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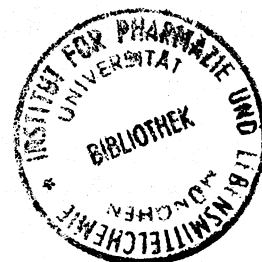
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Original Communications

- Electrochemical Syntheses, IV. Metal Carbonyl Compounds of the Iron Group Elements (In German)
J. GROBE and B. H. SCHNEIDER 1
- Electrochemical Syntheses, V. Phosphane Substituted Metal Carbonyls of the Iron Group Elements (In German)
J. GROBE and B. H. SCHNEIDER 8
- The Crystal Structures of BaSe₂ and BaSe₃
F. HULLIGER and T. SIEGRIST 14
- Acyl- and Alkylidene phosphines, XV. 2,2-Dimethylpropylidynephosphine, a Stable Compound with a Phosphorus Atom of Coordination Number 1 (In German)
G. BECKER, G. GRESSER, and W. UHL 16
- IR, ³¹P, ⁵⁵Mn and ^{185,187}Re NMR Spectroscopic Investigations of Some Carbonylmanganese and -rhenium Complexes (In German)
A. KEÇEÇI and D. REHDER 20
- On Oxidpnictides: Preparation and Crystal Structure of Ba₂Mn₂Sb₂O and Ba₂Mn₂Bi₂O (In German)
E. BRECHTEL, G. CORDIER, and H. SCHÄFER 27
- Solutions of Lithium Tetrahydrido Aluminates in Ethers: a ⁷Li and ²⁷Al NMR Study
H. NÖTH, R. RURLÄNDER, and P. WOLFGARDT 31
- Penta-Coordinated Complexes of Bis(2,4-pentanedionato) Copper(II) with Some Oxygen Donor Organic Solvents
B. P. BARANWAL, G. K. PARASHAR, and R. C. MEHROTRA 42
- The Reaction between Borontrifluoride and Sodium Diethylphosphite Synthesis and Reactions of Tris(diethylphosphitoborane) (In German)
H. BINDER and J. PALMTAG 45
- Perfluoromethyl Element Ligands, XXIV; Organotin Compounds as Reagents, III. Cleavage Reactions of the Element-Element-Bond in Compounds of the Type R_nE-ER_m (R = CH₃CF₃; E = P, As, S, Se, Te; n, m = 1, 2) (In German)
P. DEHNERT, J. GROBE, and DUC LE VAN 48
- Preparation and Crystal Structure of SbCl₃ · I₂ · 1,4-Dithiane (In German)
G. KIEL 55
- Mössbauer Spectroscopic Studies of Monosubstituted Pentacyano Ferrate(II) Complexes, Na₃[Fe(CN)₅RNH₂] · nH₂O
A. N. GARG and P. N. SHUKLA 59
- Preparation and Spectroscopical Characterisation of Tetrakis(chloro-iodo)oxalato-osmates(IV) (In German)
W. PREETZ and H. SCHULZ 62
- Preparation and Characterization of Monoorgano-bismuth(III) and Bismuth(III) Derivatives of Mercaptocarbonic Acids (In German)
U. PRAECKEL and F. HUBER 70
- Collisional Activation Mass Spectra of C₆H₆M⁺ and C₇H₇M⁺ Fragment Ions from Transition Metal π-Complexes (In German)
J. MÜLLER and F. LÜDEMANN 74
- Crystal and Molecular Structure of (Tetramethylcyclobutadiene)cis-1,2-dicyano-ethene-1,2-dithiolato-nickel(II) (In German)
R. HEMMER, H. A. BRUNE, and U. THEWALT 78
- Some New 1-D Compounds with Metal-Halide Chain
D. LAYEK and G. C. PAPAVALASSIOU 83
- Non Deprotonated Metal Complexes of the Bisamide Tetradentate Ligand N,N'-(Dipicolyl)-1,8-naphthylenediamine
TH. F. ZAFIROPOULOS, S. P. PERLEPES, P. V. IOANNOU, J. M. TSANGARIS, and A. G. GALINOS 87
- Metal-π Complexes of Benzene Derivatives, XIII. Bis(methylthio-η-benzene)chromium(0). Preparation and Function as a Bidentate Chelating Ligand (In German)
H. BURDORF and CHR. ELSCHENBROICH 94

- Stabilization of a Host-Guest Type Complex by Bifurcated Hydrogen Bonds: 18-crown-6 · (2,4-Dinitrophenylhydrazine)
R. HILGENFELD and W. SAENGER 242
- Activation of Steroid Systems to Alkylating Agents (In German)
M. WILK and K. SCHMITT 248
- A New Route to 1H-Pyrido[1,2-a]quinazolines
F. S. G. SOLIMAN, W. STADLBAUER, and TH. KAPPE 252
- Synthesis of Kaempferol-3-O-(3'',4''-di-O- α -L-rhamnopyranosyl)- β -D-galactopyranoside and its Comparison with the Natural Ascaside Isolated from *Astragalus caucasicus*
I. RIESS-MAURER, H. WAGNER, and A. LIPTÁK 257
- Isosilychristin, a New Flavonolignan from *Silybum marianum* L. Gaertn. (In German)
M. KALOGA 262
- Notes**
- Contributions to the Chemistry of Phosphorus, 89. Cyclization of a 1,3-Dihalogen-1,2,3-triorganyl-triphosphane to the Corresponding Triorganyl-cyclotriphosphane (In German)
M. BAUDLER and J. HELLMANN 266
- Preparation of Antimony(V)tetrafluoridepentafluorotellurate(VI), SbF₄OTeF₅ and Antimony(V)trifluoride-bis[pentafluorotellurate(VI)], SbF₃(OTeF₅)₂ (In German)
O. LEITZKE and F. SLADKY 268
- A New Preparative Method for Cesiumhydroxide (In German)
H. JACOBS and B. HARBRECHT 270
- Redox Properties of Platinum Uracil "Blues": A New Type of Paramagnetic Species
M. SEUL, H. NEUBACHER, and W. LOHMANN 272
- High Pressure Reactions; XIII. Synthesis of (–) Cannabidiol at High Pressure (In German)
H.-J. KURTH, D. BIENIEK, and F. KORTE 275
- Isolation of a New Natural Quinone, 2-Hydroxy-6-methoxy-3,5-dimethyl-1,4-benzoquinone, from the Potato Culture Solution of *Phoma wasabiae* Yokogi
O. SOGA and H. IWAMOTO 277
- Sulfonamidyls, 4. Ab Initio MO Calculations on Sulfonyl and Carbonyl Substituted Aminyl Radicals
H. TEENINGA, W. C. NIEUWPOORT, and J. B. F. N. ENGBERTS 279
- Erratum 282



Original Communications

- Synthesis of Sodium-Chelates of Methylene-bis-
iminodiphenylphosphorane] (In German)
R. APPEL and K. WAID 127
- Synthesis of Symmetrical Diaminocarbodiphos-
phoranes $R_2NPh_2P=C=PPh_2NR_2$ (In German)
R. APPEL and K. WAID 131
- The Crystal Structure of Methyltriphenylphos-
phonium Hexachlorotitanate (In German)
E. HEY and U. MÜLLER 135
- Preparation and Characterization of Tetrabutyl-
ammonium Tetraiodooxotechnetate(V),
(TBA)[TcOI₄] (In German)
G. PETERS and W. PREETZ 138
- Reactions of Thallium(III) Carboxylates with
Ketones (In German)
M. VOLLMERHAUS and F. HUBER 141
- Cyclic Diazastannylenes, X. The Crystal and Mole-
cular Structure of a Molecule with a Distorted
Cube-Shaped Sn₄N₃O-Cage (In German)
M. VEITH and O. RECKTENWALD 144
- On the Reaction of Aromatic Phosphane Deriva-
tives with Electrons, I. (In German)
W. KAIM 150
- Diazaborolidyl - a Stable Substituent at Sulfur
Nitrogen Compounds (In German)
W. HAUBOLD, H. G. FEHLINGER, and G. FREY 157
- Structures and Vibrational Spectra of Tetramethyl-
ammonium α -Dodecatungstosilicate and Tetra-
butylammonium β -Dodecatungstosilicate
(In German)
J. FUCHS, A. THIELE, and R. PALM 161
- Synthesis and Structure of 1,2,3-Thiadiazol- and
1,2,3-Selenadiazol-Pentacarbonyl Complexes of
the Elements Chromium and Tungsten
(In German)
V. BÄTZEL and R. BOESE 172
- On Cyanohalogenomercurates of Alkali Metals
(In German)
G. THIELE, K. BRODERSEN, and H. FROHRING 180
- Metallomethanes, IV. Molecular and Crystal Struc-
ture of Bis(chloromercuri)methane $CH_2(HgCl)_2$
(In German)
K.-P. JENSEN, D. K. BREITINGER, and W. KRESS 188
- Pt(II), Pd(II) and Cu(II) Complexes with the Ligand
4,4,5,5-Tetramethylimidazoline-1-oxyl-2-m-
pyridyl-3-oxide (In German)
K. E. SCHWARZHANS and A. STUEFFER 195
- Transition Metal Sulfur Ylide Complexes, XI.
Structure and Reactivity of η^5 -Thiacyclohexa-
dienyl-1-oxide Complexes of Chromium
(In German)
L. WEBER, D. VEHRESCHILD-YZERMANN, C. KRÜ-
GER, and G. WOLMERSHÄUSER 198
- Transition Metal Complexes of Diazenes, XVI.
Structure and Mössbauer Data of (2,3-Diaza-
nornbornene)Fe₃(CO)₉ (In German)
H. KISCH, C. KRÜGER, and A. TRAUTWEIN 205
- Electret Model for the Collective Behaviour of
Biological Systems
H. BILZ, H. BÜTTNER, and H. FRÖHLICH 208
- The Metal Complexes of Heterocyclic β -Diketones
and their Derivatives, Part VIII. Synthesis,
Structure, Proton NMR and Infrared Spectral
Studies of the Complexes of Al(III), Fe(III),
Co(III), Rh(III), In(III), and Zr(IV) with
1-Phenyl-3-methyl-4-trifluoroacetyl-pyrazolone-5
(HPMTFP)
E. CH. OKAFOR 213
- (Aminoethynyl)metallations, IX. Reactions of Yn-
amines with Cyanoketenes (In German)
G. HIMBERT and L. HENN 218
- Preparation of 1,3-Dimethyl-6-hydroxy-dihydro-
thymine by Photochemical Addition of Water to
1,3-Dimethyl-thymine (In German)
E. FAHR and P. FECHER 226
- Kinetic Studies of the Methanolysis Reaction of
Chloromethylated Phenols (In German)
G. STEIN, V. BÖHMER, W. LOTZ, and H. KÄM-
MERER 231

First Liquid Crystal Azulene Derivatives (In German) K. PRAEFCKE and D. SCHMIDT	375	Notes	
Sesquiterpene Esters of Type B from <i>Euonymus europaeus</i> L. (In German) A. RÖMER, H. THOMAS, B. KREUELS, and H. BUDZIKIEWICZ	379	A Method for the Preparation of Anhydrous Ruthenium(VIII) Oxide (In German) R. LÖSSBERG and U. MÜLLER	395
7H-Imidazo[1,2-a]- and -[1,5-a]azepine-7-ones (In German) U. WOLF	383	Photoproduction of Hydrogen from Water Catalysed by Metal Sulfur Chelates R. BATTAGLIA, R. HENNING, and H. KISCH	396
Electrochemical Properties of Pyridine and Dihydropyridine Derivatives (In German) G. ABOU-ELENIEN, J. RIESER, N. ISMAIL, and K. WALLENFELS	386	¹³ C, ¹ H Spin-Spin Coupling Constants, VIII. 2-Methyl- and 3,5-Dimethyladamantane (In German) R. AYDIN and H. GÜNTHER	398
Kinetic Investigation on the Hydrogen Transfer from Dihydropyridines to Hydrazyls (In German) G. ABOU-ELENIEN, J. RIESER, N. ISMAIL, and K. WALLENFELS	391	A Spin Trap Investigation of Azolyl Radicals V. N. BABIN, V. V. GUMENYUK, S. P. SOLODOVNIKOV, and YU. A. BELOUSOV	400
		Methoxymercuration-Demercuration of Pheromones for Double Bond Position Determination (In German) O. VOSTROWSKY and K. MICHAELIS	402



Original Communications

- Interhalogen Cations: Preparation and Crystal Structures (143 K) of $I_3Cl_2SbCl_6$, $I_3Cl_2AlCl_4$ and $I_3Br_2SbCl_6$ (In German)
S. POHL and W. SAAK 283
- Synthesis and Crystal Structure of Bis(N-methylhydroxylamido(1-)-O,N)(N-methyl-N-oxo-dithiocarbamato-O,S)-oxo-molybdenum(VI) (In German)
W. HOLZBACH, K. WIEGHARDT, and J. WEISS 289
- S_4N_4 and its Derivatives: Molecular and Crystal Structure of $S_4N_4^{2+}(FeCl_4^-)_2$ (In German)
U. THEWALT and M. BURGER 293
- Synthesis and Stabilization of (Benzoyl- and Pentafluorobenzoyloxy)diphenylphosphane and Comparison with the Corresponding Isomeric Aroyl-diphenylphosphane Oxides (In German)
E. LINDNER and J. C. WUHRMANN 297
- Electrochemical Syntheses, VI. Electrochemical Substitution of VI B-Hexacarbonyls $M(CO)_6$ ($M = Cr, Mo, W$) (In German)
J. GROBE and H. ZIMMERMANN 301
- Alkoxohalogenotellurates(IV): Preparation and Structure of Tetraphenylphosphonium Trichloro-(dioxo-ethylene-O,O')tellurate(IV) (In German)
K. BÜSCHER, S. HEUER, and B. KREBS 307
- Opening of the $B_{10}H_{10}^{2-}$ Cage to Give $B_{10}H_{14}$
H. MONGEOT and H. R. ATCHEKZAI 313
- $(\eta^3\text{-Benzyl})(\eta^4\text{-cyclooctadiene})\text{rhodium(I)}$ Complexes (In German)
H.-O. STÜHLER and J. PICKARDT 315
- Synthesis and Properties of Bi-, Tri- and Tetranuclear Transition Metal Complexes with the Organometallic Chelate Ligands $[C_5H_5M(P(OMe)_2O)_2]^\ominus$ ($M = Ni, Pd$) (In German)
H. WERNER, T. NGO-KHAC, C. FRIEBEL, P. KÖHLER, and D. REINEN 322
- ^{125}Te NMR Shifts and Te-P Coupling Constants of Phosphane Tellurides, Tellurophosphanes, and Tellurophosphane Complexes (In German)
W.-W. DU MONT and H.-J. KROTH 332
- On the Reaction of $[(CO)_4FeC(O)NMe_2]-[C(NMe_2)_3]^+$ with Some Diorganoboron Bromides (In German)
W. PETZ 335
- Enehydrazines, XXX. Phenylgous Enehydrazines without a Direct N,N-Bond (In German)
W. SUCROW and W. TURNSCHEK 339
- Thermolysis of 2,2-Dihydro-1,4,2-oxazaphosphol-4-enes, I. Dimerization of Bis(trifluoromethyl) Substituted Nitrile Ylides (In German)
K. BURGER, H. GOTH, K. EINHELLIG, and A. GIERN 345
- Thermolysis of 2,2-Dihydro-1,4,2-oxazaphosphol-4-enes, II. A Simple Synthesis for Fluorine Substituted N-Vinylimidoyl Chlorides (In German)
K. BURGER, H. GOTH, and E. BURGIS 353
- Kinetics of Oxidation of Tryptophan by Sodium Hypochlorite
TH. RAUSCH, F. HOFMANN, and W. HILGENBERG 359
- 1,4-Cycloaddition of *p*-Benzoquinone; 1,4-Naphthoquinone and N-Phenylmaleimide to 9-Vinylidene-xanthene (or Thioxanthene) Derivatives
S. B. AWAD, A. B. SAKLA, N. F. ABDUL-MALIK, and N. I. SAMAAAN 362
- Reactions of Amino Acids on 2-Methylmercaptopyridantoin Derivatives. Synthesis of Imidazoimidazoline and Imidazoquinazoline Derivatives
H. A. DABOUN, A. M. ABD-ELFATTAH, M. M. HUSSEIN, and A. F. A. SHALABY 366
- A Fundamental Study of Quantitative Desulfurization of Sulfur Containing Amino Acids by Raney Nickel and its Character
SH. OHMORI, K. TAKAHASHI, M. IKEDA, and T. UBUKA 370

Photodimerisation of 6- <i>trans</i> -Styryl-4-methoxy-2-pyrone (= 5,6-Dehydrokawain) (In German) M. KALOGA and I. CHRISTIANSEN	505	Reaction of (η^3 -Allyl)(η^5 -cyclopentadienyl) Palladium with 2,3-Bis(diphenylphosphino)-maleic Anhydride (In German) D. FENSKE and A. CHRISTIDIS	518
Contributions to the Synthesis of Cystine Peptides Illustrated by the Total Synthesis of Human Insulin (In German) B. KAMBER	508	Tl ₄ Ge ₄ Se ₁₀ , a Thallium(I) Selenogermanate with the Adamantane-Like Anion [Ge ₄ Se ₁₀] ⁴⁻ (In German) G. EULENBERGER	521
Notes			
New Phospha(III)azenes (In German) O. J. SCHERER and H. CONRAD	515	Isolation of Dihydrokaempferol from <i>Silybum marianum</i> L. Gaertn. (In German) M. KALOGA	524



Original Communications

- The Crystal Structure of $\text{Te}_6\text{O}_{11}\text{Cl}_2$ (In German)
W. ABBRIEL 405
- On Bariumthioantimonate(III) $\text{Ba}_3\text{Sb}_6\text{S}_{17}$
(In German)
W. DÖRRSCHEIDT and H. SCHÄFER 410
- Zintl Phases with Binary Anions: BaGe_2P_2 and
 BaGe_2As_2 (In German)
B. EISENMANN and H. SCHÄFER 415
- UV Photoelectron Spectra of Some Bent Bis-
(η^5 -cyclopentadienyl)Niobium and Tantalum Com-
plexes
H. VAN DAM, A. TERPSTRA, A. OSKAM, and J. H.
TEUBEN 420
- Contributions to the Chemistry of Trifluoromethyl-
seleninic Acid, Redox Processes in the
 $\text{F}_3\text{CSe}(\text{O})\text{OSCF}_n\text{Cl}_{3-n}$ System (In German)
A. DARMADI, A. HAAS, and K. TEBBE 426
- Reactions of (η - C_5H_5) $\text{Co}(\text{CO})_2$ and
(η - EtMe_4C_5) $\text{Co}(\text{CO})_2$ with Iodine and Cyanogen
Halides, XCN ($\text{X} = \text{Br}$ OR I)
M. MORÁN 431
- Reactions of Biscyclopentadienyl Vanadium with
 NO and XNO ($\text{X} = \text{Cl}$ OR Br)
M. MORÁN and M. GAYOSO 434
- 5-Chloro-5-phenyl-1-oxa-4,6-dithia-5-stannocane, a
Diplanar Transition State for the Racemisation
of the Boat-Chair Conformation in an Eight-
Membered Ring (In German)
M. DRÄGER 437
- Polymeric Dimethyl- and Diphenylglyoximate Com-
plexes of Cobalt and Iron with Pyrazine as a
Bridging Ligand. The Crystal Structure of Bis-
(dimethylglyoximate)pyrazine Cobalt(II)⁺
(In German)
F. KUBEL and J. STRÄHLE 441
- Isolable Chloro[(thio)alkoxy]triorganylphos-
phoniumchlorides as Intermediates of the Oxirane
(Thiirane)-Halogenation with Dichlorophospho-
ranes (In German)
R. APPEL and V. I. GLÄSEL 447
- Carbonylvandium, -manganese and -molybdenum
Complexes of the Ligands $o\text{-C}_6\text{H}_4\text{EPh}_2$ ($\text{E}'\text{Ph}_2$)
($\text{E}, \text{E}' = \text{P}, \text{As}, \text{Sb}, \text{Bi}$) and $\text{cis-Ph}_2\text{PCH}=\text{CHPh}_2$
(In German)
R. TALAY and D. REHDER 451
- On the Rare-Earth Pnictochalcogenides LnAsSe
R. SCHMELCZER, D. SCHWARZENBACH, and F.
HULLIGER 463
- Cyclic Boron Derivatives of Biurets
J. BIŁLAWSKI, K. NIEDENZU, A. WEBER, and W.
WEBER 470
- Organometallic Lewis Acids, V. Reactions of
Carbonyl- η^5 -cyclopentadienyl Molybdenum
Tetrafluoroborates ($\eta^5\text{-C}_5\text{H}_5$) $\text{Mo}(\text{CO})_2(\text{L})\text{FBF}_3$
($\text{L} = \text{CO}, \text{PR}_3$) with Phosphanes and Alkenes
(In German)
K. SÜNKEL, H. ERNST, and W. BECK 474
- Electrochemical Syntheses, VII. Electrochemical
Substitution Reactions of $\text{M}(\text{CO})_{6-n}(\text{PR}_3)_n$
Complexes ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) (In German)
J. GROBE and H. ZIMMERMANN 482
- A Novel Isomerization of an Electron-Rich Alkene
E. L. WEINBERG, J. TH. BURTON, M. C. BAIRD,
and M. HERBERHOLD 485
- Two-Dimensional (2D-J) NMR Spectroscopy for
Analysis of Isomers and Heterocouplings
R. BENN and W. RIEMER 488
- The Structures of $\text{S}_4\text{N}^\ominus$, $\text{S}_3\text{N}_2\text{O}_2$ and $\text{S}_4\text{N}_3^\ominus$
R. GLEITER and R. BARTETZKO 492
- The Fluctual Behaviour of the P_7 Trianion -
A Molecular Orbital Study
M. C. BÖHM and R. GLEITER 498
- Cyclisation of 1-Phenyl-4-carboxymethylmercapto-
5-aryloxy-hydantoins
A. F. A. SHALABY, M. A. ABDEL AZIZ, and S. S. M.
BOGHADADI 501

- The Crystal Structure of Potassium-bis(hexamethylenetetramine)-tris-(isothiocyanato)cuprate(II)-dihydrate,
 $K[Cu(C_6H_{12}N_4)_2(NCS)_3] \cdot 2 H_2O$, a Trigonal Bipyramidal Cupric Complex (In German)
 J. PICKARDT 649
- Temperature Dependent ESR Studies on Platinum Pyrimidine "Blues": Evidence for a Structural Instability?
 M. SEUL, H. NEUBACHER, and W. LOHMANN 651
- Could Hydrogen Peroxide Photolysis Occur in the Absence of Transition Metals?
 ST. LUŇÁK and J. VEPŘEK-ŠIŠKA 654
- On the Hydration of N-Isomeric 5-Tetrazolecarbaldehydes
 D. MODERHACK 656
- Direct Photochemical *cis-trans* Isomerization with 185 nm Radiation: A Facile Preparation of *cis*-Di-tert-butylethylene
 W. ADAM and F. YANY 658



Original Communications

- Contributions to the Chemistry of Phosphorus, 103. Tri-*tert*-butyl-diphospharsa-cyclopropane, (*t*-BuP)₂(*t*-BuAs) (In German)
M. BAUDLER and S. KLAUTKE 527
- On Aluminium Sulfide: α -Al₂S₃ and Al₂S₃(tetr.) (In German)
H. HAEFUSELER, A. CANSIZ, and H. D. LUTZ 532
- NMR Spectroscopic Studies on Chalcogen Compounds, II. ¹²⁵Te, ⁷⁷Se, ¹⁹F and ¹³C Chemical Shifts of CF₃ Substituted Selenium and Tellurium Compounds (In German)
W. GOMBLER 535
- Structure and Vibrational Spectrum of the α -Undecatungstophosphate Na₂[N(CH₃)₄HPW₁₁O₃₉ · 7 H₂O (In German)
J. FUCHS, A. THIELE, and R. PALM 544
- Sulfur-Nitrogen-Compounds, VIII. Synthesis and Characterization of Some Aromatic Sulfurdimines (In German)
G. BRANDS and A. GOLLOCH 551
- Addition Compounds of Trimethylstibine Dihalogenides and Antimony(III) Halogenides (In German)
J. WEERNER, W. SCHWARZ, and A. SCHMIDT 556
- (MePNMe)₄ · MeI and (MePNMe)₄ · 2 MeI, a Cyclo-tetra($\lambda^3, \lambda^3, \lambda^3, \lambda^5$ -) and a Cyclo-tetra($\lambda^3, \lambda^5, \lambda^3, \lambda^5$ -) phosphazane (In German)
W. ZEISS, T. KUHN, D. LUX, W. SCHWARZ, and H. HESS 561
- Separation of Calcium Isotopes with Cryptand Complexes (In German)
K. G. HEUMANN and H.-P. SCHIEFER 566
- Chemistry of Polyfunctional Ligands, 64. On Hydrido-iridium(III) Complexes of N,N-Bis-(diphenylphosphino)-*p*-tolylamine (In German)
J. ELLERMANN, L. MADER, and K. GEIBEL 571
- Rhodium(I) Catalyzed Asymmetric Hydrogenation of α -Acetamido Cinnamic Acid with Monomeric and Polymeric Aminophosphines (In German)
U. NAGEL, H. MENZEL, P. W. LEDNOR, W. BECK, A. GUYOT, and M. BARTHOLIN 578
- Solvent Effects on the Carbon - 13 NMR Chemical Shifts and Rotational Barriers of N,N-Dimethylbenzamide - Solvent Enhanced π Polarization
C. W. FONG and H. G. GRANT 585
- On the One and Two-Electron Oxidations of Water-Soluble Zinc Porphyrins in Aqueous Media
M. NEUMANN-SPALLART and K. KALYANASUNDARAM 596
- Energy Turnover of a Reaction between Radical Cation and Radical Anion (In German)
A. STANIENDA 601
- Reactions of Mesoionic Five-Membered Heterocycles with *o*-Quinonoid Compounds, IV. Mono- and Tricyclic 1,3-Thiazolium-4-olates, 1,3-Dithiolium-4-olates (In German)
W. FRIEDRICHSEN, W.-D. SCHRÖER, I. SCHWARZ, and A. BÖTTCHER 609
- Reactions of Five-Membered Mesoionic Heterocycles with *o*-Quinonoid Compounds, V. 1,3-Oxazolium-5-olates and 1,3-Thiazolium-5-olates (In German)
W. FRIEDRICHSEN, I. SCHWARZ, B. EPE, and K.-F. HESSE 622
- Cycloadditions with *o*-Benzoquinone-diimines, VI. Reactions of 1,3-Diarylbenzo[c]furans with *o*-Benzoquinone-diimines. Stable Chair and Boat Conformers in the 5,6,11,12-Tetrahydrodibenzo-[b,f][1,4]diazocin Series (In German)
W. FRIEDRICHSEN, M. RÖHE, and T. DEBAERDEMAEKER 632

Notes

- On the Crystal Structure of Mixed Phosphate/Sulfate Fluoroapatites (In German)
M. C. APPELLA and E. J. BARAN 644
- Preparation and Crystal Structure of Na₃FeSe₃ (In German)
P. MÜLLER and W. BRONGER 646

Occurrence of *trans*-3-Hexenal in *Thea sinensis* Leaves

A. HATANAKA and T. KAJIWARA 755

Studies on Wasp Venom, I. Low Molecular Weight Constituents of Venom Sac Extracts from *Paravespula vulgaris* (In German)

H. KLEIN, W. FRANCKE, and W. A. KÖNIG 757

Notes

Solvent Effects on the IR Spectra of N-Methylacetamide

J. MANZUR and G. GONZÁLEZ 763

The X-ray Structure of $\text{gem-N}_3\text{P}_3\text{Cl}_4(\text{NPPPh}_3)_2$ -Conformation of the NPPPh₃ Groups

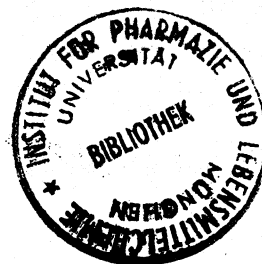
M. KRISHNATAH, L. RAMAMURTHY, P. RAMABRAHMAM, and H. MANOHAR 765

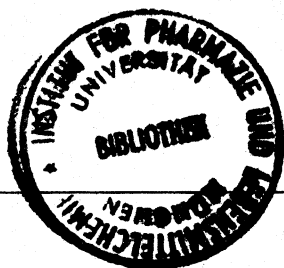
Unusual Reaction of (σ -Allyl)manganesepentacarbonyl with Bis(diphenylphosphino)-N-methyl Maleic Anhydride (In German)

D. FLENSKE, K. BRANDT, and P. STOCK 768

Silyl-Assisted Ether Cleavage in Radical Cations of Hydroxylamine Derivatives (In German)

B. CROMMER, H. SCHWARZ, A. MAAROUFI, M. T. REETZ, and K. LEVSEN 771





Original Communications

- The Stabilisation of Tris(hydrazino)phosphane by Complex Formation (In German)
H. NÖTH and V. THORN 659
- Nitrido Azido Complexes of Molybdenum(VI). Synthesis and Crystal Structure of $\text{MoN}(\text{N}_3)_3(\text{NC}_5\text{H}_5)$ (In German)
E. SCHWEDA and J. STRÄHLE 662
- Perfluoromethyl-Element Ligands, XXV. Organotin Compounds as Reagents, IV: Cleavage Reactions of the Element-Element Bond in Complexes of the Type $\text{M}(\text{CO})_5\text{ER}_2\text{E}'\text{R}'_2$ and $\text{M}(\text{CO})_5\text{ER}_2\text{E}'\text{R}'$, Respectively, with Trimethylstannane ($\text{R}, \text{R}' = \text{CH}_3$; $\text{E} = \text{P}, \text{As}$; $\text{E}' = \text{S}, \text{Se}, \text{Te}$; $\text{M} = \text{Cr}, \text{Mo}$) (In German)
J. GROBE and D. LE VAN 666
- Oligophosphine Ligands, III. Bis(3-diphenylphosphinopropyl)phenylphosphinechloroiridium(I) and its Carbonyl and Hydride Derivatives (In German)
E. ARPAC and L. DAHLENBURG 672
- Coordination Complexes of Reduced Pyrazine and Alkyl Derivatives of Boron, Aluminum, Gallium, and Indium (In German)
W. KAIM 677
- On the Mechanism of the Formation of Nitrosylvanadium Complexes from Hydroxylamine: Reversible, Intramolecular Conversion of Coordinated Nitric Oxide to a Hydroxylamido(1—) Ligand (In German)
K. WIEGHARDT and U. QUILTZSCH 683
- $\text{Ti}_2\text{Sn}_2\text{S}_5$, a Thallium(I) Thiostannate(IV) with Five-fold Coordinated Tin (In German)
G. EULENBERGER 687
- Investigations on the Course of the Hydrolysis of Some Tris(alkoxy)boranes and the Identification of Intermediates (In German)
K.-P. STEINFELDT, G. HELLER, and R. BAUMERT 691
- Lanthanide(III) Complexes of Oxamic Acid
S. P. PERLEPES, TH. F. ZAFIROPOULOS, J. K. KOVINIS, and A. G. GALINOS 697
- ^{10}B , ^{11}B , ^{13}C NMR Studies of *closo*-Pentaalkyl-1,5-dicarbapentaboranes(5) (In German)
R. KÖSTER and B. WRACKMEYER 704
- Organometalphosphine-Substituted Transition Metal Complexes, XXVII. Reactions of Pentacarbonylmanganese- and Pentacarbonylrhenium-bromide with Organoelement(IVb) Phosphines (In German)
H. SCHUMANN and H. NEUMANN 708
- Investigation on Autoxidation of Metallic Copper and Copper(I) Compounds by Different Methods (In German)
L. HORNER and E. PLIEFKE 713
- Stereoisomerism of 5-Benzylidenetetramic Acids (In German)
H.-D. STACHEL and H. POSCHENRIEDER 721
- Crystal Structure and the Radiation-Induced Free-Radical Chain Reaction of 2-Deoxy- β -D-erythro-pentopyranose in the Solid State
M. N. SCHUCHMANN, C. VON SONNTAG, YI-H. TSAY, and C. KRÜGER 726
- Phosphate Production and Analysis in the Non-Enzymatic Activation of Amino Acids by ATP when Using Hydroxylamine as a Trapping Agent
D. W. MULLINS (JR.) and J. C. LACEY (JR.) 732
- Solvent Induced Circular Dichroism in Conformational Analysis: Bile Pigments
H. LEHNER, C. KRAUSS, and H. SCHEER 735
- Benzoylation of 3-Substituted 4-Hydroxy-2-quinolones and 4-Hydroxycoumarines (In German)
W. STADLBAUER and TH. KAPPE 739
- Pseudobases from Quinolinium-Salts and Alcoxides (In German)
W.-H. GÜNDEL and H. BERENBOLD 745
- Selective Succinylation of Adenosine Catalyzed by 4-Morpholine- N,N' -dicyclohexylcarboxamidine
C. SAUER and U. SCHWABE 750

Solvent Induced Circular Dichroism in Conformational Analysis: Bile Pigments

Harald Lehner*

Institut für Organische Chemie der Universität Wien,
Währingerstraße 38, A-1090 Wien

Corinna Krauss and Hugo Scheer

Botanisches Institut der Universität München,
Menzingerstraße 67, D-8000 München 19

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Solvent Induced Circular Dichroism, Conformation, Enantiomerization, Purpurines, Bilatrienes

The applicability of solvent induced circular dichroism (SICD) for the conformational analysis of bile pigments has been investigated. The S-(—)-ethyl lactate induced rotational strengths for octaethylbilindion (**4**) and its dihydroderivative **5** are remarkably high. Related compounds, *e.g.* the isomeric purpurines **1** and **2** and formyltripyrinon **3** exhibit an optical activity which is smaller by more than one order of magnitude. **1–3** are essentially free from steric strain so that a flat arrangement of the chromophore is most likely. On the other hand the closed conformations of **4** and **5** experience considerable steric repulsion of their terminal rings, so that a helical topology is energetically favoured. This distinction is reflected in the magnitude of the SICD observed and demonstrates its applicability for the conformational analysis of bile pigments.

Introduction

Recently it has been shown that SICD of bile pigments can be useful in their conformational analysis. Thus, for all-Z-all-syn biliverdindimethylester (**6**) and the XIII α isomer, for which a helical conformation has been established by various methods [1–5], a remarkably large $\Delta\epsilon$ -value is observed in S-(—)-ethyl lactate [3, 5], while for an E,Z,Z isomer [6] no SICD could be observed under the same conditions. Hence, SICD seems an attractive method in conformational analysis. In this report more direct evidence is given for this empirical approach. It will be shown, that under appropriate conditions this method is useful for bile pigments in general.

Materials and Methods

Compounds **1–3** [7], **4** and **5** [8] and **6** [3] were prepared according to the literature. CD spectra were recorded on a Jobin Yvon Mark III instrument in thermostated ($\pm 1^\circ$) quartz cuvettes of variable path length (0,01–2,0 cm) and $c = 10^{-4}$ – 10^{-5} M. Absorption spectra were measured on a Cary 15 spectrometer in 0,5 cm quartz cuvettes at ambient temperature. (S-(—)-ethyl lactate ($[\alpha]_D^{20} = -11,1^\circ$, neat) was purchased from Fluka and distilled twice over a Vigreux column prior to use.

Results and Discussion

Since the magnitude of the SICD observables is dependent on the inducibility of the optically active solvent employed [5], measurements routinely were performed in S-(—)-ethyl lactate at 20 °C. The SICD effects exhibited by the pigments **1–6** in the spectral region 300–800 nm are outlined in Table I.

The induced optical activities of the purpurines **1** and **2** as well as that of the formyltripyrinon **3** are exceedingly small, while the data obtained for all-Z-octaethylbilindion **4** closely resemble those of all-Z-all-syn-biliverdin-IX α -dimethylester (**6**) exhibiting an induced optical activity of $\Delta\epsilon = +5,9$ and $-2,9$ at 377 and 680 nm, respectively [5]. Likewise, the ellipticities observed for the dihydroderivative **5** (*cf.* Table I) are similar to the values reported for the structurally related racem. phytychromobilindimethylester [9]. These results are in agreement with geometric considerations. There is one striking difference between the two groups of compounds **1–3** and **4–6**, respectively. In the compounds **1** and **2** a planar structure of the chromophore is readily accessible due to a lack of steric hindrance between rings A and D. In contrast to the situation in bilatrienes the fourth ring A of the purpurines has virtually no influence on the conformation of the connected chromophore consisting of rings B, C, D. Similar arguments hold for **3**, as its molecular skeleton involves only three pyrrolic units. A planar,

* Reprint requests to Dr. H. Lehner.
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Table I. $\Delta\epsilon_{\max}$ -values [$M^{-1} \text{ cm}^{-1}$] of the bile pigments 1-6 in S-(—)-ethyl lactate at 20 °C determined at the wavelength λ ([nm]).

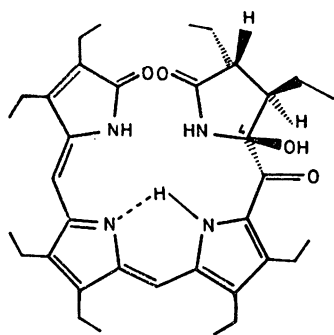
1	2	3	4	5 ^a	6 ^b
+ 0,2 (550)	— 0,2 (540)	— 0,2 (510)	— 3,4 (667)	— 5,2 (610)	— 2,9 (675)
— 0,2 (500)			+ 6,9 (366)	+ 8,7 (348)	+ 5,9 (378)

^a The corresponding data for the two synthetic isomeric phytychromobilin-dimethylesters are reported to be + 5,1 (372) and — 2,6 (610) and + 3,5 (375) and — 2,2 (610), respectively [9]. (The values at 610 nm do not represent the maximum of the long wavelength band but the edge of the recorded wavelength range.)

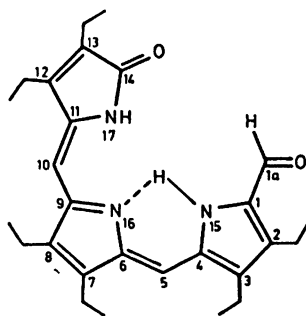
^b Values taken from ref. [5]; for the temperature dependence *cf.* Fig. 1.

closed conformation has been suggested for 3 in solution [10] and has been determined in the crystal state of an analogue [11]. By contrast, the non-bonded-interactions between the peripheral rings force all-*Z*-all-syn-biliverdindimethylester (6) and

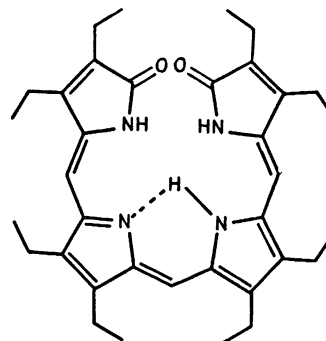
related compounds such as 4 and 5 into a helical arrangement. 4-6 can flip between two enantiomeric sets of conformations, which are both inherently chiral and separated by an activation barrier of approx. 42 kJ/mol [12].



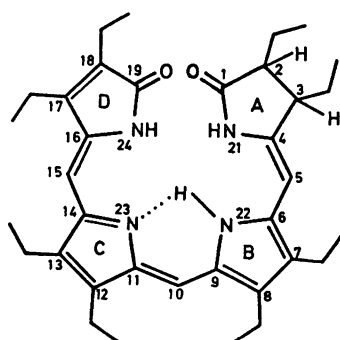
1
2 : C-4-epimer



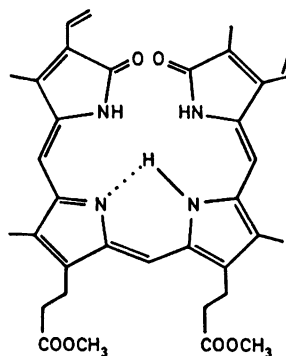
3



4



5



6

The finding of a large SICD in the twisted species of 4–6 is reminiscent of the effects observed in natural optical activity: the rotational strengths of inherently chiral chromophores are generally larger than the pertinent values for chirally perturbed symmetrical chromophores [13, 14].

Hence, the large SICD of 4–6 as compared to 1–3 is rationalized by the induction of an excess population of one enantiomeric helix, which originates from diastereomeric interactions of the optically active solvent with easily interconverting antipodal conformations of the solute. Therefore the equilibrium constant between P- and M-helices is no longer unity, but is shifted to the one or other side, so that one enantiomeric, inherently chiral species predominates. Thus, this process represents an asymmetric transformation of the first kind or enantiomerization [15]. A similar mechanism has been suggested for the intense CD in bilirubin and biliverdin induced by binding to serum albumen [16, 17].

Of course, the amount of the excess population in a given optically active solvent is not known, and it is even probable that the solute involves an ensemble of different diastereomeric conformations. In other words, although a large induced ellipticity as compared to a related non-helical molecule is indicative of a considerable amount of twisted conformers in the sample, it is by no means a proof for conformational homogeneity. For 6 *e.g.* it has been shown by fluorescence spectroscopy that its solvatochromic and thermochemical properties are due to different populations of coiled and stretched conformers [5]. Accordingly, on lowering the temperature the amount of the coiled species of 6 should increase. In fact, the SICD of 6 in ethyl lactate exhibits an extraordinarily strong temperature dependence with respect to the intensity, whereas the position and shape of the band remains unchanged (*cf.* Fig. 1). The increase of the effect on lowering the temperature reflects a shift of the conformational equilibrium to helical species, which exhibit a much larger contribution to the SICD observed than other conformers. The dependence of an induced CD on the conformation of the substrate has further been supported by incubation of 6 in liposomes of optically active lecithines [18]. In this matrix 6 exhibits chronochromic properties, which are due to a conformational transition [19].

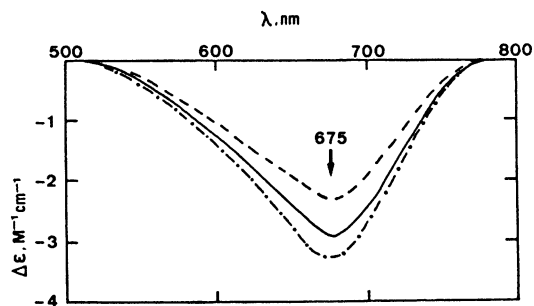


Fig. 1. SICD in the VIS absorption region of 6 in S-(—)-ethyl lactate (10^{-4} M) at 35 °C (---), 20 °C (—), and 9 °C (-·-·-). The temperature-dependence observed is fully reversible.

On the basis of these considerations the small SICD of 1–3 is not surprising. The arguments given above explain as well the negligible SICD of E,Z,Z-biliverdin [6], in which the steric repulsion between the peripheral rings is removed and of a biliverdin bridged between N-21 and N-24, in which the ready interconversion between enantiomeric helices is hindered at ambient temperature [20].

Concluding Remarks

In order to identify twisted chromophore conformations by means of SICD the induced rotational strength of a related molecule with a similar chromophore of established conformation should be known. A chromophore independent criterion based on the anisotropy factor (g), which has been fruitfully applied in natural optical activity [14], cannot be given.

Although the electronic transitions stemming from helical conformations of 4–6 and other bilatrienes should be electrically and magnetically allowed the condition $g \approx 10^{-2}$ [14] will scarcely be met. Even in the case of conformational homogeneity the enantiomeric excess population – the analogue of “enantiomeric purity” in natural optical activity – will not necessarily reach unity. Its value is not known for any given case, and it additionally changes with the optically active solvent employed.

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