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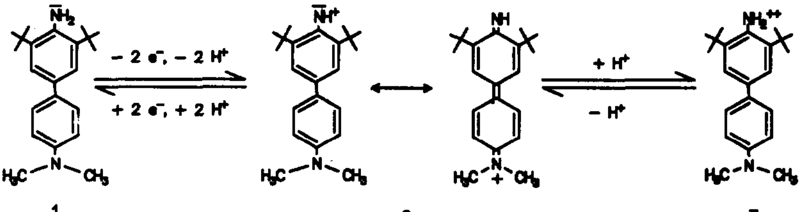
ELECTROCHEMISTRY OF ANILINES. PART 5*. SPECTROSCOPIC AND ELECTROCHEMICAL CHARACTERIZATION OF A PERSISTENT BIPHENYLYL NITRENIUM ION

Anton Rieker and Bernd Speiser
Universität Tübingen, Institut für Organische Chemie, Auf der Morgenstelle 18, D-7400 Tübingen 1, FRG

Summary – A persistent biphenylyl nitrenium ion is generated from 3,5-di-*tert*-butyl-4'-dimethylaminobiphenylyl-4-amine by anodic oxidation. It is characterized by UV and ^{1}H-NMR spectroscopic as well as electrochemical methods.

Introduction. Nitrenium ions are important intermediates in the anodic oxidation of amines. While these ions have been directly observed starting from secondary anilines[2, 3], no characterization of nitrenium ions derived from primary anilines has been reported to our knowledge. Stabilization of these species may be attempted by increasing the resonance system and/or substitution with strongly electron donating groups. Persistency may be obtained by preventing dimerization through bulky *ortho*-substituents. In this paper, we report on the spectroscopic and electrochemical characterization of a persistent biphenylyl nitrenium ion **2** derived from 3,5-di-*tert*-butyl-4'-dimethylaminobiphenylyl-4-amine (**1**). The characterization of **2** (and other nitrenium ions of this type) by chemical reactions will be published separately.



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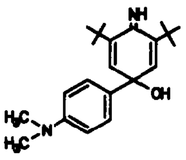

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Results and Discussion. Aniline **1** (for synthesis and purification of this compound, see[4]) was anodically oxidized in acetonitrile/0.1 M NEt_4ClO_4 at a platinum electrode (potential: +1.0 V *vs.* SCE) in a three compartment cell in the presence of a ten-fold excess of 2,6-lutidine (lu). After 2 F/mole were passed, the current reduced to its background value. The resulting deep purple solution was investigated by UV and ^{1}H-NMR spectroscopy as well as cyclic voltammetry and coulometry. Separation of the product from the supporting electrolyte without decomposition was not possible.

UV *spectroscopy* reveals a single band at $\lambda_{max} = 502$ nm corresponding to the purple colour of the solution. Upon addition of aqueous perchloric acid the solution turns into an orange brown ($\lambda_{max} = 464$ nm). This absorption corresponds to dication **3**, formed by protonation of **2**. The protonation is reversible: after addition of more lu the purple colour of **2** shows up again.

Of course, the site of protonation may also be the $(CH_3)_2N$ group or there may be an equilibrium between the forms protonated at either one of the two nitrogen atoms. No distiction between these possibilities can be made from the UV spectra alone. Species **3** has also been obtained by anodic or chemical oxidation of aniline **1** in neutral acetonitrile[5]. It has been confirmed by spectroelectrochemistry that the UV spectrum of **3** is identical to that of the two-electron oxidation product of **1**[5].

^{1}H-NMR *spectra* of **2** were recorded in CD_3CN. Compared to both **1** and iminoquinol **4** (Table 1) the signals are shifted downfield, as is expected for a distribution of the positive charge over both rings of the biphenyl system

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*Part 4: Ref.[1]

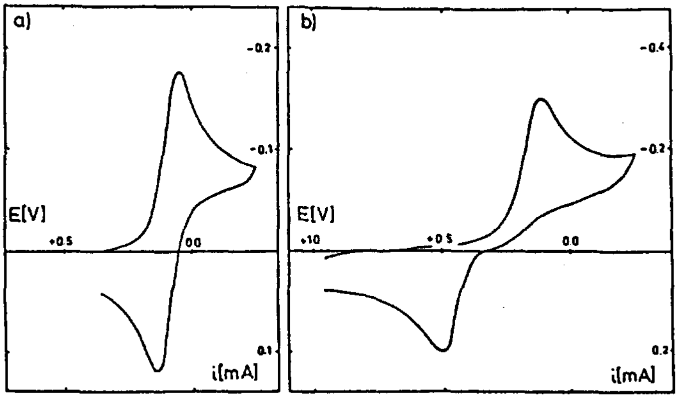

Figure 1: Cyclic voltammograms of **2** in neutral [a)] and acidic [b)] acetonitrile.

and the $(CH_3)_2N$ substituent (only two of the possible resonance structures of **2** are shown above). Two *t*-butyl signals are observed, indicating a non-linear structure of the $-NH^+$ (=NH) moiety.

Cyclic voltammetry of **2** shows a reversible one-electron reduction at $E^0 = +0.111$ V (Figure 1a). The peak potential difference ΔE_p is 61 ± 4 mV, while the peak current ratio $i_p^{ox}/i_p^{red} = 0.88 \pm 0.05$. The deviation of this value from unity indicates slow decomposition of the resulting nitryl radical. A combination[6] of the CV results with chronoamperometric data gives $n = 0.8 \pm 0.2$.

After addition of acetic acid — which does not protonate **2**, as shown by the fact that the UV spectrum of the solution does not change — the chronoamperometric reduction current increases to twice its value. A cyclic voltammogram of this solution is shown in Figure 1b. The reduction peak is shifted to more positive values due to a fast follow-up reaction. During the reverse scan, the oxidation peak of **1** is found. Thus, in a moderately acidic medium **2** is reduced in an overall two electron transfer to the aniline **1**.

Table 1: ^{1}H-NMR shift values of **1**, **2**, and **4** (δ in ppm from TMS).

	protons				
compound	*t*-butyl	$(CH_3)_2N$	ring B$^{a)}$	ring A$^{b)}$	N-H
1$^{c)}$	1.44	2.91	7.13$^{d)}$	7.36	4.21
2$^{e)}$	1.45/1.49	3.59	7.82$^{d)}$	7.61	11.86
4$^{c)}$	1.30	2.91	6.84$^{d)}$	6.10	9.95

$^{a)}$ ring bearing $(CH_3)_2N$; $^{b)}$ ring bearing *t*-butyl groups; $^{c)}$ in $CDCl_3$; $^{d)}$ A_2B_2 system, $J \approx 9$ Hz; $^{e)}$ in CD_3CN.

This result is confirmed by ***bulk electrolysis*** and ***constant potential coulometry***: aniline **1** is oxidized to **2** as described above. To the resulting solution acetic acid is added. After reduction at +0.05 V and passage of 82 % of the oxidation charge, 82 % of the aniline is recovered with some material lost due to diffusion into the counter electrode compartment.

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