

## Radical anions and dianions of 3,3'-bi(2-R-5,5-dimethyl-4-oxopyrrolinyldene) 1,1'-dioxides

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3,3'-Bi(2-R-5,5-dimethyl-4-oxopyrrolinyldene) 1,1'-dioxides (R = CF<sub>3</sub>, Me, Ph, and Bu<sup>t</sup>), which represent cyclic nitrons linked by the conjugated C=C bond, were shown to be strong electron-acceptors. The mechanism of their electrochemical reduction is the EE-type process including the consecutive formation of radical anions and dianions, which are stable under standard conditions. The radical anions of dinitrons, which are stable at 298 K and whose nitron group is not a part of the aromatic  $\pi$ -system and is not conjugated with it, were obtained for the first time and characterized by ESR spectroscopy in combination with quantum-chemical calculations.

**Key words:** 3,3'-bi(2-R-5,5-dimethyl-4-oxopyrrolinyldene) 1,1'-dioxides, cyclic nitrons, electrochemical reduction, radical anions, dianions.

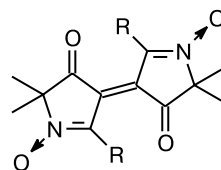
An interest in studying stabilized radical ions of cyclic nitrons is related, first of all, to problems of revealing possible routes of formation of stable nitroxyl radicals from nitrons.<sup>1</sup>

The necessary condition for the efficient use of cyclic *N*-oxides as precursors of nitroxyl radicals is their ability to undergo redox transformations under mild conditions involving no nucleophilic (electrophilic) reagents, which participate in the reaction, and retaining unchanged the structure of initial *N*-oxides.

Potentials of the electrochemical reduction (PER) of *N*-oxides vary in rather wide limits: the PER of heteroaromatic *N*-oxides, viz., phenazine, acridine, quinoxaline, and pyrazine derivatives, change from –0.85 V to –1.90 V (in DMF vs. saturated calomel electrode (SCE)),<sup>2–4</sup> and the PER of acyclic  $\alpha$ -aryl-*N*-alkyl(aryl)nitrons and cyclic nitrons, viz., pyrroline and isoindole derivatives, range from –1.80 V to –2.30 V (in DMF vs. SCE).<sup>5–8</sup> In aprotic media, the first step of reductive electrode processes of mono- or *N,N*-dioxides is a one-electron process.\* However, the formation of cyclic *N*-oxide radical anions (RA) stable at 298 K are very rare, and the first wave of their reduction is irreversible.<sup>2,4–6,8</sup> The reversible electrochemical reduction (ECR) of 1,1,3-triphenyl-*N*-oxide was mentioned.<sup>5</sup> However, the ESR spectrum of the corresponding RA was not detected down to –40 °C. In turn, the ECR of *N*-oxides of phenazine, acridine, quinoxaline,

and pyrazine are characterized by the corresponding RA, and the coupling constants with the <sup>14</sup>N nuclei and protons of the aromatic system were determined.<sup>3</sup> Published data on the formation of stable RA of mono- or dinitrons, in which the nitron group is not directly conjugated with the aryl fragment, are lacking.

3,3'-Bi(2-R-5,5-dimethyl-4-oxopyrrolinyldene) 1,1'-dioxides **1–4** formed due to the smooth oxidation of the corresponding pyrrolinones<sup>9</sup> have the  $\pi$ -conjugation chain including both nitron groups. The extension of the graph of the  $\pi$ -system of the corresponding derivatives compared to the initial pyrrolinones should enhance the electron-acceptor ability of dimers **1–4** and favor the stabilization of their RA, which should be sufficient for measuring ESR spectra. Therefore, we studied the peculiarities of ECR of compounds **1–4** in DMF by cyclic voltammetry (CV).



R = CF<sub>3</sub> (**1**), Me (**2**), Bu<sup>t</sup> (**3**), Ph (**4**)

### Experimental

Cyclic voltammograms of dinitrons **1–4** were detected using an SVA-1BM modified electrochemical system with the tri-

\* The first step of the electrochemical reduction of  $\alpha$ -phenyl-*N*-*tert*-butylnitron and some  $\alpha$ -aryl-*N*-*tert*-butylnitrons is a two-electron process.<sup>7,8</sup>

angular pulse of potential sweep. A cell with a 5-mL working volume was used. It was connected to the system *via* the three-electrode scheme and equipped with the salt bridge filled with a solution of the supporting electrolyte in DMF for connection of the working solution and reference electrode. A stationary needle-like Pt electrode with a surface of 8 mm<sup>2</sup> was used as the working electrode, a Pt wire was the auxiliary electrode, and an aqueous saturated calomel electrode served as reference. An 0.1 M solution of Et<sub>4</sub>NClO<sub>4</sub> in DMF was used as the supporting electrolyte, and oxygen was removed by bubbling argon through the working solution. The concentration of the depolarizer was 1 · 10<sup>-3</sup> mol L<sup>-1</sup>.

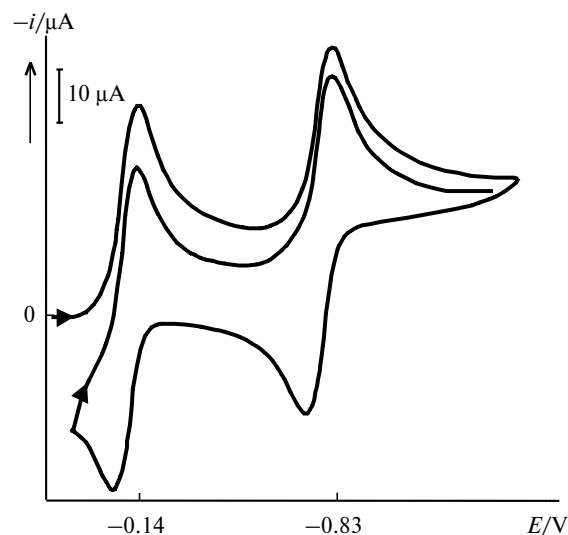
ESR spectra of paramagnetic intermediates of reduction processes were measured on a Bruker ESP-300 radiospectrometer equipped with a double resonator. Compounds **1–4** were reduced at potentials of the corresponding peaks in combination with ESR spectrometric measurements under anaerobic conditions at 298 K in a three-electrode cell, whose cathodic area was placed in the front shoulder of the spectrometer cavity. The *g* factors of paramagnetic species were calculated relatively to the reference (MnO), which was placed in the back shoulder of the cavity. ESR spectra of the samples under study and reference were measured successively in each shoulder without re-adjusting of the microwave bridge. Numerical simulation of the spectra was performed using the WINSIM-32 program with the LMB1 algorithm of multiparametric optimization.

In order to establish the structural features and to determine the energies of bonding molecular orbitals in compounds **1–4**, their RA, and dianions (DA), we performed quantum-chemical calculations of the corresponding forms. The neutral forms and DA were calculated by the RHF method, and RA were calculated by both the UHF and RHF methods for comparison. All calculations were carried out in the PM3 approximation (MOPAC 6.0 program) with the full optimization of geometry and restrictions by symmetry for the Me groups in position 5 of the pyrrolinone cycles and for the substituents in position 2 according to their local dynamic symmetry (*C*<sub>3v</sub> for the CF<sub>3</sub>, Me, and Bu<sup>t</sup> groups, and *C*<sub>2v</sub> for Ph). No restrictions for rotation of the substituents relative to the pyrrolinone cycles were applied.

The solvent (DMF) was purified by distillation *in vacuo* over P<sub>2</sub>O<sub>5</sub>. The characteristics and procedure of synthesis of compounds **1–4** have been described previously.<sup>9</sup>

## Results and Discussion

Cyclic voltammograms of compounds **1–4** are similar. In all cases, we observed two reversible cathodic peaks of the diffusional nature ( $I_p^{C_1}/I_p^{A_1} = 1$ ,  $I_p^{C_1}v^{-1/2} = \text{const}$ ,  $I_p^{C_2}/I_p^{A_2} = 1$ ,  $I_p^{C_2}v^{-1/2} = \text{const}$ , where  $I_p$  is the current in the maximum of the peak, and  $v$  is the potential sweep) related to the ECR of **1–4** to RA and DA according to the EE-type electrode process (an example of the voltammogram for compound **1** is presented in Fig. 1). The PER values for compounds **1–4** are presented in Table 1 along with the values of Koopmans electron affinity ( $-\epsilon_{\text{LUMO}}$ ) calculated for neutral forms **1–4** by the RHF/PM3 method.



**Fig. 1.** Cyclic voltammogram of compound **1** ( $C = 1 \cdot 10^{-3}$  mol L<sup>-1</sup>, DMF,  $v = 0.08$  V s<sup>-1</sup>, supporting electrolyte 0.1 M Et<sub>4</sub>NClO<sub>4</sub>).

According to the CV data (see Table 1), the electron-acceptor ability of compounds **1–4** with the variation of substituents decreases in the order CF<sub>3</sub> > Bu<sup>t</sup> > Ph > Me. The PER value of the most electron-withdrawing trifluoromethyl-substituted compound **1** is close to the PER of tetracyanethylene (−0.16 V in DMF vs. SCE).<sup>11</sup> The calculated Koopmans electron affinities (see Table 1) agree well with the PER values and reflect rather correctly the change in the electron-acceptor ability in the series **1–4**.

According to the X-ray diffraction data,<sup>10</sup> compounds **2–4** in the solid phase contain planar pyrrolinone cycles turned relatively to each other by the angle proportional to the effective volume of the R substituent. In the series R = Me, Ph, and Bu<sup>t</sup>, the dihedral angles between the cycles are equal to 32, 42.8, and 51.5°, respectively. The equilibrium conformations of compounds **1–4** (an example for the trifluoromethyl derivative of ylidene **1** is shown in Fig. 2) calculated by the RHF/PM3 method are

**Table 1.** Cathodic ( $E^{C_i}$ ) and anodic ( $E^{A_i}$ ) potentials\* of the peaks and Koopmans electron affinity ( $\epsilon_{\text{LUMO}}$ ) of compounds **1–4**

| Com-<br>pound | $-E_p^{C_1}$ | $-E_p^{C_2}$ | $-E_p^{A_1}$ | $-E_p^{A_2}$ | $-\epsilon_{\text{LUMO}}/\text{eV}$ |
|---------------|--------------|--------------|--------------|--------------|-------------------------------------|
|               | V            |              |              |              |                                     |
| <b>1</b>      | 0.13         | 0.83         | 0.06         | 0.76         | 2.226                               |
| <b>2</b>      | 0.50         | 1.14         | 0.43         | 1.07         | 1.895                               |
| <b>3</b>      | 0.44         | 1.07         | 0.37         | 1.00         | 1.804                               |
| <b>4</b>      | 0.47         | 0.99         | 0.40         | 0.92         | 1.795                               |

\* Versus SCE on the Pt electrode in an 0.1 M solution of Et<sub>4</sub>NClO<sub>4</sub> in DMF,  $C = 10^{-3}$  mol L<sup>-1</sup>, potential sweep  $v = 0.08$  V s<sup>-1</sup>, index "i" denotes the number of the peak in order of increasing the absolute potential value.

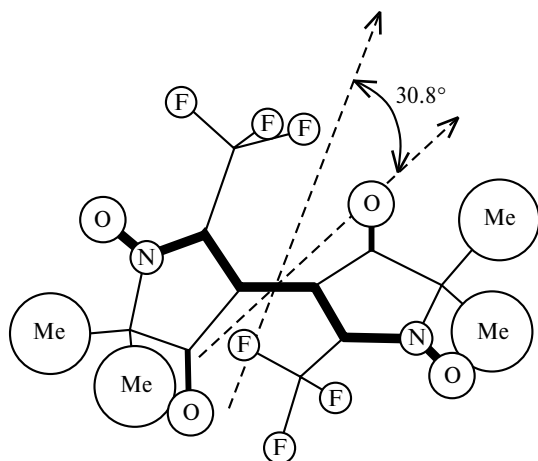


Fig. 2. Equilibrium conformation of the neutral form of dinitron 1 calculated by the RHF/PM3 method.

also substantially nonplanar, and the dihedral angles between the pyrrolinone cycles in the series  $R = \text{Me}$ ,  $\text{CF}_3$ ,  $\text{Ph}$ , and  $\text{Bu}^t$  are equal to 30.1, 30.8, 37.2, and 55.1°, respectively. In addition, the pyrrolinone cycles are characterized by small out-of-plane distortions, which increase with an increase in the corresponding dihedral angles between the cycles.\* The out-of-plane distortions of the pyrrolinone cycles remarkably decrease on going from neutral forms 1–4 to their RA and DA, whose pyrrolinone fragments are planar according to the calculation, but the dihedral angles between them are great. In the case of RA 2, 1, 3, and 4, the corresponding values are equal to 37, 45.9, 53, and 67.7°.

Figure 3, *a* shows the correspondence of the PER of compounds 1–4 and their adiabatic electron affinity  $A_{\text{ad}}$ , which is determined as the difference between the total energies of the neutral forms and the corresponding RA in the calculated equilibrium conformations. The  $A_{\text{ad}}$  values were calculated as  $A_{\text{ad}}^{\text{UHF}} = E_{\text{RHF}}^0 - E_{\text{UHF}}^{\text{AP}}$  and  $A_{\text{ad}}^{\text{RHF}} = E_{\text{RHF}}^0 - E_{\text{RHF}}^{\text{AP}}$ , where  $E_{\text{RHF}}^0$  and  $E_{\text{UHF}}^{\text{AP}}$  ( $E_{\text{RHF}}^{\text{AP}}$ ) are the total energies of neutral forms 1–4 and RA, respectively, in the corresponding Hartree–Fock approximation. The RHF and UHF calculations are well consistent with experiment. The qualitative correspondence is also observed for the potentials of the second reduction peaks and adiabatic electron affinity of RA 1, 2, and 4 (see Fig. 3, *b*).\*\* According to the calculations, the  $A_{\text{ad}}$  values for these RA are negative. At the same time, the second reduction peaks are reversible in all cases, indicating stability of DA 1–4, and the second peak potentials are very low and do not exceed –1.14 V (for DA 2, see Table 1). It is most probable that the stabilization of

\* This type of distortions for equilibrium structures 2–4 calculated by the PM3 method has previously been mentioned.<sup>9</sup>

\*\* The  $A_{\text{ad}}$  value of compound RA 3 is not presented because the calculated equilibrium geometry of DA 3 is not stationary.

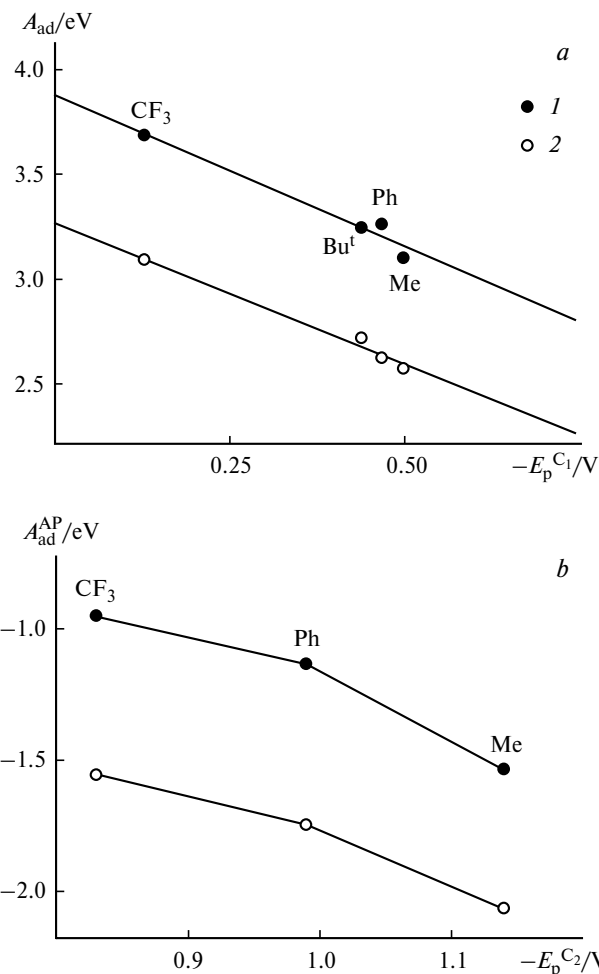


Fig. 3. Correspondence of the potentials of the first cathodic peaks ( $E_p^{C1}$ ) and adiabatic electron affinity ( $A_{\text{ad}}$ ) of the neutral forms of compounds 1–4 (*a*) and the potentials of the second cathodic peaks ( $E_p^{C2}$ ) and adiabatic electron affinity ( $A_{\text{ad}}^{\text{AP}}$ ) of RA 1, 2, and 4 (*b*): calculations by the UHF (1) and RHF methods (2).

DA 1–4 in DMF is facilitated, to a great extent, by solvation and the absence of electrophilic admixtures in the solvent used. Such a situation is typical, for example, of the first two one-electron steps of reduction of nitrobenzene. For the latter in pure anhydrous solvents, such as DMF or liquid ammonia, the reduction peaks corresponding to the formation of its RA and DA are reversible, while in the presence of admixtures, the second reduction peak corresponding to DA formation becomes irreversible.<sup>12,13</sup> For ECR at the potential of the second reduction peak, no changes in the shape of ESR signals are observed. This means that the electronic shells of the corresponding DA are, most likely, in the singlet state.

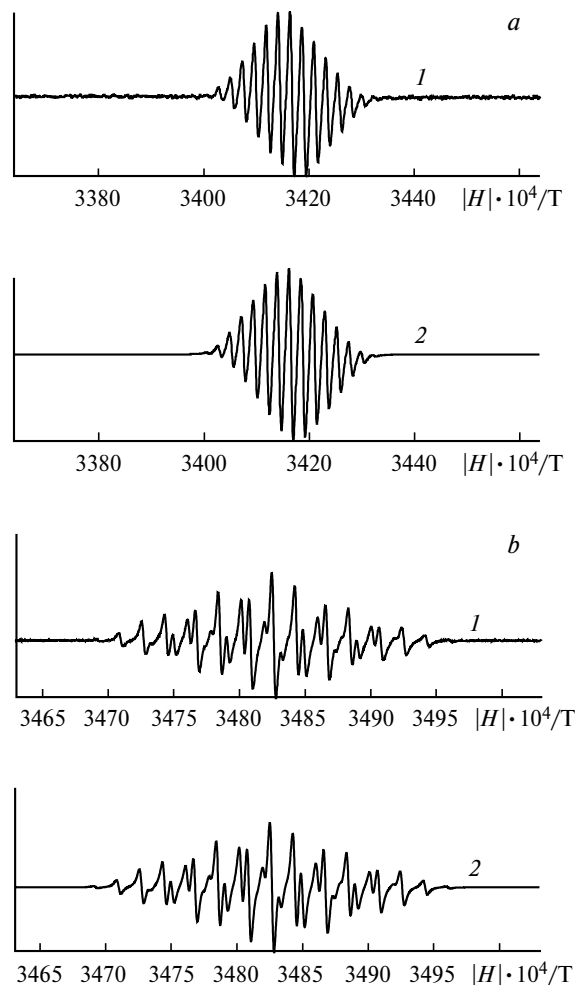
For the ECR of compounds 1–4 at the potential of the first cathodic peak, the ESR spectra of the corresponding RA were detected. Their characteristics are presented in Table 2. The  $g$  factors of RA 1–4 are very close

**Table 2.** Characteristics of the ESR spectra\* of RA 1–4

| Compound | R               | IHFC constants/mT                                  |
|----------|-----------------|--|
| 1        | CF <sub>3</sub> | 0.444 ( <sup>14</sup> N), 0.228 ( <sup>19</sup> F) |
| 2        | Me              | 0.408 ( <sup>14</sup> N), 0.174 ( <sup>1</sup> H)  |
| 3        | Bu <sup>t</sup> | 0.433 ( <sup>14</sup> N)                           |
| 4        | Ph              | 0.424 ( <sup>14</sup> N)                           |

\* RA were generated in  $1.5 \cdot 10^{-3}$  M (0.1 M Et<sub>4</sub>NClO<sub>4</sub>, DMF) solutions of 1–4 at the potentials of the first reduction peak.

and amount to  $2.0033 \pm 0.0004$ . For all RA (see Table 2), both N atoms are spectroscopically equivalent, and the ESR spectra exhibit the characteristic quintet with a ratio of hyperfine components of 1 : 2 : 3 : 2 : 1. The isotropic hyperfine coupling (IHFC) with the nuclei of the R substituent is manifested in the case of RA 1 and 2 (Fig. 4, *a*, *b*). All <sup>19</sup>F or <sup>1</sup>H nuclei in the corresponding RA are dynamically equivalent both within the trigonal



**Fig. 4.** ESR spectra of RA 1 (*a*) and 2 (*b*) obtained for the ECR of compounds 1 and 2 in DMF (1) at the potential of the first cathodic peaks (298 K) and their mathematical models (2).

rotors, namely, the CF<sub>3</sub> and CH<sub>3</sub> groups and between the rotors. The hyperfine splitting is characterized by a septet with the binomial ratio of intensities, *i.e.*, at 298 K the CF<sub>3</sub> and CH<sub>3</sub> groups rotate in the regime of fast three-point exchange. In the case of RA 3 and 4, no IHFC with the <sup>1</sup>H nuclei of the *tert*-butyl and phenyl groups are observed. According to the data of UHF/PM3 calculations of the geometry of RA 4, the benzene rings in its equilibrium conformation are deviated from the plane of the pyrrolinone cycles by an angle of 37.8°. For this reason, most likely, the IHFC constants with the protons of the phenyl fragments are vanishingly small.

Analysis of spin populations on the 2s-AO of <sup>14</sup>N in the calculated conformations of RA 1–4 shows that the N atoms should be equivalent spectroscopically, which is confirmed by the ESR spectroscopic data. The equilibrium conformations are characterized by the C<sub>2</sub> symmetry.

In the case of RA of trifluoromethyl-substituted compound 1, the IHFC constant with the <sup>14</sup>N nuclei is maximum and decreases in the series of RA 2–4 with a decrease in the effective dynamic volume of the R substituent, *i.e.*, in the series Bu<sup>t</sup> > Ph > Me. To study in detail the spatial-dynamic structure of RA 1–4 in the liquid phase, one has to analyze the temperature plots of the line shape of the ESR spectra and IHFC constants, which is beyond the bounds of this work and will be reported elsewhere. Note that the IHFC constants with the <sup>14</sup>N nuclei of radical anions 1–4 with the variation of the R substituent range within  $3.6 \cdot 10^{-2}$  mT. The small interval of changing the constants and their absolute values of ~0.4 mT (see Table 2) suggest that RA 1–4 are  $\pi$ -radicals with the spin-polarization mechanism of IHFC with <sup>14</sup>N nuclei, and the O←N=C=C=C=N→O fragment is the unified radical center.

Thus, we have demonstrated by the CV method that 3,3'-bi(2-R-5,5-dimethyl-4-oxopyrrolinylidene) 1,1'-dioxides (R = CF<sub>3</sub>, Me, Ph, and Bu<sup>t</sup>) are characterized by a significant electron-acceptor ability compared with that for tetracyanethylene. The dinitron radical anions, which are stable at 298 K and whose nitron group is not a part of the aromatic  $\pi$ -system and is not conjugated with it, were characterized for the first time.

## References

1. I. G. Kursakina, V. F. Starichenko, I. A. Kirilyuk, and I. A. Grigor'ev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 2009 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 1774 (Engl. Transl.)].
2. H. Miyazaki, T. Kubota, and M. Yamakawa, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 780.
3. K. Nishikida, T. Kubota, H. Miyazaki, and S. Sakata, *J. Magn. Reson.*, 1972, **7**, 260.

4. H. Miyazaki, T. Kubota, and Y. Matsuhisa, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 3850.
5. K. Ashok, P. M. Scaria, P. V. Kamat, and M. George, *Can. J. Chem.*, 1987, **65**, 2039.
6. I. M. Sosonkin, V. N. Belevskii, G. N. Strogov, A. N. Domarev, and S. P. Yarkov, *Zh. Org. Khim.*, 1982, **18**, 1504 [*J. Org. Chem. USSR*, 1982, **18**, 1313 (Engl. Transl.)].
7. G. L. McIntire, H. N. Blount, H. J. Stronks, R. V. Shetty, and E. V. Janzen, *J. Phys. Chem.*, 1980, **84**, 916.
8. T. H. Walter, E. E. Bankroft, G. L. McIntire, E. R. Davis, L. M. Gierasch, H. N. Blount, H. J. Stronks, and E. V. Janzen, *Can. J. Chem.*, 1982, **60**, 1621.
9. V. A. Reznikov, V. V. Martin, and L. B. Volodarskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 1398 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 1261 (Engl. Transl.)].
10. T. V. Rybalova, Yu. V. Gatilov, V. A. Reznikov, N. V. Pervukhina, and A. B. Burdukov, *Zh. Strukt. Khim.*, 1997, **38**, 775 [*Russ. J. Struct. Chem.*, 1997, **38** (Engl. Transl.)].
11. Ch. K. Mann and K. K. Barnes, *Electrochemical Reactions in Nonaqueous Systems*, Marcel Dekker, New York, 1970.
12. W. H. Smith and A. J. Bard, *J. Am. Chem. Soc.*, 1975, **97**, 5203.
13. B. S. Jensen and V. D. Parker, *J. Chem. Soc., Chem. Commun.*, 1976, **10**, 367.

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