Brief Communications

Reversible dimerization of 9-cyano-10-methylacridinyl radical

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The electrochemical reduction of the 9-cyano-10-methylacridinium cation in acetonitrile yielded the corresponding radical, which was rather stable at 20 °C and gave a resolved ESR spectrum. This radical reversibly dimerized in the temperature range from 20 to −30 °C.

Key words: acridine, hydride transfer, dimerization, radical, ESR spectroscopy, electroreduction.

The transfer of a hydride-type active hydrogen from an sp^3-hybridized carbon atoms occurring in many chemical and biochemical processes is actively discussed in the literature.[1—5] Compounds of the dihydropyridine series, in particular, 9,10-dihydroacridine derivatives, are widely used as models convenient for mechanistic studies of hydride transitions.[2,5]

Previously, it has been shown that oxidation of 9-cyano-10-methyl-9,10-dihydroacridine (**1**) follows a stepwise EPE path (electron—proton—electron) including intermediate formation of a radical cation (**2**) and radical (**3**). The 9-cyano-10-methylacridine (**4**) is formed as the final product[6,7] (Scheme 1).

A cyclic voltammetry study of this process has shown that cation **4** in MeCN—0.1 *M* Et_4NClO_4 is reversibly reduced at a potential of −0.42 V *vs.* Fc/Fc^+ to give neutral 9-cyanoacridinyl radical **3**, which lies on the reaction coordinate of the stepwise hydride transfer.

The reduction of cation **4**, obtained by the synthetic route, in an electrochemical cell placed in the cavity of an ESR spectrometer resulted in a spectrum (a_N^{10}, 0.38 mT; a_N^{CN}, 0.149 mT; $a_{3\,H}^{Me}$, 0.3 mT; $a_{2\,H}^{1,8}$, 0.3 mT; $a_{2\,H}^{3,6}$, 0.236 mT) corresponding to the previously reported[8,9] 9-cyanoacridinyl radical **3**. As the temperature is reduced from ~20 to −30 °C, the intensity of the ESR signal decreases due to the formation of dimers; when the

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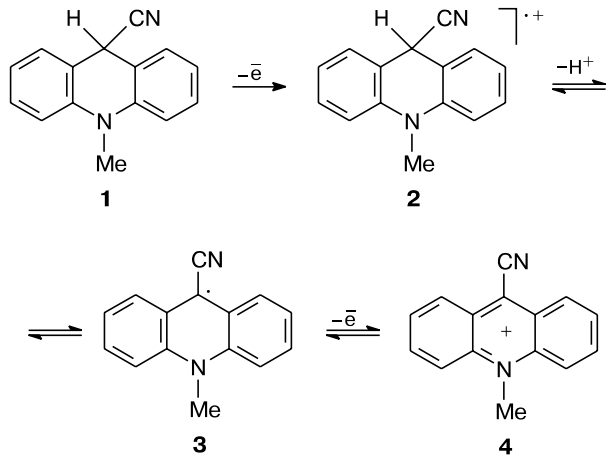
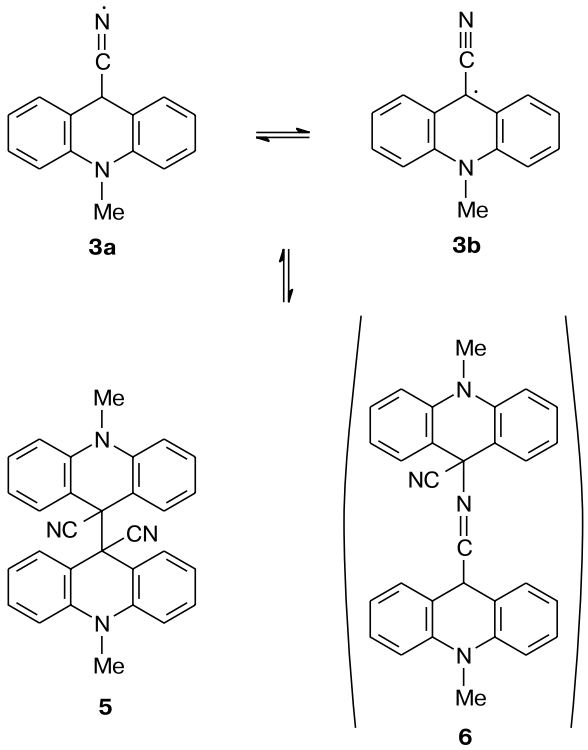
Scheme 1



temperature is raised again, the spectrum returns to the initial state. Thus, dimerization of radical **3** is reversible, and at room temperature, the equilibrium is shifted toward the radical monomer. The presence of the cyano group in position 9 of acridine stabilizes radical **3** through charge and spin density delocalization. This is indicated by the much more positive reduction potential of cation **4** with respect to unsubstituted *N*-methylacridinium cation (−0.82 V). The nitrile group appears to participate directly in the dimerization. The formation of two dimerization products, namely, compounds **5** and **6**, may be expected (Scheme 2).

Scheme 2



The existence of the dimer—monomer equilibrium for 9-cyanoacridinyl radical may imply the presence of such equilibrium also for other acridine derivatives. The available published data[4–10] suggest a shift toward the dimers upon a decrease in the steric restrictions and electron-withdrawing properties of the 9-substituent in the acridinyl radical.

Experimental

Cyclic voltammograms were recorded using a PI-50-1 potentiostat with an H 307/2 *xy*-recorder. A glassy carbon disc electrode (2 mm in diameter) was used as the working electrode. The ferrocene—ferricenium system was used as the internal standard with an $Ag/AgNO_3$ reference electrode in acetonitrile. Dissolved oxygen was removed by bubbling argon through the solution at 22 °C. ESR studies combined with electrolysis were carried out in a setup comprising a CE/X-2544 ESR spectrometer, a PI-50-1 potentiostat, and an electrochemical cell. A platinum plate served as the working electrode, a platinum wire was an auxiliary electrode, and a silver wire was used as the reference electrode. The solutions were deaerated by the freezing—evacuation—thawing cycle repeated three times. The 9-cyano-10-methylacridinium cation was prepared by a reported procedure.[6]

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