

treating (*Z*)-2-bromo-2-buten-1-ol⁷ sequentially (-78 °C, ether-THF) with 3 equiv of *t*-BuLi, 1 equiv of lithium thienylcyanocuprate,⁸ 2 equiv of Me₃SiCl⁹ and 1 equiv of 2-cyclopentenone. Chromatographic purification provided cyclopentanone **8** in 40–45% yield.¹⁰ Protection of the primary alcohol of **8** as a triisopropylsilyl (TIPS) ether¹¹ and subsequent regioselective enolization (-78 °C, THF) of **9**¹² with Masamune's base¹³ provided, after *in situ* triflation¹⁴ (Tf = SO₂CF₃), the enol triflate **10**. This intermediate was contaminated with ca. 10% of its double-bond regioisomer.¹⁵ Carbonylation of **10** [5% Pd(PPh₃)₄, CO (1 atm), DMF, 55 °C]¹⁶ in the presence of *N,O*-dimethylhydroxylamine provided amide **11**. Acylation of **11**¹⁷ with the aryllithium dianion prepared from 2-(trimethylacetamido)-bromobenzene¹⁸ gave enone **12** in an overall yield of 63% from cyclopentanone **9**.

Enone **12** was epoxidized with good facial selectivity (10–13:1) at -23 °C (*t*-BuOOH, Triton B) to give **13**, which afforded styrene **14** upon subsequent reaction with 3 equiv of (methylene)triphenylphosphorane (THF, -78 → 23 °C). Desilylation of **14** with (*n*-Bu)₄NF followed by chlorination of the liberated alcohol (MsCl, DMF, LiCl, -23 → 23 °C) afforded the allylic chloride **15**. Although direct bis-aminolysis of **15** with NH₃ was not clean, the desired cyclization was accomplished by sequential treatment of **15** (DMF, 23 °C) with the sodium salt of trifluoroacetamide,¹⁹ followed by cleavage of the resulting bicyclic amide with KOH (EtOH-H₂O, 80 °C). This sequence delivered the azabicyclic amine **16** in 35% overall yield from enone **12**.

The pivotal rearrangement of **16** was occasioned under standard mild conditions [paraformaldehyde (1.5 equiv), camphorsulfonic acid (1.0 equiv), Na₂SO₄ (2 equiv), CH₃CN at reflux]¹ to provide a single crystalline product **17** in 88% yield. Hydrolysis of this intermediate with a large excess of KOH in EtOH-H₂O (2:1) at reflux provided, in 70% yield, (±)-dehydrotubifoline (**3**). The synthetic product was identical with an authentic sample prepared by acid treatment of natural akuammicine.²⁰

The chemistry outlined herein defines a short, highly stereocontrolled, new strategy for preparing *Strychnos* alkaloids. The overall yield of (±)-dehydrotubifoline from 2-cyclopentenone was 6%, and this conversion was accomplished in only 12 chemical operations. Besides the key aza-Cope-Mannich rearrangement step (**16** → **17**), other notable transformations include 1,4-addition of a 1-hydroxy-2-butenyl cuprate (**7** → **8**) and formation of an unsaturated *N*-methyl-*N*-methoxyamide by palladium-catalyzed carbonylation-aminolysis of an enol triflate (**10** → **11**). The extension of this approach to the preparation of strychnine and other complex *Strychnos* alkaloids is under investigation.

Acknowledgment. The support of PHS Grant NS-12389 is

(7) Readily available in 90% overall yield from methyl *trans*-crotonate by bromination, dehydrobromination (Et₃N, pentane, reflux), and (*i*-Bu)₂AlH (-78 °C, CH₂Cl₂) reduction.

(8) Lipshutz, B. H.; Koerner, M.; Parker, D. A. *Tetrahedron Lett.* **1987**, *28*, 945.

(9) (a) Chuit, C.; Foulon, J. P.; Normant, J. F. *Tetrahedron* **1980**, *36*, 2305. (b) Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* **1985**, *26*, 6019. (c) Alexakis, A.; Berlan, J.; Besace, Y. *Tetrahedron Lett.* **1986**, *27*, 1047.

(10) Yields are reported for isolated compounds purified by flash chromatography on silica gel. All new compounds showed ¹H NMR, ¹³C NMR, IR, and high-resolution mass spectra in complete accord with their assigned structures.

(11) Ogilvie, K. K.; Thompson, E. A.; Quilliam, M. A.; Westmore, J. B. *Tetrahedron Lett.* **1974**, 2865.

(12) For an alternate, longer preparation of **9**, see ref 6.

(13) Masamune, S.; Ellingboe, J. W.; Choy, W. *J. Am. Chem. Soc.* **1982**, *104*, 5526.

(14) McMurry, J. E.; Scott, W. J. *Tetrahedron Lett.* **1983**, *24*, 979.

(15) These isomers have been separated by careful chromatography on silica gel (hexane) to give **10** in 71% yield and >40:1 isomeric purity. In early experiments this mixture was carried forward, and subsequent purified intermediates contained only a few percent of the undesired regioisomer.

(16) For the preparation of simple α,β -unsaturated amides in this way, see: Cacchi, S.; Morera, E.; Ortari, G. *Tetrahedron Lett.* **1985**, *26*, 1109.

(17) Levin, J. I.; Turos, E.; Weinreb, S. M. *Synth. Commun.* **1982**, *12*, 989.

(18) Wender, P. A.; White, A. W. *Tetrahedron* **1983**, *39*, 3767.

(19) Hawkins, J. M.; Fu, G. C. *J. Org. Chem.* **1986**, *51*, 2820.

(20) Smith, G. F.; Wröbel, J. T. *J. Chem. Soc.* **1960**, 792.

gratefully acknowledged as is fellowship support for J.M.F. from the American Cancer Society (PF-3171). NMR and mass spectra were determined at Irvine with spectrometers acquired with the assistance of NSF shared instrumentation grants. We thank Dr. Susan Vice for her early efforts on this project, Mr. Steven Knight for optimizing the preparation of **10** and **11**, and Professor E. Wenkert and J. Lévy for samples of natural akuammicine.

Spectra of the Solvated Electron in the Presence of Sodium Cation in Tetrahydrofuran and in Its α,α' -Methylated Derivatives[†]

Piotr Piotrowiak* and John R. Miller

*Electron Transfer and Energy Conversion Group
Chemistry Division, Argonne National Laboratory
Argonne, Illinois 60439*

Received January 7, 1991

We report the first optical absorption spectra of a solvated electron with clearly resolved structures. The results presented in this communication were obtained via time-resolved pulse radiolysis experiments on tetrahydrofuran (THF), mixed *cis*- and *trans*-2,5-dimethyltetrahydrofuran (2,5-DMTHF), and 2,2,5,5-tetramethyltetrahydrofuran (2,5-TMTHF) solutions containing millimolar concentrations of sodium salts.

It has been known for quite some time that the properties of the solvated electron in solutions of electrolytes in moderately polar solvents differ considerably from its properties in the same solvents but in the absence of electrolytes.^{1,2} Specifically, for sodium salts in tetrahydrofuran (THF), the absorption maximum occurs at 880 nm (1.41 eV), compared with 2120 nm (0.58 eV) for e⁻_{sol} in neat THF.³ This phenomenon is attributed to the formation of a new species (e⁻,M⁺).⁴ The magnitude of the spectral shift is not a monotonic function of the radius of the bare cation⁵ and is, for example, smaller for lithium than for sodium. It appears to depend critically on the degree of solvation of the alkali-metal cation, which controls the equilibrium distance between the positive charge and the electron.

In this study we investigated the influence of the structure of the solvent molecule on the spectral and kinetic properties of the (e⁻,Na⁺) moiety. 2,5-DMTHF and 2,5-TMTHF were selected as interesting media since their dipole moments and dielectric constants are similar to those of unsubstituted THF, yet their ability to tightly solvate alkali-metal cations is significantly diminished as a result of the steric hindrance generated by the presence of two or four methyl groups in the α positions.

Our time-resolved pulse radiolysis experiments were performed on purified samples of the above ethers that contained 5–20 mM sodium salts. Tetraphenylboron sodium was used as the source

[†] Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Science, US-DOE, under Contract No. W-31-109-ENG-38.

(1) Klosterboer, J. G.; Gilling, L. J.; Rettschnick, R. P. H.; Van Voorst, J. D. W. *Chem. Phys. Lett.* **1971**, *8*, 457.

(2) Gilling, L. J.; Klosterboer, J. G.; Rettschnick, R. P. H.; Van Voorst, J. D. W. *Chem. Phys. Lett.* **1971**, *8*, 462.

(3) Bockrath, B.; Dorfman, L. M. *J. Phys. Chem.* **1973**, *77*, 1002.

(4) The species (e⁻,M⁺) is often regarded as an "ion pair" composed of the solvated electron and the solvated metal cation. However, it should be pointed out that there is no experimental evidence (results of the present study included) that would prove the validity of this structure and would rule out the possibility of a spherically symmetric, hydrogen-like, geometry of the (e⁻,M⁺) moiety, with the solvated metal cation residing in the center and the electron delocalized over its solvation shell. Therefore, in our description of (e⁻,M⁺), we will refrain from using the term "ion pair", which implies a nonconcentric, axial arrangement of the components.

(5) Bockrath, B.; Dorfman, L. M. *J. Phys. Chem.* **1975**, *79*, 1509.

(6) Ramme, G.; Fisher, M.; Claesson, S.; Szwarc, M. *Proc. R. Soc., Ser. A* **1972**, *327*, 467.

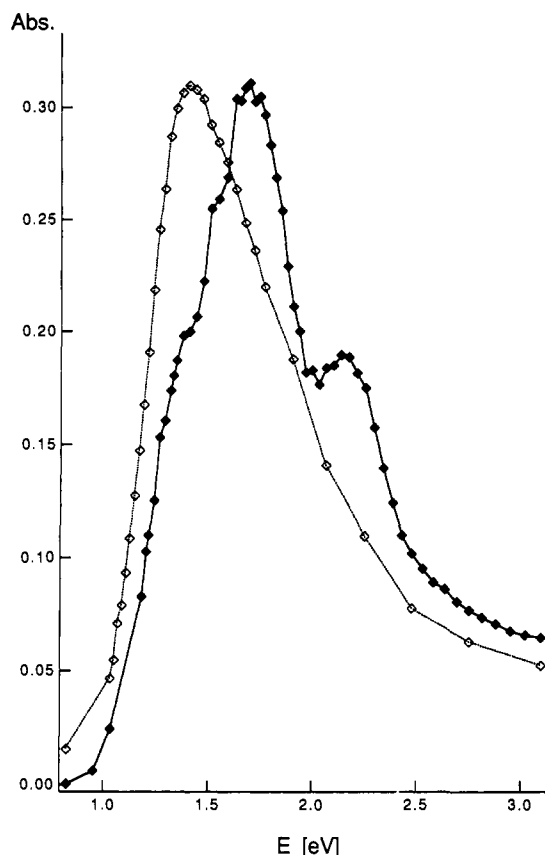


Figure 1. Room temperature spectra of (e^-, Na^+) in 2,5-DMTHF (solid line) and THF (dotted line). The scaling is arbitrary.

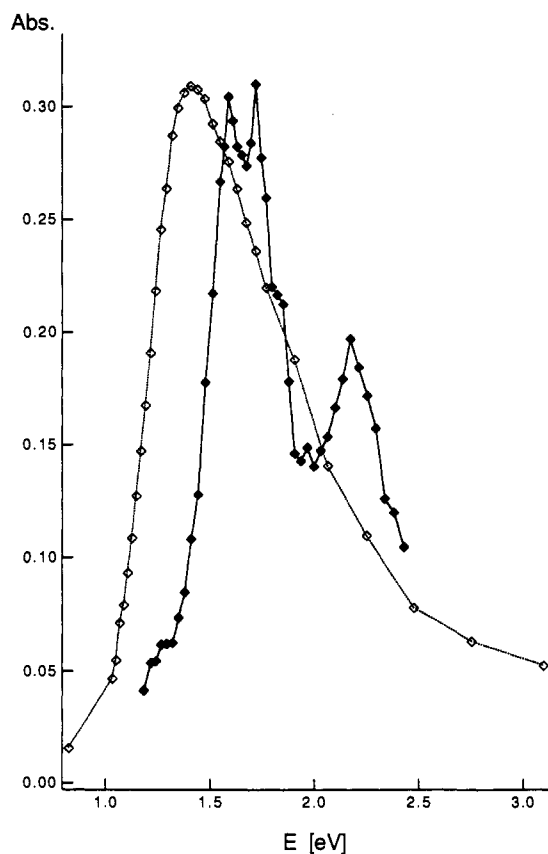


Figure 2. Room temperature spectra of (e^-, Na^+) in 2,5-TMTHF (solid line) and THF (dotted line). The scaling is arbitrary.

of Na^+ cations in the THF and 2,5-DMTHF measurements. Due to its insolubility in 2,5-TMTHF, the much more soluble tetra-

kis[3,5-bis(trifluoromethyl)phenyl]boron sodium was used instead. The experimental details will be published later.

The optical absorption spectrum of (e^-, Na^+) in 2,5-DMTHF consists of two clearly resolved peaks at 575 (2.15 eV) and 735 nm (1.69 eV) and a shoulder at longer wavelengths (Figure 1). The main peak is blue-shifted by 0.28 eV in comparison with the same salt in THF. There are three resolved peaks at 570 (2.17 eV), 720 (1.72 eV), and 780 nm (1.59 eV) in 2,5-TMTHF (Figure 2). The blue shift is not very different from the one in 2,5-DMTHF (the two highest peaks are shifted by 0.31 and 0.18 eV with respect to THF), but the spectral features are much sharper and the overall width of the spectrum is greatly reduced. While the possibility of a fast exchange between different sites remains open, the temporal behavior of the spectra down to approximately 1 ns supports the notion of a single chemical species (e^-, Na^+) being responsible for all the bands. Unfortunately, the assignment of the observed bands in terms of several bound \rightarrow bound electronic transitions and one bound \rightarrow continuum transition remains a nontrivial and ambiguous task, especially if (e^-, Na^+) is not spherically symmetric.

The results of the variable-temperature work, as well as measurements of electron attachment rates to various scavengers, will be presented in a more comprehensive article.

We will gladly make available the complete set of experimental data points to interested researchers.

Acknowledgment. We thank Mr. William Mulac for the excellent design of the collinear pulse radiolysis cell. We are indebted to Mr. George Cox and Mr. Donald Ficht for the consistent high quality of the LINAC beam.

Registry No. THF, 109-99-9; *cis*-2,5-DMTHF, 2144-41-4; *trans*-2,5-DMTHF, 2390-94-5; 2,5-TMTHF, 15045-43-9; Na^+ , 17341-25-2.

Continuously Variable Hg-S Coordination in the Low-Dimensional Organic Metal (BEDT-TTF) $Hg_{0.776}(SCN)_2$ and Its Description by the Bond Valence Sum Method

Philip Coppens,* Ivana Cisarova,[†] Xianhui Bu, and Peter Sommer-Larsen[‡]

Chemistry Department
State University of New York at Buffalo
Buffalo, New York 14214
Received January 28, 1991

Composite crystals consist of two or more sublattices coexisting in the same crystal. The chemical composition of the crystal is therefore a function of the ratio of the sublattice volumes and is nonstoichiometric when the sublattices are incommensurate.¹ Examples are the organic superconductor (BEDT-TTF) $Hg_{2.89}Br_8$ ² and the metal (BEDO-TTF) I_3 .³ (BEDT-TTF = 3,4:3',4'-bis(ethylenedithio)-2,2',5,5'-tetrathiafulvalene, below referred to as ET; BEDO-TTF = 3,4:3',4'-bis(ethylenedioxo)-2,2',5,5'-tetrathiafulvalene.) The composite metal (ET) $Hg_{0.776}(SCN)_2$, synthesized by Wang et al.,⁴ is particularly unusual as the Hg

* Author to whom correspondence should be addressed.

[†] Permanent address: Institute of Physics, Department of Structures and Bonding, Czechoslovakian Academy of Sciences, Na Slovance 2, 180 40 Praha 8, Czechoslovakia.

[‡] Permanent address: Department for General Chemistry, The Royal Danish School of Pharmacy, DK-2100 Copenhagen, Denmark.

(1) Petricek, V.; Maly, K.; Coppens, P.; Bu, X.; Cisarova, I.; Frost-Jensen, A. *Acta Crystallogr.* **1991**, *A47*, 210-216.

(2) Lyubovskaya, R. N.; Zhilyaeva, E. I.; Petsoskii, S. I.; Lyubovskii, R. B.; Atovmyan, L. O.; D'yachenko, O. A.; Takhirov, T. G. *JETP Lett.* **1987**, *46*, 149-152.

(3) Cisarova, I.; Maly, K.; Bu, X.; Frost-Jensen, A.; Sommer-Larsen, P.; Coppens, P. *Chem. Mater.*, in press.