Journal of Fluorine Chemistry 131 (2010) 451–454

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Graphical Abstracts/J. Fluorine Chem. 131 (2010) 451–454

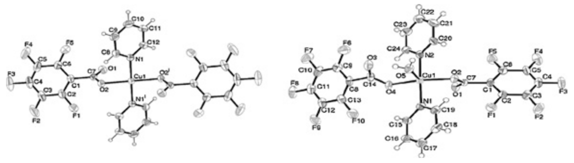
J. Fluorine Chem., 131 (2010) 456

Segregated aromatic π–π stacking interactions involving fluorinated and non-fluorinated benzene rings: $Cu(py)_2(pfb)_2$ and $Cu(py)_2(pfb)_2(H_2O)$ (py = pyridine and pfb = pentafluorobenzoate)

Raj Pal Sharma[a], Anju Saini[a], Sukhjinder Singh[a], Paloth Venugopalan[a], William T.A. Harrison[b]

[a]*Department of Chemistry, Panjab University, Chandigarh 160014, India*

[b]*Department of Chemistry of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland, United Kingdom*



Two new copper(II)pentafluorobenzoate complexes with pyridine $[Cu(py)_2(pfb)_2]$ (**1**) and $[Cu(py)_2(pfb)_2(H_2O)]$ (**2**) (where py = pyridine and pfb = pentafluorobenzoate) were isolated and structurally characterized. Detailed packing analysis of both complexes **1** and **2** show segregated aromatic π–π stacking interactions in which (py + py) and (pfb + pfb) ring-pairings are observed.

J. Fluorine Chem., 131 (2010) 461

First principle lattice energy calculations for enatiopure and racemic crystals of α-(trifluoromethyl)lactic acid: Is self-disproportionation of enantiomers controlled by thermodynamic stability of crystals?

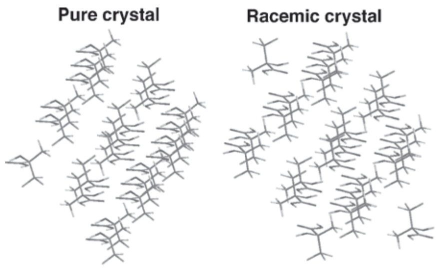
Seiji Tsuzuki[a], Hideo Orita[a], Hisanori Ueki[b], Vadim A. Soloshonok[cd]

[a]*National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan*

[b]*International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-1, Namiki, Tsukuba, Ibaraki 305-0044, Japan*

[c]*Department of Chemistry and Biochemistry, University of Oklahoma, Norman, OK 70319, United States*

[d]*Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of the Ukraine, Murmanska Street, Kyiv-94 02660, Ukraine*



Structures of enantiopure and racemic crystals.

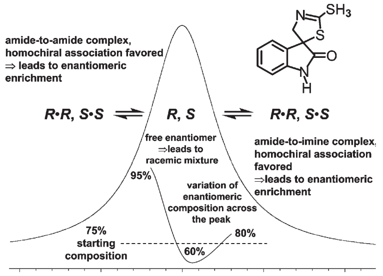
J. Fluorine Chem., 131 (2010) 467

NMR spectral enantioresolution of spirobrassinin and 1-methoxyspirobrassinin enantiomers using (*S*)-(−)-ethyl lactate and modeling of spirobrassinin self-association for rationalization of its self-induced diastereomeric anisochronism (SIDA) and enantiomer self-disproportionation on achiral-phase chromatography (ESDAC) phenomena

Karel D. Klika[a], Mariana Budovská[ab], Peter Kutschy[b]

[a]*Department of Chemistry, University of Turku, Vatselankatu 2, FIN-20014 Turku, Finland*

[b]*Institute of Chemical Sciences, Faculty of Science, P.J. Šafárik University, Moyzesova 11, 040 01 Košice, Slovak Republic*



Spirobrassinin not only exhibits the phenomenon of ESDAC (whereby the enantiomeric composition of a non-racemic mixture varies during chromatography), but is exceptional in that the enantiomeric composition rises twice across the eluting band.

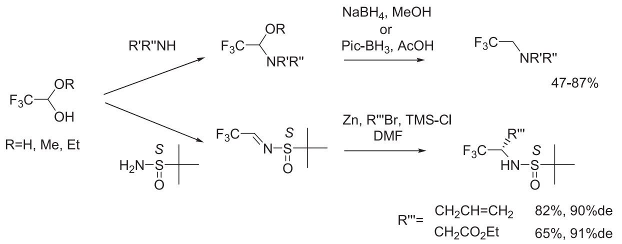
doi:10.1016/S0022-1139(10)00068-0

J. Fluorine Chem., 131 (2010) 477

Trifluoroacetaldehyde: A useful industrial bulk material for the synthesis of trifluoromethylated amino compounds

Hideyuki Mimura[a], Kosuke Kawada[a], Tetsuya Yamashita[b], Takeshi Sakamoto[b], Yasuo Kikugawa[b]

[a]*Research Laboratory, TOSOH F-TECH, Inc., 4988 Kaisei-cho, Shunan, Yamaguchi 746-0006, Japan*
[b]*Faculty of Pharmaceutical Sciences, Josai University, 1-1 Keyakidai, Sakado, Saitama 350-0295, Japan*



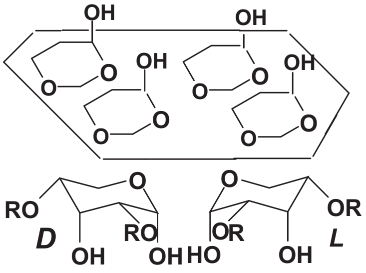
J. Fluorine Chem., 131 (2010) 487

Concept of Absolute Enantioselective Separation

Roman Bielski[a], Michal Tencer[bc]

[a]*Value Recovery, Inc., 510 Heron Drive, Suite 301, Bridgeport, NJ 08014, USA*
[b]*University of Ottawa, School of Information Technology and Engineering, Ottawa, 800 King Edward Av., ON, K1N 6N5 Canada*
[c]*MST Consulting, Ottawa, ON, Canada*

If a chiral molecule is oriented in two perpendicular directions that are parallel to the surface, the energy of interactions of opposite enantiomers with the surface is different. One of the ways to accomplish such orientation is to design a chiral surface which fits into the structure of only one enantiomer. The requirements and consequences of the relevant separation process we call Absolute Enantioselective Separation are discussed.

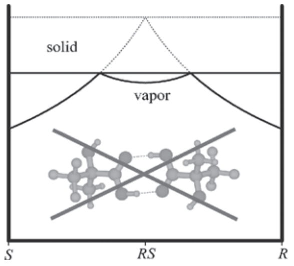


J. Fluorine Chem., 131 (2010) 495

Chirality-dependent sublimation of α-(trifluoromethyl)-lactic acid: Relative vapor pressures of racemic, eutectic, and enantiomerically pure forms, and vibrational spectroscopy of isolated (*S*,*S*) and (*S*,*R*) dimers

Merwe Albrecht[a], Vadim A. Soloshonok[bc], Lena Schrader[a], Manabu Yasumoto[d], Martin A. Suhm[a]

[a]*Institut für Physikalische Chemie, Universität Göttingen, Tammannstr. 6, D-37077 Göttingen, Germany*
[b]*Department of Chemistry and Biochemistry, The University of Oklahoma, Norman, OK 73019-3051, USA*
[c]*Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of the Ukraine, Murmanska Street, Kyiv-94 02660, Ukraine*
[d]*Central Glass Co., 2805 Imafuku-nakadai Kawagoe-shi, Saitama 350-1151, Japan*



Do gas phase dimers play a role in the chirality-dependent sublimation of α-(trifluoromethyl)-lactic acid? We show that this is not the case and that thermodynamically controlled sublimation at low temperature exhibits the expected eutectic behavior typical for immiscible solids of enantiomerically pure and racemic crystals.

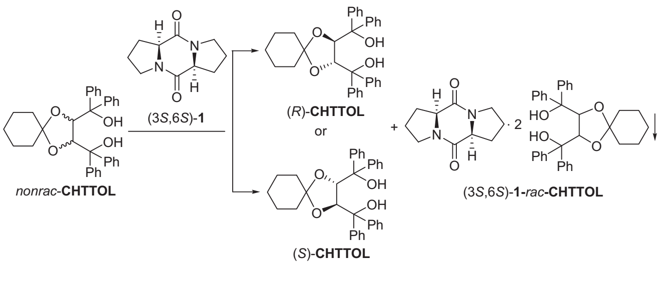
J. Fluorine Chem., 131 (2010) 505

Second example for the heterocomplexation of chiral diols and complete disproportionation of enantiomers for non-racemic 2,3-*O*-cyclohexylidene-1,1,4,4-tetraphenylthreitols

Xiaoyun Hu, Zixing Shan, Wei Li

Department of Chemistry, Wuhan University, Luojia Mountain, Wuhan 430072, China

Highly effective separation of the excess enantiomer from the racemate non-racemic was successfully realized for 2,3-*O*-cyclohexylidene-1,1,4,4-tetraphenylthreitol *via* heterocomplexation.

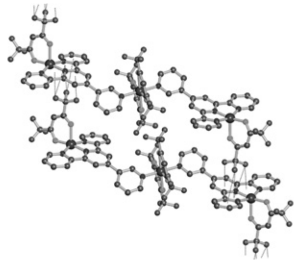


J. Fluorine Chem., 131 (2010) 510

The relevance of the fluorine interactions in the supramolecular structure of a complex constructed from copper(II) hexafluoroacetylacetonate and the 4′-(3-pyridyl)-2,2′:6′,2″-terpyridine ligand. Novel C–F/π synthons involving the π-system of the terpyridine moieties and those of the hexafluoroacetylacetonate chelate rings

Juan Granifo[a], Dominique Toledo[a], María Teresa Garland[b], Ricardo Baggio[c]

[a] *Departamento de Ciencias Químicas, Facultad de Ingeniería, Ciencias y Administración, Universidad de La Frontera, Temuco, Chile*
[b] *Departamento de Física, Facultad de Ciencias Físicas y Matemáticas and CIMAT, Universidad de Chile, Santiago de Chile, Chile*
[c] *Departamento de Física, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina*



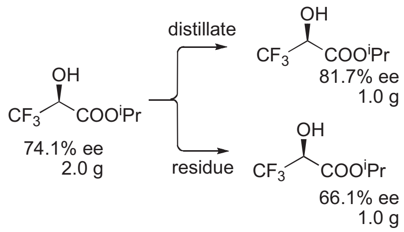
The 4′-(3-pyridyl)-2,2′:6′,2″-terpyridine (pyterpy) ligand reacts with Cu(hfacac)$_2$ (hfacac = hexafluoroace-tylacetonate) to produce the novel compound $[Cu_3(hfacac)_4(\mu\text{-pyterpy})_2][Cu(hfacac)_3]_2$. The packing motif is fixed by C–H···O, C–H···F, F···F and a variety of unusual inter-ion C–F···π interactions.

J. Fluorine Chem., 131 (2010) 517

Discrimination of enantiomeric excess of optically active trifluorolactate by distillation: Evidence for a multi-center hydrogen bonding network in the liquid state

Toshimasa Katagiri[a], Satoshi Takahashi[a], Akio Tsuboi[b], Miki Suzaki[b], Kenji Uneyama[a]

[a] *Department of Applied Chemistry, Faculty of Engineering, Okayama University, Tsushimanaka 3-1-1, Kita-ku, Okayama 700-8530, Japan*
[b] *Science and Technology Research Center, INC, Mitsubishi Chemical Group, 3-10 Ushiodori, Kurashiki 712-8054, Japan*



Multi-center hydrogen bonding network of trifluorolactate is survived in the liquid state to promote self-disproportionations of enantiomers via distillations.

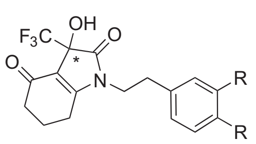
J. Fluorine Chem., 131 (2010) 521

Self-disproportionation of enantiomers of heterocyclic compounds having a tertiary trifluoromethyl alcohol center on chromatography with a non-chiral system

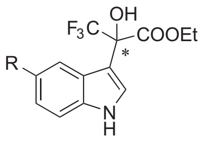
Shinichi Ogawa, Takayuki Nishimine, Etsuko Tokunaga, Shuichi Nakamura, Norio Shibata

Department of Frontier Materials, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso, Showa-ku, Nagoya 466-8555, Japan

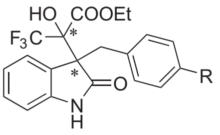
Self-disproportionation of heterocycle enantiomers having a tertiary trifluoromethyl alcohol center on achiral silica-gel stationary phase is discussed.



1: R=OMe
2: R=H



3: R=H
4: R=OMe



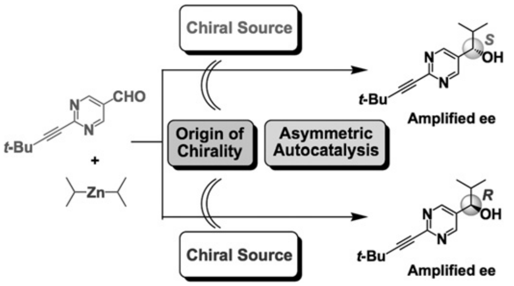
5: R=OMe
6: R=Br

J. Fluorine Chem., 131 (2010) 525

Amplification of chirality as a pathway to biological homochirality

Tsuneomi Kawasaki, Kenso Soai

Department of Applied Chemistry and Research Institute for Science and Technology, Tokyo University of Science, Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan



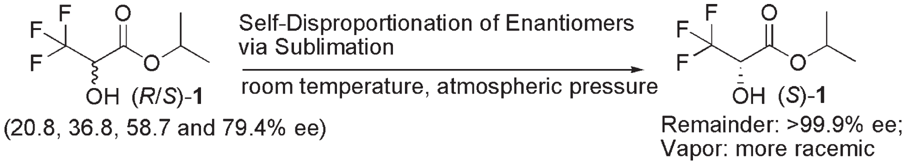
Amplification of enantiomeric purity is key feature for the chemical evolution of biological homochirality. The diastereomeric interaction enables the modification of enantiomeric excess during some chemical processes. In asymmetric autocatalysis of 5-pyrimidyl alkanol, extremely low ee can be amplified to achieve almost enantiomerically pure chiral organic compound.

J. Fluorine Chem., 131 (2010) 535

Self-disproportionation of enantiomers of isopropyl 3,3,3-(trifluoro)lactate via sublimation: Sublimation rates vs. enantiomeric composition

Manabu Yasumoto[b], Hisanori Ueki[c], Taizo Ono[d], Toshimasa Katagiri[e], Vadim A. Soloshonok[af]

[a]*Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of the Ukraine, Murmanska Street, Kyiv 94 02660, Ukraine*
[b]*Central Glass Co., 2805 Imafuku-nakadai Kawagoe-shi, Saitama 350-1151 Japan*
[c]*National Institute for Materials Science, 1-1, Namiki, Tsukuba, Ibaraki 305-0044, Japan*
[d]*National Institute of Advanced Industrial Science and Technology (AIST), 2266-98 Anagahora, Shimoshidami, Moriyama-ku, Nagoya, Aichi Prefecture 463-8560, Japan*
[e]*Okayama University, Tsushimanaka 3-1-1, Okayama 700-8530, Japan*
[f]*Department of Chemistry and Biochemistry, The University of Oklahoma, Norman, OK 73019, United States*

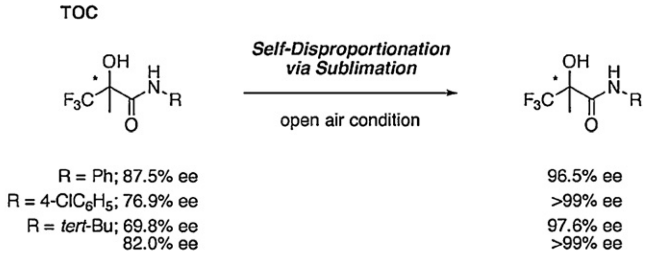


J. Fluorine Chem., 131 (2010) 540

Self-disproportionation of enantiomers of α-trifluoromethyl lactic acid amides via sublimation

Manabu Yasumoto[a], Hisanori Ueki[b], Vadim A. Soloshonok[cd]

[a]*Central Glass Co., 2805 Imafuku-nakadai Kawagoe, Saitama 350-1151, Japan*
[b]*International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-1, Namiki, Tsukuba, Ibaraki 305-0044, Japan*
[c]*Department of Chemistry and Biochemistry, University of Oklahoma, Norman, OK 73019, USA*
[d]*Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of the Ukraine, Murmanska Street, Kyiv 94 02660, Ukraine*



N-Phenyl-, *N*-(4-Cl-C_6H_5)-, and *N*-*tert*-Bu-α-trifluoromethyl lactic acid amides were found to strongly exhibit the phenomenon of self-disproportionation of enantiomers (SDE) via sublimation. The results described in this paper support the hypothesis that compounds containing –CF_3 group directly bonded to a stereogenic carbon center can induce a SDE effect.

J. Fluorine Chem., 131 (2010) 545

Attempts to explain the self-disproportionation observed in the partial sublimation of enantiomerically enriched carboxylic acids

Aurélien Bellec[ab], Jean-Claude Guillemin[ab]

[a]*École Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, Avenue du Général Leclerc, CS 50837, 35708 Rennes Cedex 7, France*
[b]*Université européenne de Bretagne, France*

In standard conditions and with a continuous condensation of the sublimate, the partial sublimation of samples of enantioenriched mandelic acid unambiguously occurs with the formation of a gas phase with the composition of the vapor eutectic.