aqueous solution proton transfer can be expected for the following conditions: (a) volume of moiety is large compared with the volume of the substituent; (b) electron directing power of the substituent is strong; and (c) substituent does not replace a hydrogen atom which could formerly engage in strong hydrogen bonding to the solvent.

(32) M. Taagepera, W. G. Henderson, R. T. Brownlee, J. L. Beauchamp. D. Holtz, and R. W. Taft, *J. Am. Chem. Soc.*, **94**, 1369 (1972).

(33) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **93**, 7139 (1971).

(34) J. D. Payzant, R. Yamdagni, and P. Kebarle, *Can. J. Chem.*, **49**, 3308 (1971).

(35) P. Kebarle in "Environmental Effects on Molecular Structure and Properties", B. Pullman, Ed., D. Reidel Publishing Co., Dodrecht, Holland, 1976.

(36) K. Hiraoka, E. P. Grimsrud, and P. Kebarle, *J. Am. Chem. Soc.*, **96**, 3359 (1974).

(37) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **95**, 3504 (1973).

(38) J. B. Cumming, M. French, and P. Kebarle, to be submitted for publication.

(39) Experiments to measure the binding energies $XC_6H_4COO^-$–HOH are presently under way. The experimental difficulty in series of this type is that the phenolate or benzoate anion A^- should not be produced by proton abstraction from the respective acid, AH, since in the presence of AH the major proton held dimers are AHA^- and not A^-HOH even when a large excess of HOH is used. This again is a consequence of the hydrogen bond following the acidity. The acidity of the phenols and benzoic acids being much larger than that of HOH leads to the dominance of the AHA^- clusters.

(40) See, for example, E. M. Arnett, F. M. Jones III, M. Taagepera, S. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Am. Chem. Soc.*, **94**, 4724 (1972).

(41) E. M. Arnett, L. E. Small, D. Oancea, and D. Johnston, *J. Am. Chem. Soc.*, submitted for publication.

(42) The above discussion of the substituent entropy effects in aqueous solution was conceived by the present authors on the basis of the mentioned studies of hydrogen bonding $A^- \cdots HOR$ in the gas phase. An examination of the literature showed that similar ideas were expressed earlier.[3] Repetition of the argument in the present form is thought to be useful, since its acceptance does not seem to be widespread.[43]

(43) T. M. Krygowsky and W. R. Fawcett, *Can. J. Chem.*, **53**, 3622 (1975).

(44) F. G. Bordwell, J. E. Bartmess, G. E. Drucker, Z. Margolis, and W. S. Matthews, *J Am. Chem. Soc.*, **97**, 3226 (1975).

(45) W. R. Davidson and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 6125 (1976).

(46) W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 2191 (1970).

(47) *The error* introduced by *the point dipole approximation used* in conventional electrostatic calculations increases with the distance over which the actual charges of the molecule are distributed. A conventional correction is to use higher moments like quadrupole moment, etc. However, the use of net atomic charges as in structure IX is a method that is satisfactory and is more natural to the chemist.

(48) Good theoretical ab initio calculations[49] of $M^+ \cdots OH_2$ ($M^+ = Li^+ \ldots Cs^+$) have shown that the bonding is essentially electrostatic. Thus, Mulliken population analysis showed[49] that there is an electron transfer of only 0.018 and 0.004 e from the water molecule to the Li^+ and K^+ ions, respectively. Therefore application of the Lewis acid/base concept to systems like K^+ and OH_2 with the implied sharing of the pair donated by the base is not helpful, but rather misleading. The situation should be very similar for acetonitrile and Me_2SO.

(49) E. Clementi and H. Popkie, *J. Chem. Phys.*, **57**, 1077 (1972); H. Kistenmacher, H. Popkie, and E. Clementi, *ibid.*, **58**, 1689 (1973); **59**, 5892 (1973).

(50) J. Hine, "Physical Organic Chemistry", McGraw-Hill, New York, N.Y., 1962.

(51) L. R. Mahoney, private communication.

(52) D. H. Fine and J. B. Westmore, *Chem. Commun.*, 273 (1969).

(53) J. H. Richardson, L. M. Stephenson, and J. T. Brauman, *J. Chem. Phys.*, **62**, 1580 (1975).

(54) L. M. Branscomb, *Phys. Rev.*, **148**, 11 (1966).

(55) NOTE ADDED IN PROOF. (a) The prognosis about the propable inapplicability of the ΔE calculations (with STO-3G basis sets) to the isodesmic reactions (eq 1) involving negative ions has proven incorrect. Radom has published such calculations using the closed-shell procedure. In fact Radom's publication includes calculations for proton transfer between some substituted phenols that are generally in good agreement with results in Table IV (L. Radom, *J. Chem. Soc., Chem. Commun.*, 403 (1974)).

(b) A recent reexamination[56] of the assumption $\Delta S°_1 \approx 0$ for the reactions (eq 1) involving proton transfer in negative ions has shown that the resulting error introduced in the $\Delta H°_1$ can be significant. In particular the reaction: $Cl^- + AH = HCl + A^-$, which involves our primary standard HCl, generally has a $T\Delta S° \approx 2$–3 kcal/mol at 600 K because of the appearance of two (external) rotations in HCl which are generally only partially canceled by disappearance of (internal) rotations in $AH \rightarrow A^-$. For this reason the $D(AH) - EA(A)$ values given in Tables III and VI are generally too low by about 2 kcal/mol. For example, the new[57] $D - EA$ for phenol is 34.6 ± 2 kcal/mol and not 33.3 kcal/mol as shown in Tables III and VI.

(56) J. B. Cumming and P. Kebarle, *J. Am. Chem. Soc.*, to be submitted for publication.

Regio- and Stereoselectivity of Chiral Binaphthyl Reductive Aminoalkylation. Rotational Conformation and Electron Distribution of Alkali-Metal Biarylides

O. Eisenstein,[1a] J. P. Mazaleyrat,[1b,d] M. Tordeux,[1c] and Z. Welvart*[1b]

Contribution from the Groupe de Recherche No. 12 and C.E.R.C.O.A., C.N.R.S.,
94320 Thiais, France, and Laboratoire de Chimie Théorique, Bat. 490,
91405 Orsay, France.

Received June 7, 1976

Abstract: The reductive aminoalkylation of 1,1′-binaphthyl by alkali metals and aminonitriles occurs in position 4. According to Hückel calculations, the high regioselectivity and the lack of asymmetric induction, when the reaction is performed with chiral binaphthyl, are in agreement with a flattened intermediate alkali metal binaphthylide. The product obtained by deuterolysis is *trans*-4-aminoalkyl-3-deuterio-3,4-dihydro-1,1′-binaphthyl. The high stereoselectivity of the deuteration and its regioselectivity in an unusual position can be explained by an orbital overlap stabilization of the transition state.

The reactivity of the alkali-metal biphenylide was uncertain for a long time[2,3] as shown by the conflicting results reported on the reduction of the parent hydrocarbon.[4] But a recent work of Harvey et al.[5] proves that this reagent behaves like radical anions derived from other aromatics. These react where electron density is highest and this can be determined by simple Hückel calculations.[2,6-8]

However other problems concerning the reactivity of radical anions formed from diaryl-type aromatic hydrocarbons also have to be elucidated.

(1) The electron distribution in these compounds is conformation dependent and it has been suggested that the twisting of the neutral molecule and of the corresponding radical anion and radical cation could be different.[9] The twisting of the radical anions has to be taken into account in a study of their reactivity.

(2) Some of these aromatics are chiral, and it is therefore worthwhile to examine if in the corresponding radical anion reactions asymmetric induction occurs. Only very few results concerning the properties of chiral radical anions have been reported.[10]

These problems are examined in the present work and 1,1′-binaphthyl, an easily resolvable aromatic hydrocarbon,[11] is used. The reaction studied is a reductive aminoalkylation[12,13] which involves radical anion intermediates similarly to the alkali-metal reductions[2,3,6-8] and the reductive alkylations.[5,14,15] The various steps of this reduction are described in Scheme I.

Scheme I. Reductive Aminoalkylation of Aromatic Hydrocarbons

$$\text{(a) ArH} + \text{M} \rightleftharpoons \underset{\mathbf{1}}{\text{ArH}^{-\cdot}, \text{M}^{+}}$$

$$\text{(b) } \underset{\mathbf{1}}{\text{ArH}^{-\cdot}, \text{M}^{+}} + \underset{\mathbf{2}}{\text{RCN}} \rightarrow \text{ArH} + \text{RCN}^{-\cdot}, \text{M}^{+} \rightarrow \text{R}\cdot + \text{MCN}$$

$$\text{(c) } \underset{\mathbf{1}}{\text{ArH}^{-\cdot}, \text{M}^{+}} + \text{R}\cdot \rightarrow \underset{\mathbf{3}}{\text{RArHM}}$$

$$\text{(d) RArHM} \xrightarrow[\text{or } D_2O]{H_2O} \underset{\mathbf{4}}{\text{RArHH(D)}} + \text{MOH(D)}$$

ArH = naphthalene, anthracene, or in the present work 1,1′-binaphthyl; R = dialkylamino alkyl groups; in the present work $(CH_3)_2N$-C-$(CH_3)_2$.

The steps determining product formation are the radical anion–aminoalkyl radical collapse and protonation (or deuteration) (steps c and d in Scheme I). The structure of product (or products) **4** yields valuable information on the structure and reactivity of the intermediate radical anion **1** and of the organometallic **3**.

Results

When a reductive aminoalkylation of binaphthyl is performed in such a way that the nascent lithium binaphthylide **1** reacts immediately with aminonitrile **2**, the ^{1}H NMR spectra of the crude amines show clearly the presence of only two products, amine **4** and imine **5**. Imine **5** is obtained by reaction of aminonitrile **2** with lithium metal (Scheme II). A similar reaction has already been reported.[12]

Scheme II. Reaction of Lithium Metal with Aminonitrile **2**

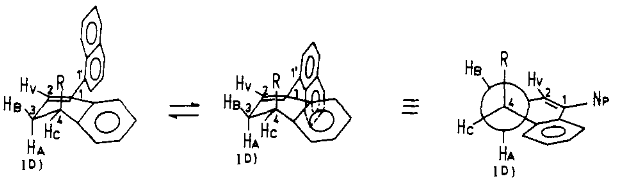
$$2\underset{\mathbf{2}}{(CH_3)_2NC(CH_3)_2CN} + 2\ Li \rightarrow LiCN$$

$$+ [(CH_3)_2NC(CH_3)_2]_2C{=}NLi \xrightarrow{H_2O} \underset{\mathbf{5}}{[(CH_3)_2NC(CH_3)_2]_2C{=}NH}$$

The structural proofs of compound **4** are related below.

^{1}H NMR Identification of Compound 4. The data of the ^{1}H NMR spectra of the main product **4** and of its deuterated analogue **4d** at 40 and 100 °C are reported in Table I. The temperature dependence of the spectra, illustrated in Figure 1, shows the presence of two rotamers **4′** and **4″** (Scheme III), exchanging slowly on a ^{1}H NMR time scale at room temperature. Rotational diastereoisomers such as **4′** and **4″** have been separated by column chromatography.[18] However this was not possible with compound **4**. A sharp melting point is obtained and no separation of the two isomers can be detected by TLC. The failure to separate the two rotamers can be explained in terms of fast exchange rates on a laboratory time scale between **4′** and **4″**.[19]

Scheme III. Structure of Compound 4. According to Previous Work,[13,17] Pseudo-Axial Position Is Assumed for the R Group



4′ 4″ 4

R = $(CH_3)_2N-\overset{1}{C}(CH_3)_2$

Np = Naphthyl

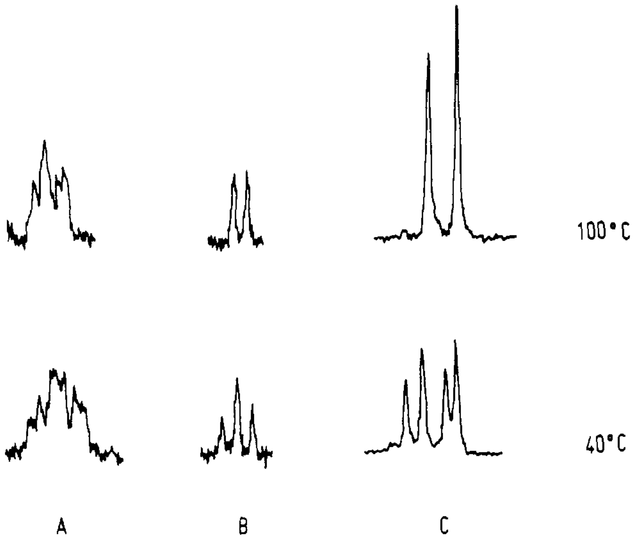


Figure 1. The temperature dependence of the ^{1}H NMR spectra of compounds **4** and **4d**: A, vinylic proton H_V of compound **4**; B, vinylic proton H_V of compound **4d**: C, the $C(CH_3)_2$ moiety signal (A, Varian A60 spectrometer; B and C, Jeol C 60 HL spectrometer).

The ^{1}H NMR data of compounds **4** and **4d** are consistent (a) with the 4 position of the aminoalkyl group R, (b) with the conjugated 1,2 position of the double bond, and (c) with a stereospecific substitution of H_A by deuterium.

This confirms the regioselectivity of the binaphthyl radical anion–aminoalkyl radical collapse (Scheme I, step c), and the high regio- and stereoselectivity of the deuteration of the organometallic intermediate **3** (Scheme I, step d).

Reaction Involving Chiral Binaphthyl. The reductive aminoalkylation of the chiral binaphthyl was performed below 0 °C. At that temperature the half-life time of chiral binaphthyl is about 130 h, but the reaction is almost immediate. The reaction was performed in such a way that the produced alkali metal binaphthylide could be immediately quenched by the aminoalkyl radical produced from aminonitrile (see Experimental Section, procedure a).

The Importance of the Experimental Conditions. The ratio of the main products **4**/**5** depends on the experimental conditions. The kinetic orders of the two competitive processes as shown in Schemes I and II are different.

When the reaction is performed in such a way that the alkali-metal binaphthylide is preformed before reacting with α-aminonitrile **2**, compound **5** is no longer produced. However, even this process yields secondary products owing to a transformation of the lithium binaphthylide into lithium perylenide. This transformation can be followed by a change in color: from red-brown, the lithium binaphthylide solution turns purple, the color of the alkali-metal perylenide, and from this solution perylene could be isolated.[20] This purple solution, reacting with aminonitrile, does not lead to compound **4**.

Discussion

The Aminoalkylation Step. In order to correlate the observed regioselectivity of the reductive aminoalkylation and the spin density distribution of the lithium binaphthylide, the actual twisting of this radical anion has to be taken into consideration. Lithium binaphthylide is expected to be markedly twisted, since in the parent hydrocarbon the planar conformation of the two naphthalene nuclei is 22 kcal/mol less stable than that of the almost perpendicular one.[21] The estimated twist angle is about 75°.[20,22]

Extended Hückel calculation (Figure 2) illustrates clearly the conformational dependence of the electron distribution: a flattening of the molecule reverses the spin densities at the

Table I. The ^{1}H NMR Data of Compounds **4** and **4d** in Toluene-d_8 at 40 °C

Type		Aromatic	H_V[a]	H_A[a]	H_B[a]	H_C[a]	$N(CH_3)_2$	$C(CH_3)_2$
Ratio	**4**	11	1		3		6	6
	4d	11	1		2		6	6
Aspect and coupling constants[b]	**4**	Multiplet	Large partly split triplet[c,d] $^3J_{H_VH_B} = 7$[e] $^3J_{H_VH_A} = 3$[e]	Multiplet $^2J_{H_AH_B} = 16$ $^3J_{H_AH_C} = 8$ $^3J_{H_AH_V} = 3$[f]	Multiplet $^2J_{H_BH_A} = 16$ $^3J_{H_BH_C} = 1$ $^3J_{H_BH_V} = 7$[f]	Multiplet $^3J_{H_CH_A} = 8$ $^3J_{H_CH_B} = 1$	Singlet	4 singlets[d]
	4d	Multiplet	Triplet[c] $^3J_{H_VH_B} = 7$	None	Unresolved multiplet[g]	Large singlet[h]	Singlet	4 singlets[d]
Chemical shifts[i,j]		6.7; 8.3 (6.5; 8.1)	5.9 (6.03)	2.5	3.35	3.07	2.18 (2.31)	1.23; 1.11; 0.93; 0.82 (1.23; 1.13; 1.00; 0.92)

[a] See Scheme III for the significance of H_V, H_A, H_B, and H_C. [b] In hertz, determined at 100 °C, in well-resolved spectra. [c] This structure of triplet arises from the two superimposed doublets for rotamers **4'** and **4''**. A temperature increase simplifies this signal, which appears at 100 °C as a quartet for compound **4** and as a doublet for compound **4d** (see Figure 1). [d] By raising the temperature to 100 °C, the exchange rates between the two rotamers **4'** and **4''** increase and only two methyl signals are observed for the two methyl groups of the $C(CH_3)_2$ moiety. These two methyl groups are diastereotopic because of the presence of an asymmetric carbon in position 4 (see Scheme III) and they remain nonequivalent even at high temperature. [e] According to Karplus[16] the lower value represents the coupling with H_A (dihedral angle ~90°) (Scheme III). [f] By irradiation of H_V, the 7- and 3-Hz couplings disappear. [g] Width at half height ~12 Hz, this signal sharpens by irradiation of H_V. [h] Width at half height ~4 Hz, this signal is not alterated by irradiation of H_V. [i] In parts per million downfield from the internal Me_4Si standard. [j] In $CDCl_3$ for values within brackets.

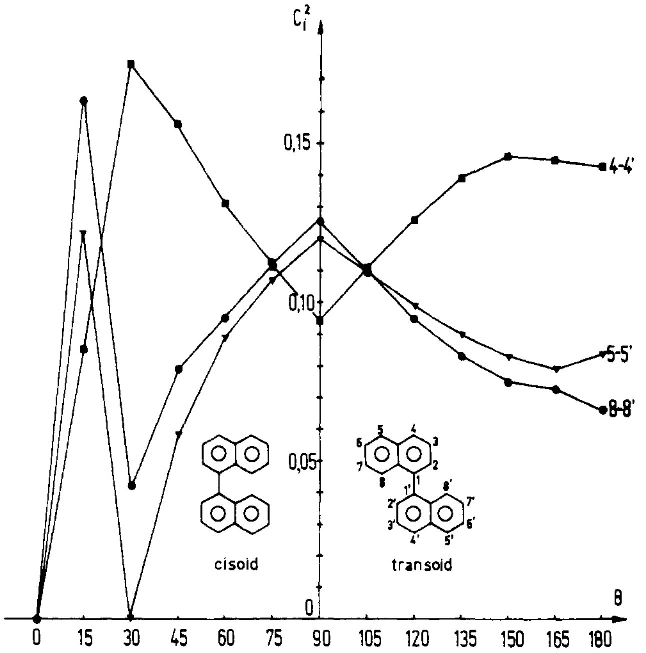


Figure 2. Correlation between the electron distribution and twist angle (θ) of alkali-metal binaphthylide by extended Hückel calculation: $\theta = 0°$, cisoid conformation; $\theta = 180°$, transoid conformation.

positions 4, 5, and 8, and the spin density becomes considerably higher about carbon 4 than at the other positions when the twist angle deviates strongly from 90°.[23]

ESR spectroscopy is generally used to establish experimentally the electron distribution of radical ions. There is an excellent correlation between the hyperfine splitting constants and the calculated electron densities.[8,24-26]

Unfortunately, however, ESR spectra reported for the alkali-metal binaphthylide are contradictory. Three positions, with approximately equal charge densities, have been proposed by Solodovnikov et al.[27] Their spectral data correspond to a highly twisted alkali-metal binaphthylide (Figure 2, positions 8, 5, 4). Only one position of high electron density (position 4) has been proposed by Fu et al.;[28] the ESR spectrum agrees with a nearly planar conformation (see Figure 2). Hnoosch and Zingaro[29] have found also a high hyperfine splitting constant for only one position, but their constant is very different from the previous one.[30]

The conflicting results illustrate the difficulty in obtaining from not a totally resolved ESR spectrum a correlation between electron distribution and hyperfine splitting constants.

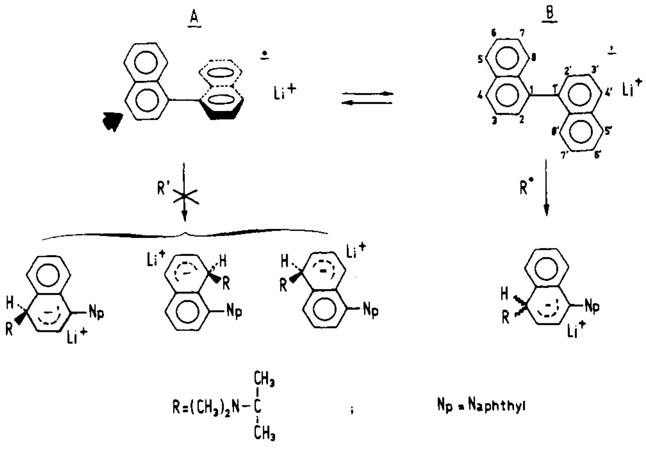
Information on the conformation of the lithium binaphthylide can be obtained by a comparison of the present chemical results with a Hückel calculation as illustrated in Figure 2.

The regioselectivity of the reductive aminoalkylation at position 4 can be explained by a flattening of the molecule, which increases the charge density at this position; however, it was not possible to determine the direction of flattening.

The lack of asymmetric induction is discussed hereafter.

If the radical anion prepared from the chiral binaphthyl remains twisted, an asymmetric induction can be predicted[31] (Scheme IV).

Scheme IV. Correlation between the Geometry of Lithium Binaphthylide and Asymmetric Induction



A front side attack (black arrow in Scheme IV) is hindered only by half of an aromatic nucleus and will occur more readily than a back side attack, which is inhibited by one and a half nuclei. Therefore during the aminoalkylation process, the formation of a chiral center is expected as illustrated in part A of the Scheme IV.

Obviously the hypothesis of a planar conformation leads to opposite conclusions. Attacks on either side are equally probable and the low energy of the resulting conformation involves fast racemization[32] (part B of Scheme IV: this scheme represents a transoid twisting, but obviously the same prediction remains valid for a cisoid conformation).

Therefore, the observed lack of stereoselectivity is also consistent with a flattening of the binaphthyl radical anion.

It is possible that flattening occurs as soon as the binaphthyl reduction step (Scheme I, step a), since the binaphthyl which is recovered from the reaction mixture is racemic (see Experimental Section). However, partial or total racemization may also take place during the work-up process of the reaction mixture.[33]

In a planar conformation, the increased nonbonding interactions can be compensated by a stabilization due to electron delocalization.[34] However, the degree of flattening could not be estimated.

The Protonation Step. The dihydrobiphenyllithium or -sodium **3** (Scheme **I**, ArH = diphenyl) is protonated and alkylated[5] in the usual way for allylic carbanions,[36] resulting in the formation of the less stable unconjugated hydrocarbon. But the dihydrobinaphthylsodium or -lithium **3** presently studied (Scheme I, ArH = binaphthyl) leads to the more stable conjugated product **4**.

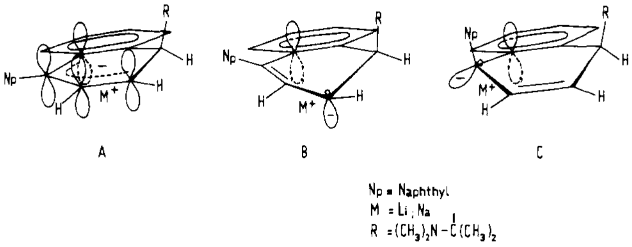
The formation of this product is certainly not due to an equilibration, since deuteration is stereoselective, i.e., without a random redistribution of the deuterium.

The high stereoselectivity of this reaction can be explained as follows.

It is well established that protonation by water involves tight ion pairs rather than loose ion pairs or free ions, since the cation stabilizes the concentration of negative charge on the oxygen atom.[37] Therefore, in order to understand the observed stereoselectivity, the tight ion pair structure must be examined.

Assuming that the most stable conformation is the one with a quasi-axial aminoalkyl group[13,17] and that the tight ion pair is "under the roof" where solvation is not possible,[38] the metallic ion has to be in a trans position relative to the dialkylaminoalkyl R group (Scheme V).

Scheme V. Structure of the Tight Ion Pair **3** (A, planar anion with delocalized sp^2 orbitals; B, trans localized sp^3 orbital in position 3; C, trans localized sp^3 orbital in position 1. For sake of clarity, only one of the aromatic nuclei π-orbitals is represented.)



If the deuteration involves such an ion pair, D_2O has to arrive on the side where the metallic ion is located. Therefore, deuteration occurs in a stereoselective way relative to the R group.

Regioselectivity is the direct consequence of a high trans stereoselectivity. Even if the allylic ion pair is planar (Scheme V, A), some electron localization has to take place in the transition state of the deuteration. The overlap of the localized sp^3 orbital by the π orbitals of the aromatic nucleus can be an important stabilizing factor (Scheme V).

If the localized orbital is assumed to be trans orientated, there is an excellent overlap in position 3 where the localized orbital is parallel to the π orbitals (Scheme V, B), but there can be no overlap in position 1, where the two orbitals are nearly perpendicular (Scheme V, C). This is the reason why the B-like transition state which leads to the conjugated product is the most stable.[39] Orbital overlap has been recognized as an important factor in determining the reaction rate and stereoselectivity.[40]

A quite similar explanation has been proposed for the stereoselectivity of the alkyl and aminoalkyl 9,10-dihydroanthracylsodium[13,41] and for the regioselectivity of the aminoalkyl-dihydronaphthylsodium[42] deuterations. However, it must be emphasized that the selectivity presently observed is considerably higher than the previously reported cases and that it is independent of the metallic ion.[43]

Conclusions

The present results concerning the reductive aminoalkylation of binaphthyl illustrate the usefulness of Hückel calculations in an approximate evaluation of the radical anion geometry from the chemical reactivity.

It can be assumed that the flattening of the radical anion is responsible for the high regioselectivity and the lack of asymmetric induction in the aminoalkylation step. There is also a direct correlation between the unusual regioselectivity and the stereoselectivity of the protonation step. Therefore both steps indicate a direct correlation between regio- and stereoselectivities and such correlations are probably more frequent than it is usually assumed.[45]

Experimental Section

Calculations. Calculations were performed with EXTHUC Program (ICON 8 version).[46]

4-(2-Dimethylaminoisopropyl)-3,4-dihydro-1,1′-binaphthyl (4). (a) In a flame-dried vessel and under a dry argon atmosphere, 1.21 g (0.0108 mol) of aminonitrile **2** dissolved in 50 mL of THF is stirred with 0.16 g (0.023 g atom) of lithium for 10 min at 0 °C. The surface of the lithium turns yellow; 2.44 g (0.0096 mol) of crystalline 1,1′-binaphthyl is subsequently added. The solution turns immediately dark green, but is stirred for 1 h more at 0 °C in order to complete the reaction. The mixture is then quenched with 5 mL of water and the solution turns light yellow-green. After the usual workup (extraction with dilute hydrochloric acid and neutralization with dilute sodium hydroxyde) 1 g of neutral product and 1.98 g of crude amines are isolated. The ^1H NMR spectrum in $CDCl_3$ of this crude product contains only the signals of amines **4** and **5** in a ratio 65:35 as measured from the peak height of the sharp $N(CH_3)_2$ signals at 2.14 and 2.31 ppm.

A second preparation is performed with 300 mg of aminonitrile, 610 mg of binaphthyl, and 50 mg of lithium yields 500 mg of crude amines. The TLC separation of the products, using Kieselgel F 254, PSC Fertigplatten Merck, and 80% pentane-20% ether mixture as solvent, provides the following fractions (detected by UV light) in order of decreasing R_f: (1) three purple and blue spots, 3 mg; (2) yellow-violet spots, 20 mg; the ^1H NMR spectrum of the latter fraction displays aromatic and vinylic protons, two peaks at 2.25 (weak) and 2.17 ppm (strong). (According to the signals of different $N(CH_3)_2$ groups, this fraction could be a mixture of two products resulting from the reductive aminoalkylation of binaphthyl); (3) almost pure **4** (69 mg); (4) 287 mg of pure **4**; (5) 56 mg of product **5**.

(b) Lithium binaphthylide is prepared by stirring for 1 h at room temperature 5 g (0.02 mol) of 1,1′-binaphthyl and 0.17 g (0.024 g atom) of lithium in 100 mL of THF. To the red-brown solution, 1.21 g (0.0108 mol) of α-dimethylamino isobutyronitrile **2** is added and the solution turns dark green. The whole mixture is stirred 1 h more and quenched with 5 mL of water; the solution turns yellow.

The THF is removed under reduced pressure and the remaining product is dissolved in ether. By shaking with 20% aqueous hydrochloric acid, amine **4** hydrochloride precipitates. After dilute sodium hydroxide neutralization and ether extraction, 2.2 g of pure amine **4** is obtained (60% yield). From the remaining mother liquor 1.19 g of impure amine **4** is recovered.

From the ether solution of neutral products, pure binaphthyl can be recovered by crystallization in benzene.

Amine **4**: mp 142 °C (after crystallization in ethanol). Anal. Calcd for ($C_{25}H_{27}N$): C, H, N (for ^1H NMR spectrum see Figure 1 and Table I). Analytical TLC (silica gel) using various solvents (pentane, ether, ethyl acetate) proves the purity of the product; no separation of the two rotamers **4′** and **4″** can be detected.

***trans*-3-Deuterio-4-(2-dimethylaminoisopropyl)-3,4-dihydro-1,1′-binaphthyl (4d).** As in (b), but using 3 mL of D_2O instead of H_2O. Reaction b repeated, but 0.48 g of sodium was used instead of 0.17 g of lithium and 3 mL of D_2O instead of H_2O, mp 142 °C (ethanol). The ^1H NMR data are in Table I. The mass spectrum of this compound at 70 eV shows a base peak *m/e* 86, $(CH_3)_2N^+{=}C(CH_3)_2$, and a small molecular peak at *m/e* 342, corresponding to the monodeuterated product. The d_1 percentage estimated from the (M − 15) peaks (loss of a methyl) is 92%.

Conversion of Lithium Binaphthylide into Lithium Perylenide. Reaction b is repeated, but the red-brown solution of lithium binaphthylide is stirred overnight. The solution turns purple. The addition of aminonitrile gives a dark green solution from which, by the usual workup, a new product is isolated. Its ^1H NMR spectrum displays nine aromatic signals (a broad multiplet between 7.1 and 8.2 ppm), one vinylic signal (a quartet at 6.67 ppm, J = 7 and 3 Hz), three allylic or benzylic proton resonances (a broad signal between 2.3 and 3.7 ppm), a sharp signal for $N(CH_3)_2$ at 2.28 ppm, and two diastereotopic methyl signals at 0.93 and 0.84 ppm (internal Me_4Si standard in $CDCl_3$ solution).

The decrease in the number of aromatic protons relative to compound **4** and the presence of only two diastereotopic methyl signals instead of four is in agreement with the structure of a compound resulting from the reductive aminoalkylation of perylene. The presence of this compound can be detected in the crystallization mother liquor in the preparation of compound **4** by method b, but it is absent in method a.

Reaction with the Chiral Binaphthyl. Binaphthyl was resolved by Pincock's method;[11] the sample of (−)-(*R*)-1,1′-binaphthyl used in the reaction has $[\alpha]^{25}$ −82.8° at 589 nm in benzene (Perkin-Elmer 141 M polarimeter, 1-dm long tube; *c* 0.007 g/mL), so the optical purity of our sample is 36%.[11]

The reductive aminoalkylation was performed according to method a. The recovered 1,1′-binaphthyl and amine **4** do not show rotation from 546 to 589 nm (absorption prevents measurement at 435 and 365 nm).

Di(α-dimethylaminoisopropyl)ketimine (5). α-Dimethylaminoisobutyronitrile **2** (2 g, 0.02 mol) and 0.21 g (0.03 g atom) of lithium in 12 mL of THF are stirred overnight. After quenching the reaction with 1 mL of H_2O, the product is dissolved in ether, washed with water, dried, and distilled: bp 150 °C (20 mm); yield, 1.3 g (76%); Anal. Calcd for ($C_{11}N_3H_{25}$): C, N, H; ^1H NMR spectrum (in $CDCl_3$, Me_4Si as internal reference), two peaks of equal intensity at 2.14 ppm for $N(CH_3)_2$ and 1.25 ppm for $C(CH_3)_2$, and a broad signal at 9.35 ppm for N–H; IR 1608 (strong) C=N stretching,[47] 3400 cm^{-1} (weak) N–H stretching;[48] mass spectrum, no molecular peak at 70, 18, or 12 eV, base peak at 70 eV *m/e* 86, corresponding to $(CH_3)_2$-$N^+{=}C(CH_3)_2$, other principal peaks *m/e* 70, 85, 112, 139, 154.

Acknowledgment. We are grateful to Professor R. Hoffmann (Cornell University) for the EXTHUC Program, to Dr. Chenon, Dr. Gaudry, and Dr. Marquet (C.N.R.S., Thiais) for helpful comments, and to Dr. de Villardi for linguistic criticism of the manuscript.

References and Notes

(1) (a) Laboratoire de Chimie Théorique; (b) address for correspondence: Groupe de Recherche No. 12; (c) C.E.R.C.O.A.; (d) part of the Ph.D. Thesis of J. P. Mazaleyrat, April 30, 1974, No. CNRS A.O. 7747.

(2) A. Streitwieser Jr. and S. Suzuki, *Tetrahedron*, **16**, 153 (1961).

(3) S. Hayano and M. Fujihira, *Bull. Chem. Soc. Jpn.*, **44**, 2046 (1971).

(4) I. P. Egorov, E. P. Kaplan, Z. I. Letina, V. A. Shiapochnikov, and A. D. Petrov, *J. Gen. Chem. USSR*, **28**, 3284 (1958); W. Hückel and R. Schwen, *Chem. Ber.*, **89**, 150 (1956).

(5) D. F. Lindow, C. N. Cortez, and R. G. Harvey, *J. Am. Chem. Soc.*, **94**, 5406 (1972).

(6) H. E. Zimmerman, *Tetrahedron*, **16**, 169 (1961).

(7) A. Streitwieser, Jr., "Molecular Orbital Theory for the Organic Chemist", Wiley, New York, N.Y., 1961, p 425.

(8) N. L. Holy, *Chem. Rev.*, **74**, 243 (1974].

(9) F. C. Adam and L. J. Aarons, *Can. J. Chem.*, **50**, 1427 (1972); R. Stosser, P. Janietz, C. Jung, J. Sauer, and J. Preidel, *J. Prakt. Chem.*, **315**, 629 (1973); L. O. Wheeler, K. S. V. Santhanam, and A. J. Bard, *J. Phys. Chem.*, **70**, 404 (1966).

(10) W. Bruning and S. I. Weissman, *J. Am. Chem. Soc.*, **88**, 373 (1966); R. Chang and S. I. Weissman, *ibid.*, **89**, 5968 (1967); S. I. Weissman and R. Chang, *ibid.*, **94**, 8683 (1972); O. Ito, A. Tajiri, and M. Hatano, *Chem. Phys. Lett.*, **19**, 125 (1973).

(11) R. E. Pincock and K. R. Wilson, *J. Am. Chem. Soc.*, **93**, 129 (1971); *ibid.*, **97**, 1474 (1975).

(12) C. Fabre and Z. Welvart, *Tetrahedron Lett.*, 3801 (1967).

(13) C. Fabre, M. Hadj Ali Salem, and Z. Welvart, *Bull. Soc. Chim. Fr.*, 3814 (1972); *ibid.*, 3820 (1972).

(14) R. G. Harvey, *Synthesis*, 161 (1970); R. G. Harvey, L. Arzadon, J. Grant, and K. Urberg, *J. Am. Chem. Soc.*, **91**, 4535 (1969).

(15) R. G. Harvey, *J. Org. Chem.*, **36**, 3306 (1971).

(16) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry", Holden Day, San Francisco, Calif., 1966, p 108.

(17) A. W. Brinkmann, M. Gordon, R. G. Harvey, P. W. Rabideau, J. B. Stothers, and A. L. Ternay Jr., *J. Am. Chem. Soc.*, **92**, 5912 (1970); D. Cohen, L. Hewitt, and I. T. Millar, *Chem. Ind.* (*London*), 1532 (1966); J. MacMillan and E. R. Walker, *Chem. Commun.*, 1031 (1969); M. L. Caspar, J. N. Seiber and K. Matsumoto, Abstracts, 146th National Meeting of the American Chemical Society, Denver, Colo., 1964, No. C-30.

(18) W. T. Ford, T. B. Thompson, K. A. J. Snoble, and J. M. Timko, *J. Am. Chem. Soc.*, **97**, 95 (1975).

(19) Taking into account the chemical shift difference $\Delta\nu$ (1.2 and 4.2 Hz at 60 MHz, respectively) of the coalescent diastereotopic methyl signals, and their line widths (1.2 and 2.2 Hz), a rough evaluation of the activation energy at the coalescence temperature (70 and 65 °C, respectively) can be calculated as ca. 20 kcal/mol from Jaeschke et al.'s diagram (A. Jaeschke, M. Muensch, H. G. Schmid, H. Friebolin, and A. Mannschreck, *J. Mol. Spectrosc.*, **31**, 14 (1969)).

(20) S. P. Solodovnikov, S. T. Ioffe, Yu. B. Zaks, and M. I. Kabachnik, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 442 (1968).

(21) A. K. Colter and L. M. Clemens, *J. Phys. Chem.*, **68**, 651 (1964); R. E. Carter and L. Dahlgren, *Acta Chem. Scand.*, **23**, 504 (1969).

(22) X-ray analysis shows a cis configuration with an angle of 68° between the planes of the two naphthalene residues (K. A. Ker and J. M. Robertson, *J. Chem. Soc. B*, 1146 (1969)). However, a value of 48° was calculated from molecular Kerr constants (R. J. W. Lefevre, A. Sundaram, and K. M. S. Sundaram, *J. Chem. Soc.*, 3180 (1963)).

(23) Applying the known cosine correlation between a twist angle and bond integrals (cf. ref 7, p 105) even a simple Hückel calculation demonstrates clearly the strong increase of the charge density differences at positions 4, 5, and 8, but in the proximity of the perpendicular conformation a reverse order in charge densities does not appear.

(24) J. R. Bolton in "Radical Ions", E. T. Kaiser and L. Kevan, Ed., Interscience, New York, N.Y., 1968, pp 1–33.

(25) F. Gerson and J. Hammons in "Nonbenzenoid Aromatics", Vol. 2, J. P. Snyder, Ed., Academic Press, New York, N.Y., 1971, pp 82–159; ref 7, pp 150–165.

(26) Reference 7, pp 153–164.

(27) S. P. Solodovnikov and M. I. Kabachnik, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 458 (1973).

(28) K. H. Fu, H. Y. Sheng, and C. L. P'an, *Chem. Abstr.*, **64**, 18 747h (1966).

(29) M. H. Hnoosh and R. A. Zingaro, *J. Am. Chem. Soc.*, **92**, 4388 (1970).

(30) The attribution[29] of the highest electron density to position 8 is based on Fukui et al.'s (*J. Chem. Phys.*, **22**, 1433 (1954)) calculations of the electron distribution of naphthalenes α-substituted by electron-withdrawing groups. Extended Hückel calculations predict the *same* position for the highest electron density with 90° twist angle between the two naphthalene nuclei (see Figure 2).

(31) Geometric enantiomerism is not always most appropriate for asymmetric induction, however there are several reports on such an induction in the reaction of atropisomers as well as in the transformation of an axial asymmetry into a centroasymmetry (H. Joshua, R. Gans, and K. Mislow, *J. Am. Chem. Soc.*, **90**, 4884 (1968); K. Mislow, V. Prelog, and K. Scherrer, *Helv. Chim. Acta*, **41**, 1410 (1958); J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions", Prentice-Hall, Englewood Cliffs, N.J., 1971, p 384.

(32) F. H. Westheimer in "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, N.Y., 1956, pp 523–555.

(33) A recent communication (O. Ito and M. Hatano, *Chem. Lett.*, 39 (1976)) which appears after the submission of the present work for publication points out the fast racemization of alkali-metal binaphthylide.

(34) Calculations predict a 1–2 kcal/mol stabilization of the planar conformation in biphenyls *p,p*′-substituted by electron donating *and* electron withdrawing groups (J. Pedersen, *Acta Chem. Scand.*, 3181 (1972)). In the completely planar anions obtained by reduction of the cyclooctatetraene octadehydro[24]annulene, the stabilization of the π-electron system overrides important strain energies.[35]

(35) Reference 7, p 282, and R. M. McQuikin, P. J. Garratt, and F. Sondheimer, *J. Am. Chem. Soc.*, **92**, 6682 (1970).

(36) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", 2nd ed, Cornell University Press, Ithaca, N.Y., 1969, pp 826 ff; G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955); J. Hine, *ibid.*, **88**, 5525 (1966); R. B. Bates, D. W. Cosselink, and J. A. Kaczynski, *Tetrahedron Lett.*, 199 (1967).

(37) S. Bank and B. Bockrath, *J. Am. Chem. Soc.*, **93**, 430 (1971).

(38) D. Nicholls and M. Szwarc, *J. Am. Chem. Soc.*, **88**, 5757 (1966).

(39) The C-like transition state (Scheme V) should also be destabilized by the nonbonding interactions of the 1,4-quasi-diaxial substituents (E. J. Panek and T. J. Rodgers, *J. Am. Chem. Soc.*, **96**, 6921 (1974)), but these inter-

actions are not important enough to destabilize this type of transition state in the reductive alkylation of diphenyl.
(40) A. Streitwieser Jr., R. A. Caldwell, and M. G. Granger, *J. Am. Chem. Soc.*, **86**, 3574 (1964); P. Lansbury, *Acc. Chem. Res.*, **2**, 211 (1969); C. Fabre, M. Hadj Ali Salem, J. P. Mazaleyrat, A. Tchapla, and Z. Welvart, *J. Organomet. Chem.*, **87**, 9 (1975); M. Daney, R. Lapouyade, M. Mary, and H. Bouas Laurent, *ibid.*, **92**, 267 (1975).
(41) R. G. Harvey and L. Arzadon, *Tetrahedron*, **25**, 4887 (1969); R. Lapouyade and P. Labandibar, *Tetrahedron Lett.*, 1589 (1970); R. Lapouyade, P. Labandibar, and H. Bouas Laurent, *ibid.*, 979 (1971); R. Lapouyade, M. Mary, H. Bouas Laurent, and P. Labandibar, *J. Organomet. Chem.*, **34**, 3958 (1969).
(42) C. Fabre, M. Hadj Ali Salem, and Z. Welvart, *Bull. Soc. Chim. Fr.*, 3825 (1972).
(43) However, in complete agreement with a referee's comment, we have to point out that the actual role of the protonating agent also has to be elucidated; these reagents play an important role in the regio- and stereoselectivities of benzylic-type carbanion protonation.[44]
(44) G. A. Russel, *J. Am. Chem. Soc.*, **81**, 2017 (1959); R. G. Harvey, D. F. Lindow, and P. W. Rabideau, *ibid.*, **94**, 5412 (1972); R. G. Harvey, D. F. Lindow, and P. W. Rabideau, *Tetrahedron*, **28**, 2909 (1972).
(45) A regio- and stereoselectivity correlation has already been proposed in nucleophilic reactions with hard and soft bases (Y. Maroni-Barnaud, M. C. Roux-Schmitt and J. Seyden-Penne, *Tetrahedron Lett.*, 3129 (1974); J. G. Kyriakakou, M. C. Roux-Schmitt, and J. Seyden-Penne, *Tetrahedron*, **31**, 1883 (1975).
(46) R. Hoffmann, *J. Chem. Phys.*, **29**, 1397 (1963).
(47) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Methuen, 1964, p 267.
(48) Reference 47, p 252.

Electrogenerated Chemiluminescence. 29. The Electrochemistry and Chemiluminescence of Chlorophyll a in *N,N*-Dimethylformamide Solutions

Tetsuo Saji and Allen J. Bard*

Contribution from the Department of Chemistry, University of Texas at Austin, Austin, Texas 78712. *Received September 9, 1976*

Abstract: The electrochemistry and ecl of chlorophyll a (Chl a) have been studied in highly purified DMF solutions. Cyclic voltammetric and coulometric experiments demonstrate that both the radical anion, (Chl a)$^{-}\cdot$, and the dianion, (Chl a)$^{2-}$, are fairly stable even under bulk electrolysis conditions in the absence of proton donors and oxygen. The protonation of (CHl a)$^{-}\cdot$ and (Chl a)$^{2-}$ by hydroquinone was also studied. Luminescence was observed for the reduction of Chl a in the presence of oxygen, but not for the Chl a anion-cation annihilation in the absence of oxygen. Chemiluminescence on mixing a solution of (Chl a)$^{-}\cdot$ and oxygen was also observed.

Chlorophyll a (Chl a) plays an important role in photosynthesis in the initial redox events following the absorption of light. Thus the nature and reactions of the oxidized and reduced forms of Chl a and the potentials associated with the electron-transfer processes of this molecule have been the subject of a number of investigations. Several authors have discussed the electrochemical behavior of Chl a.[1-7] The oxidation[5-7] of Chl a in aprotic solvents (e.g., CH_2Cl_2) occurs with the reversible formation of the radical cation which is stable even for time scales characteristic of bulk electrolysis. The reduction, which has been studied at a mercury electrode, shows two one-electron waves, similar to those observed with other metal porphyrins.[8,9] These latter results suggested that the radical anion formed at the first wave [(Chl a)$^{-}\cdot$] was not very stable. Thus Berg and Kramarčzyk[3] observed some reoxidation of (Chl a)$^{-}\cdot$ in *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (Me_2SO) using the Kalousek commutator technique and estimated the half-life of the radical anion as between 0.01 and 0.1 s. The second reduction wave for Chl a was irreversible. Similarly, Kiselev et al.[4] reported, by using cyclic voltammetry, that the first reduction wave of Chl a in DMF was quasireversible and the second wave was irreversible. Felton et al.[2] reported that controlled-potential coulometric reduction of Chl a at a Pt electrode in Me_2SO at potentials of the first wave yielded an n_{app} value of 1.1 to 1.3. However, the solution produced by reduction could neither be reduced further at potentials of the second wave nor oxidized at potentials at the foot of the first wave. Spectroscopic examination of the reduced solution suggested that (Chl a)$^{-}\cdot$ decomposed by loss of a hydrogen atom (at the 10 position) to form the phase test intermediate; the hydrogen atom acceptor was not identified. The instability of (Chl a)$^{-}\cdot$ and (Chl a)$^{2-}$ as compared with the relative stability of the reduced forms of other metalloporphyrins and the free porphins[8-11] suggested that further investigation of the electrochemical reduction of chlorophyll be undertaken.

The question of ecl in chlorophyll systems is also of interest. Radical ion annihilation luminescence has been observed for α, β, γ, δ, tetraphenylporphin (TPP),[10] and for PtTPP and PdTPP.[11] Fairly extensive experiments in our laboratories failed to show ecl from Chl a in several solvents with careful purification and deaeration.[12] However, Krasnovskiĭ and Litvin[13] reported studies of Chl a in DMF with LiCl supporting electrolyte in which ecl was observed both upon cycling the potential of a Pt electrode between the oxidation and reduction waves (i.e., radical ion annihilation ecl) and upon reduction of Chl a in the presence of oxygen.

In this paper we describe experiments which demonstrate that both (Chl a)$^{-}\cdot$ and (Chl a)$^{2-}$ are quite stable in purified DMF and discuss the conditions for observing chemiluminescence in (Chl a)-containing systems.

Experimental Section

Chlorophyll a Separation.[14-15] Chl a was isolated from spinach leaves. After extraction with 80% acetone, the pigments were adsorbed on talc, eluted with ethyl ether, and separated by chromatography on a column of fine powdered sugar. To remove yellow compounds, the adsorbed pigments were washed with 1:1 *n*-pentane:benzene. Chl a and Chl b were further separated chromatographically by washing with *n*-pentane containing 0.5% 1-propanol. The Chl a zone was eluted with ethyl ether and dried on a vacuum line for 1 day, then stored in a drybox under a helium atmosphere. The final separation was carried out under subdued light, and the Chl a was stored in the dark.

Reagents. DMF was first purified by stirring for several days over molecular sieves and then using the procedure reported previously, method A.[16] For further purification, the solvent containing supporting electrolyte was treated with neutral alumina as recommended