; Liu Yan-Ling; Zhao Xuan; Zheng Xiao-Ke; Feng Wei-Sheng; Cao Yan-Gang; et al
From Journal of natural products (2020), 83(4), 1118-1130, Language: English, Database: MEDLINE

This paper describes the isolation and characterization of 17 new and 12 known terpenoids from the fruit of Gardenia jasminoides. The structures of eight new triterpenoids and nine new monoterpenoids, including their absolute configurations, were defined by spectroscopic analysis in combination of quantum chemical electronic circular dichroism (ECD), vibrational circular dichroism (VCD), and gauge-independent atomic orbital (GIAO) NMR calculations. The cytoprotective effects of the isolated compounds against lipopolysaccharide (LPS)-induced apoptosis in normal rat kidney tubule epithelioid (NRK 52e) cells were investigated in vitro. Compounds 10, 18, 20, 21, 24, and 26 exhibited significant protective effects with EC50 values from 14.2 nM to 1.6 μM.

47. Vibrational optical activity: From discovery and development to future challenges

By Nafie Laurence A
From Chirality (2020), 32(5), 667-692, Language: English, Database: MEDLINE

Vibrational optical activity (VOA) consisting of infrared vibrational circular dichroism (VCD) and vibrational Raman optical activity (ROA) was predicted, discovered, and confirmed between 1971 and 1975. My path to VOA was mentored by three pioneers of chirality and vibrational spectroscopy: Professors Albert Moscowitz, Warner L. Peticolas, and Philip J. Stephens, and while they are no longer alive today, the Chirality Medal, my award address, and this paper are dedicated to each of them. Since the discovery of VOA, a number of key advances have made possible the current era of widespread applications. The principal instrumental advances were Fourier-transform VCD (FT-VCD) and multichannel charge coupled detector (CCD) ROA. Computational advances include the first complete quantum chemistry formulation of VCD leading to the magnetic field perturbation (MFP) and the nuclear velocity perturbation (NVP) theories. The strength of VOA is the comparison between measured and calculated spectra that enables the determination of absolute configuration and solution-state conformations. More recently, VCD has uncovered supramolecular chirality in amyloid fibrils and ROA to high-order protein structure. Future challenges for VOA include describing the effects of weak intermolecular interactions, transfer of chirality, solvent effects, supramolecular chirality, and the generation of nuclear velocity electron current density.

48. Optically tunable terahertz chiral metasurface based on multi-layered graphene

By Masyukov Maxim; Vozianova Anna; Grebenchukov Alexander; Gubaidullina Kseniya; Zaitsev Anton; Khodzitsky Mikhail; Vozianova Anna; Grebenchukov Alexander; Khodzitsky Mikhail
From Scientific reports (2020), 10(1), 3157, Language: English, Database: MEDLINE

Active manipulation of the polarization states at terahertz frequencies is crucially helpful for polarization-sensitive spectroscopy, having significant applications such as non-contact Hall measurements, vibrational circular dichroism measurements and anisotropy imaging. The weakness of polarization manipulation provided by natural materials can be overcomed by chiral metamaterials. Chiral metamaterials have a huge potential to achieve the necessary polarization effects, hence they provide the basis for applications such as ultracompact polarization components. Terahertz chiral metamaterials that allow dynamic polarization modulation of terahertz waves are of great practical interest and still challenging. Here, we show that terahertz metasurface based on the four conjugated "petal" resonators integrated with multi-layered graphene (MLG) can enable dynamically tunable chiroptical response using optical pumping. In particular, a change of ellipticity angle of 20° is observed around 0.76 THz under optical pumping by a 980 nm continuous wave (CW) laser. Furthermore, using temporal coupled-mode theory, our study also reveals that the chiroptical response of the proposed multi-layered graphene-based metasurface is strongly dependent on the influence of optical pumping on the loss parameters of resonance modes, leading to actively controllable polarization states of the transmitted terahertz waves. The present work paves the way for the realization of fundamental terahertz components capable for active polarization manipulation.

49. Solid-state synthesis of cyclo LD-diphenylalanine: A chiral phase built from achiral subunits

By Perez-Mellor Ariel; Le Barbu-Debus Katia; Zehnacker Anne
From Chirality (2020), 32(5), 693-703, Language: English, Database: MEDLINE

The solid-state structure of LL/DD or LD/DL diphenylalanine diluted in KBr pellets is studied by infrared (IR) absorption and vibrational circular dichroism (VCD) spectroscopy. The structure depends on the absolute configuration of the residues. The natural LL diphenylalanine exists as a mixture of neutral and zwitterionic structures, depending on the humidity of the sample, while mostly the zwitterion is observed for LD diphenylalanine whatever the experimental conditions. The system undergoes spontaneous cyclization upon heating at 125°C, resulting to the formation of a diketopiperazine (DKP) dipeptide as the only product. The reaction is faster for LD than for LL diphenylalanine. As expected, LL and DD diphenylalanine react to form the LL and DD enantiomers of cyclo diphenylalanine. Interestingly, the DKP dipeptides formed from the LD or DL diphenylalanine show unexpected optical activity, with opposite VCD spectra for the products formed from the LD and DL reagents. This is explained in terms of chirality synchronization between the monomers within the crystal, which retain the symmetry of the reagent, resulting to the formation of a new chiral phase made from transiently chiral molecules.

50. Water-Soluble Glutamic Acid Derivatives Produced in Culture by Penicillium solitum IS1-A from King George Island, Maritime Antarctica

By Rodriguez Julie P G; Bernardi Darlon I; Gubiani Juliana R; Morais-Urano Raquel P; Bertonha Ariane F; Bandeira Karin F; Bulla Jairo I Q; Berlinck Roberto G S; Magalhaes de Oliveira Juliana; Ferreira Antonio G; et al
From Journal of natural products (2020), 83(1), 55-65, Language: English, Database: MEDLINE

A new method of screening was developed to generate 770 organic and water-soluble fractions from extracts of nine species of marine sponges, from the growth media of 18 species of marine-derived fungi, and from the growth media of 13 species of endophytic fungi. The screening results indicated that water-soluble fractions displayed significant bioactivity in cytotoxic, antibiotic, anti-Leishmania, anti-Trypanosoma cruzi, and inhibition of proteasome assays. Purification of water-soluble fractions from the growth medium of Penicillium solitum IS1-A provided the new glutamic acid derivatives solitumine A (1), solitumine B (2), and solitumidines A-D (3-6). The structures of compounds 1-6 have been established by analysis of spectroscopic data, chemical derivatizations, and vibrational circular dichroism calculations. Although no biological activity could be observed for compounds 1-6, the new structures reported for 1-6 indicate that the investigation of water-soluble natural products represents a relevant strategy in finding new secondary metabolites.

51. Diterpenoids with inhibitory activity of nitrite production from Croton floribundus

By Queiroz Suzana Aparecida S; Pinto Meri Emili F; Bobey Antonio F; Russo Helena M; Batista Andrea N L; Batista Joao M Jr; Codo Ana C; Medeiros Alexandra I; Bolzani Vanderlan S
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ETHNOPHARMACOLOGICAL RELEVANCE: Croton floribundus Spreng. (Euphorbiaceae), popularly known as Capixingui, stands out due to its widespread use in traditional medicine to treat wounds, syphilis, hemorrhoids, eye diseases and as a purgative. AIM OF THE STUDY: To characterize clerodanes diterpenes from C. floribundus and to evaluate the effects of the fraction and diterpenes (1-5) on inhibition of nitrite production. MATERIALS AND METHODS: The hydroethanolic root extract of C. floribundus was fractionated on a solid phase extraction column to obtain the fraction named Fr80%. From this, five compounds were obtained and characterized. The absolute configuration of compound 1 was determined by a combination of electronic and vibrational circular dichroism spectroscopies. Additionally, compounds 1-5 were evaluated for their inhibitory effects on nitrite production induced by lipopolysaccharide (LPS) in RAW 264 macrophage cell. RESULTS: Five clerodane diterpenoids were characterized, and the absolute stereochemistry of 1 was established as 3R,4R,5R,8R,9R,10S,12S. The IC50 values obtained through inhibition of nitrite production were 28.52 ± 2.21 μM (1), 40.26 ± 2.79 μM (2), 25.47 ± 2.16 μM (3), 35.78 ± 2.93 μM (4) and 40.58 ± 4.78 μM (5). In the tested concentrations, the samples presented low toxicity in macrophages. CONCLUSIONS: Four new diterpenes were characterized from C. floribundus, these being croflorins A-D (1-4) and a known halimane (5). These compounds exhibited inhibitory effect on nitrite production.