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Carbon- and SO₂-locked diarylnitroxides: quantum chemical consideration, synthesis and electrochemistry

Oleg A. Levitskiy,^[a] Dmitry A. Dulov,^[a] Alexey V. Bogdanov^[a] and Tatiana V. Magdesieva^{*[a]}

Abstract: Selection of linkers connecting two phenyl rings as a part of molecular design of diarylnitroxides with increased kinetic stability of redox forms was performed using quantum chemical estimation of the geometry and oxidation potential values. It revealed that introduction of the carbon bridge cannot be considered as efficient “instrument” for structural tuning of the nitroxide properties since altering neither the length of the bridge nor its position results in significant changes in the oxidation potential, in contrast to a heteroatomic bridge, which makes more perturbation in the electronic structure of diarylnitroxide. To support the prediction, new SO₂-bridged diarylnitroxide was synthesized and characterized using spectral and electrochemical methods. It is extremely stable in benzene solution, exhibits the maximal anodic potential value achieved for reversibly oxidized nitroxides to date (1.33 V, Ag/AgCl/KCl) and seems promising as cathodic redox active material providing maximal potential gap as compared to the previously reported compounds.

Introduction

Nitroxides, due to their unusual stability among the family of organic radicals, are a subject of unceasing research interest for many years. They are widely used in various practical areas, e.g., as building blocks for molecular magnetic materials^[1–4], redox active electrode materials^[5,6], spin labels and radical scavengers^[7–10], etc. Wide possibilities for fine structural tuning of aromatic nitroxides provide a strategy for modulating of crystal packing, spin density distribution, redox-potential values and other important properties required for each particular practical task.

Many practical applications of organic molecules are based on their redox-properties. Efficient functioning of mediators, electroactive electrode materials, redox catalysts, photoredox conversion systems, etc. requires an explicit value of a redox potential. In this connection, targeted molecular design and synthesis of libraries of new nitroxides with unusual structural features and various substituents covering wide redox potentials range is a topical problem.

In our recent publications, we focused on the molecular design of diarylnitroxides with increased thermodynamic and kinetic stability of both the radical species and their oxidized and reduced forms^[11–14]. New type of nitroxyl radicals, so called “twisted” diarylnitroxides, has been suggested and turned out to be promising, as follows from the results obtained.

The present paper is the further development of the research on structural tuning of stability and redox properties of diarylnitroxides. As an “instrument”, an insertion of different linkers “locking” two phenyl rings was chosen and its influence on the oxidation potential of the nitroxide was investigated. Prior to synthesis, quantum chemical calculations were performed, to select the structure providing the sufficient stability and the oxidation potential value which will allow broadening the available potential range. As a result, the SO₂-locked diarylnitroxide was obtained and fully characterized. It is extremely stable in benzene solution and exhibits completely reversible oxidation at 1.33 V (vs. Ag/AgCl/KCl). To the best of our knowledge, this is the maximal anodic potential value achieved for reversibly oxidized nitroxides to date.

It should be mentioned that the types of diarylnitroxides containing additional linker between aromatic rings synthesized to date are rather limited. The mostly investigated are diphenylidihydroacridine type derivatives with various alkyl or aryl substituents at 10-position^[15,16]. Polyradical systems of this type are also known^[3,17]. Diarylnitroxides containing Si and Ge bridging atoms were also synthesized recently and the effect of the heteroatom on the electrochemical properties of the radicals was studied^[18]. These radical derivatives are stable in non-halogenated solvents and in the solid state. Delocalization of unpaired electron on the Si and Ge atoms was confirmed using the ESR data. To our knowledge, this is the only publication on the diarylnitroxides with a bridging heteroatom. Meanwhile, the introduction of various heteroatoms into organic compounds backbone is of particular interest since this can be expected to provide unusual electronic properties of the molecule.

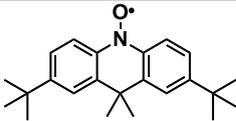
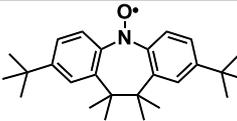
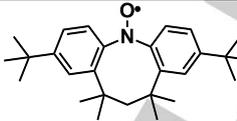
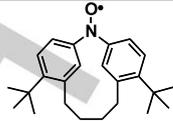
Results and Discussion

Choosing an appropriate bridge to be introduced in a diarylnitroxide is not an easy task. On the one hand, the bridge can be considered as an additional “instrument” for altering the conjugation degree between the NO group and the aromatic rings. On the other hand, it may result in an increase of sterical tension of a molecule. Thus, an optimization of the type and the length of the bridge providing an optimal torsion angle between the rings is necessary. Carbon bridges will be considered first.

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Supporting information: ¹H, ¹³C, HSQC, HMBC NMR, HRMS and IR spectra, voltammograms and mathematical analysis of the experimental data for this article is given via a link at the end of the document.

Table 1. Calculated oxidation potential values (vs. Ag/AgCl, KCl) for 4,4'-di(*tert*-butylphenyl)nitroxides with various carbon bridges; C-C-N-O and C'-C'-N-O torsion angles (θ) between the N-O group and two phenyl rings.

				
	1	2	3	4
E^{ox}, V	0.598	0.752	0.742	0.606
θ in radical	0	+29; +6	+26; -26	+36; -36
θ in oxidized form	0	+23; +5	+26; -26	+34; -34

Carbon bridges

For quantum chemical estimation, several model structures were chosen (Table 1). The position of the bridge (*ortho* or *meta*) and its length were varied. Nitroxide **1** (the 9,10-dihydroacridine derivative) has a planar and rigid structure and it can be taken as a starting point for estimation of the influence of the conjugation on the oxidation potential of diarylnitroxides. The *tert*-butyl groups in the *para*-positions and two methyl groups instead of hydrogen atoms in the α -positions of the 2,2'-bridges (in structures **1-3**, see Table 1) are necessary to prevent the destruction channel leading to quinoid-type structures (due to significant spin density in the *ortho*- and *para*- positions) which is typical for diarylnitroxides^[19].

For estimation of the oxidation potential values, a new approach suggested in ref^[20] was used. It was shown that a combination of "Priroda" program package at the PBE/L2 level of theory with continuum solvation model (in the form of the two-step procedure) provides a low-cost and reliable methodology for calculation of the standard redox potentials for nitroxides (for both alkyl and aryl type) in acetonitrile solution. A mean absolute deviation from the experimental values of 33 mV was observed^[20].

Nitroxide **2** has a longer linker and it is not planar. However, the torsion angles between the NO group and the phenyl rings are relatively small. Interestingly, the angles for two rings (CCNO and C'C'N'O') differ significantly, the structure is asymmetric, and both rings are twisted in the same side relatively to the NO plane. The introduction of an additional CH₂ group in the bridge (nitroxide **3**) negligibly influences either sterical tension of the molecule or the oxidation potential of **2** and **3**. Structure **4** has a longer linker in 3,3' – positions providing more space for rotation; as a result, the both torsion angles are increased. Lowering the conjugation degree of the NO moiety with the phenyl rings increases spin density on the NO facilitating its oxidation. Importantly, the torsion angles in the oxidized and in the neutral forms of nitroxides **2-4** are almost identical. This means that sterical tension of the bridged structures **2-4** prevents planarization of the molecule, which would be favorable for resonance stabilization of the cationic form.

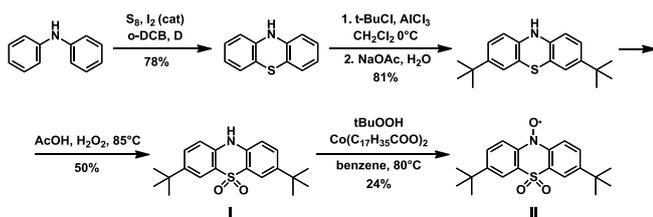
Thus, the introduction of the carbon bridge in diarylnitroxides reduces possibilities for "self-tuning" of the molecule to stabilize

the oxidized form of the nitroxide, via an increase in the conjugation between the NO group and phenyl rings, contrary to the twisted nitroxides with bulky *ortho*-substituents suggested and synthesized in ref.^[13]. Furthermore, the oxidation potential is only slightly varied with a variation of the length and position of the bridge. These facts allowed concluding that synthesis of the diarylnitroxides with the bridges of aforementioned types is inexpedient.

One can expect that a heteroatom-containing bridge would be more promising since a heteroatom could make more perturbation in the electronic structure of the diarylnitroxide without significant increase in the sterical restriction of the molecule. Indeed, quantum chemical estimation of the oxidation potential value for previously unreported SO₂-locked di(*tert*-butylphenyl)nitroxide (performed using the aforementioned approach^[20]) gave the value of $E^{\text{ox}} = 1.241 \text{ V}$ (vs. Ag/AgCl/KCl). This value is much more anodic than that previously measured for other nitroxides, both of aryl and alkyl type, which exhibit reversible oxidation (for comparison: for TEMPO: $E^{\text{ox}} = 0.7 \text{ V}$; for 4,4'-dianisyl nitroxide: $E^{\text{ox}} = 0.6 \text{ V}$; the closest value was obtained for twisted 2-^tBu-4'-CF₃-diphenyl nitroxide, $E^{\text{ox}} = 1.230 \text{ V}$ in the similar conditions, see review article^[19]). This means that the new compound is worth to be synthesized since it might be of interest as cathodic redox material providing much higher potential gap as compared to the previously reported compounds.

Heteroatom-containing bridge

Diarylnitroxides with heteroatom-containing bridge have not been reported yet. The only exception is aforementioned Si and Ge-containing biphenyl-9,10-dihydroacridin-10-yloxy derivatives^[21]. The attempt to synthesize an oxygen-locked diarylnitroxide has been reported^[22] but it was unsuccessful: corresponding phenoxazinyl radicals were formed instead of the nitroxide. Diarylnitroxides with sulphur-containing bridge locking the *ortho*-positions of the phenyl rings have not been synthesized yet though their precursors (various phenothiazines) are well-known and widely investigated (due to their application in luminescent materials^[23,24]).



Scheme 1. Preparation of I and II.

Synthesis of heteroatom-bridged diarylnitroxide was performed as presented in Scheme 1.

Synthesis of 3,7-di-*tert*-butyl-phenothiazine has been previously reported [25]; however, its further oxidation required careful consideration. The sulfur bridge can be selectively oxidized with hydrogen peroxide in acetic acid yielding previously unreported diaryl amine I with the SO₂ linker. Compound I was isolated and fully characterized using spectral methods (see the Experimental Section and the Supporting Information). Amines of this type are of interest due to their antimycobacterial properties (see, e.g., ref. [26]). Besides, sulfone-locked triaryl amines were utilized for fabrication the materials with improved electron affinities and an electron dominant transporting ability [27,28]. The detailed investigation of the properties of new sulfone-locked diphenylamine will be the subject of the forthcoming paper.

To convert the sulfone-locked diphenylamine to the corresponding nitroxide, various oxidants were tested. Commonly used oxidants such as *meta*-chloroperoxybenzoic acid (mCPBA) gave a complicated mixture of products; oxidation with hydrogen peroxide in the presence of NaWO₄ gave no targeted nitroxide, the starting compound was isolated instead. Application of the *t*-BuOOH/Co(C₁₇H₃₅COO)₂ oxidative system described in [29] allowed obtaining the targeted nitroxide in 24% yield. The identity of 3,7-di-*tert*-butyl-10H-phenothiazine-N-oxyl 5,5-dioxide II was proved by the ESI-HRMS data (see the Experimental Section and SI).

Bridged diarylnitroxide II was fully characterized using ESR and UV-Vis spectroscopy as well as with cyclic voltammetry. The purity of the isolated radical species was proven by the ESR through spin counting, to determine the spin concentration of the nitroxide samples (for more details, see the Experimental Section and the SI).

Experimental and simulated ESR spectra for nitroxide II are given in Fig.1. The characteristic triplet signal due to the spin splitting on the N atom can be observed, the a_N constant is equal to 7.95 G. The value is much lower than that observed for twisted 2,4'-di-*tert*-butylphenyl nitroxide (10.34 G [13]) and for diphenyl-9,10-dihydroacrydin-10-N-oxyl (8.82 – 9.94G [15,16]). This comparison indicates that the spin density in nitroxyl radical II is significantly delocalized due to almost planar structure and significant electron-withdrawing effect of the SO₂ moiety. Digital simulation showed that the spectral pattern observed is consistent with the additional spin splitting of each triplet component on the couple of *ortho* protons ($a(H_{ortho}) = 2.16$ G), as well as on two pairs

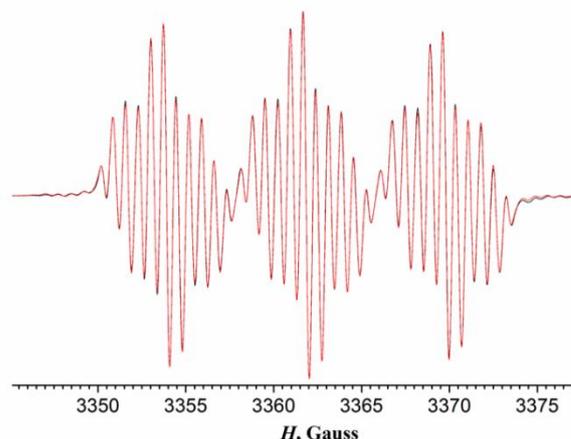


Figure 1. Experimental (black line) and simulated (red line) ESR spectra of II.

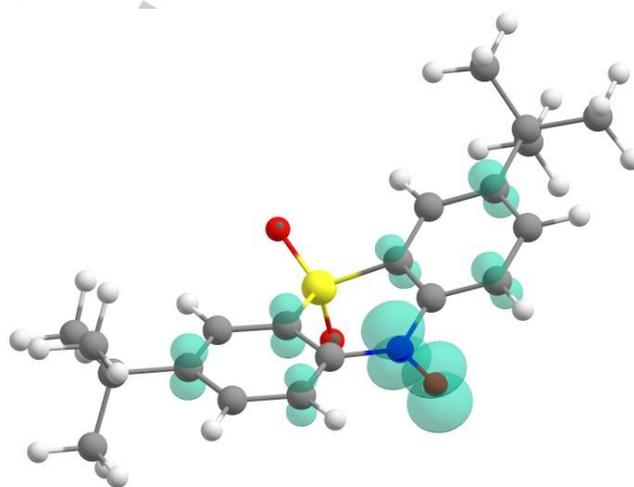


Figure 2. DFT calculated spin density distribution in II.

of *meta* protons (with the $a(H_{meta})$ values of 0.78 G and 0.59 G). The experimental data are in good agreement with the DFT calculated spin density distribution in the SO₂-bridged nitroxide (see Fig.2). Interestingly, the simulated structure of the nitroxide is not planar, contrary to 9,9-dimethylacridine-N-oxyl containing carbon (CMe₂) bridge between the rings. The UV/Vis spectrum for the diarylnitroxide with the SO₂ bridge (shown in Figure 3) is quite typical for aryl nitroxides. It exhibits an intensive peak at 223 nm, a broad intensive peak around 330 nm, and a set of much less intensive peaks in 437–500 nm region. Comparison with the UV-Vis data previously reported for 4,4'-di(*tert*-butylphenyl)nitroxide [13] indicates that the insertion of the SO₂ bridge does not principally change the spectrum pattern (for exact λ_{max} values, see SI).

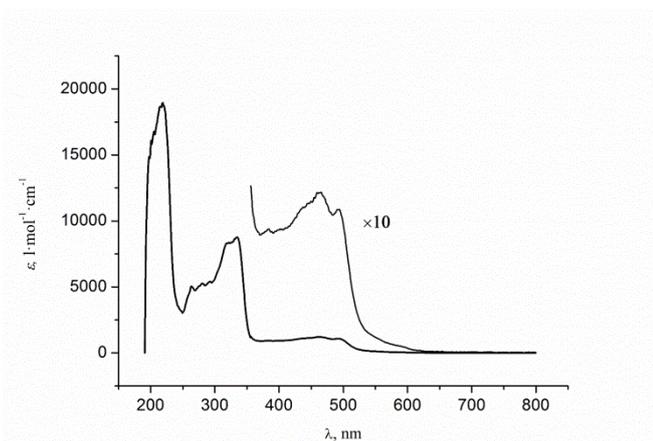


Figure 3. The UV-Vis spectrum of **II** in MeCN.

The most interesting is the weak absorption peak in the visible region since it is mainly associated with free-radical electrons located in the SOMOs. The λ_{\max} for the absorption in visible region for the SO_2 -bridged nitroxide (430–500 nm) is blue-shifted as compared to λ_{\max} for 4,4'- and 2,4'-di(*tert*-butylphenyl)nitroxides (460–530 nm) [13] and red-shifted relatively to that for alkyl derivatives (428–468 nm) [30], though the ϵ values are significantly higher for aromatic than for aliphatic (ϵ 4–10) compounds due to spin delocalization.

Though there are some descriptions of fluorescent nitroxide radicals in the literature [18], nitroxide **II** exhibit no fluorescence. Electrochemical investigation of SO_2 -locked nitroxide **II** was performed at a Pt disc electrode in acetonitrile solution using cyclic voltammetry. The CV curves are given in Fig.4. Oxidation is one-electron and reversible, even at low scan rates (50 mV/s) direct/reverse peak current ratio is close to unity. Peak separation is 70 mV at a scan rate of 100 mV/s. Linear dependence $\ln i^{\text{ox}}$ vs. $\ln v$ is observed; the slope of the linear fit is close to 0.5 indicating that the peak current is proportional to the square root of the scan rate, typically for diffusion-controlled processes. Semi-differential voltammograms are well fitted with the theoretical curve for electrochemically reversible process (see SI). This allowed estimation of the diffusion coefficient; the value of $D = 4.5 \cdot 10^{-6} \text{ cm}^2/\text{s}$ was obtained; that is lower than that for the twisted 2,4'-di(*tert*-butylphenyl)nitroxide ($1.4 \cdot 10^{-5} \text{ cm}^2/\text{s}$, [12]).

The standard heterogeneous rate constant for the electron transfer for the SO_2 -locked nitroxide's oxidation was determined using the Nicholson method [31]. The value obtained ($k_s = 0.022 \text{ cm/s}$) is close to that previously reported for the twisted 2,4'-di(*tert*-butylphenyl)nitroxide ($k_s = 0.017 \text{ cm/s}$, [12]) and is in the similar range with the standard rate constant measured for TEMPO ($k_s = 0.10 \text{ cm/s}$ [32]). This indicates that the electron transfer is sufficiently fast making the compound suitable for practical application.

The robustness of the nitroxide and stability of its oxidized form (the oxoammonium cation) were estimated by multiple cycling in the potential range of 1.0 – 1.6 V (vs. Ag/AgCl/KCl). Neither

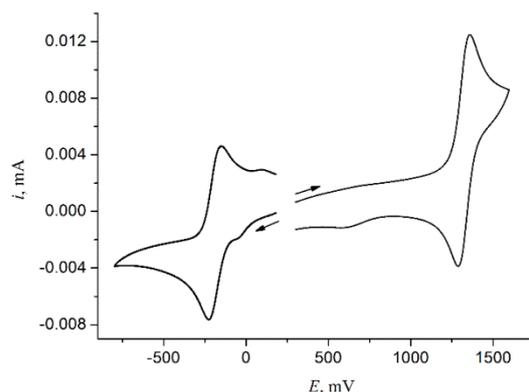


Figure 4. Voltammetric curve for oxidation and reduction of nitroxide **II** (Pt, 100 mV/s, MeCN, 0.05 M Bu_4NBF_4 , vs. Ag/AgCl/KCl).

peak current values nor $E_{\text{pa}}/E_{\text{pc}}$ values were changed (see SI). Formal peak potential value observed for the oxidation is 1.33 V which is in good agreement with the computationally predicted value (1.241 V, see above) confirming the reliability of the approach. Comparison with 4,4'-di(*tert*-butylphenyl)nitroxide indicates that insertion of the SO_2 bridge shifts the oxidation potential for 430 mV into anodic region. The difference in the oxidation potentials between twisted 2,4'-di(*tert*-butylphenyl)nitroxide and the SO_2 -locked nitroxide **II** is lower (290 mV). Thus, twisting of the molecule changes the oxidation potential of the nitroxide symbolically to the insertion of the electron withdrawing group.

Reduction of the SO_2 -bridged nitroxide **II** is also one-electron and quasi-reversible; the formal peak potential value is -0.190 V. Significant anodic shift is attributed to the presence of an electron-withdrawing SO_2 moiety. A small pre-peak of unknown nature can be also observed in the voltammogram.

Stability tests

In a crystalline form, sulfone-locked nitroxide **II** can be kept for months in air without any noticeable degradation. To quantify stability of the radical in solution, kinetic measurements in toluene and in benzene were performed using a spin-counting method. The degassed sample was kept in the sealed ESR tube at room temperature without light protection for a month and the amount of radical species was monitored periodically. The results obtained are given in Table 2.

Table 2. Kinetic measurements of the stability of 4,4'-di(*tert*-butylphenyl)nitroxide and its sulfone-locked counterpart **II** in degassed solution at room temperature.

The radical	II		4,4'-(t^{Bu} Ph) $_2$ NO	
	Benzene	Toluene	Benzene	Toluene
$k_t, 10^{-3} \text{ h}^{-1}$	2.1±0.1	22.1±0.5	1.1±0.1	6±1

As follows from the kinetic data obtained, stability of radical **II** in benzene is high enough for practical application. The kinetic decay constant measured in benzene is of one order of magnitude lower than that in toluene. Probably, the main decay channel of **II** in toluene solution is an H-atom abstraction since this solvent is prone to be an H-atom-donor. Comparison of the bridged nitroxide **II** and 4,4'-(^tBuPh)₂NO showed that their stability in benzene is similar. Both radicals have almost planarized structure providing high spin delocalization onto N-aromatic moiety; the presence of an electron withdrawing SO₂ group additionally facilitates such delocalization. Comparison of the a_N values (7.95 G for **II** and 9.74 G for 4,4'-(^tBuPh)₂NO [13]) supports the conclusion. Noteworthy, spin or charge delocalization over the prolonged conjugated system commonly decreases the reactivity and facilitates stabilization of the species. For diarylnitroxides, it is not the case since delocalization over the aromatic rings gives rise to a "different" type of reactivity at different atomic centers [14]. Steric protection of carbon atoms bearing significant spin density by incorporation of bulky ^tBu-substituents in the *para* positions of the aromatic rings provides kinetic stabilization.

To make a high stability of nitroxide **II** more "visual", the estimation of the τ_{1/2} value was performed. The half-life time of 330 h (two weeks, in benzene solution at room temperature without light protection) was obtained. This testifies in favor of a suitability of **II** for practical application.

Conclusions

Molecular design of diarylnitroxides containing different linkers connecting two phenyl rings was performed, supported with quantum chemical estimation of oxidation potential values for the new structures. A number of carbon-containing bridges were investigated; the position of the bridge (*ortho* or *meta*) and its length were varied. As a starting point for the estimation of the influence of the conjugation on the oxidation potential of the diarylnitroxide, diphenyl-9,10-dihydroacridine-N-oxyl with planar and rigid structure was taken. It was shown that the introduction of the carbon bridge in diarylnitroxides reduces possibilities for "self-tuning" of the molecule to stabilize the oxidized form of the nitroxide, as compared to the twisted nitroxides with bulky *ortho*-substituents. Furthermore, altering the length of the bridge (containing 1-4 carbon atoms) or its position (2,2' or 3,3') results in only minor changes in the nitroxide's oxidation potential value. These facts allowed concluding that the introduction of the carbon bridge in diarylnitroxides can not be considered as an efficient "instrument" for structural tuning of the nitroxide properties and synthesis of the diarylnitroxides with the bridges of aforementioned types is inexpedient.

Contrary to the aforementioned structures, quantum chemical calculations performed for the diphenylnitroxide with the SO₂-containing bridge showed that the compound might be promising as a redox-active cathodic material. SO₂-locked 4,4'-di(*tert*-butylphenyl)nitroxide **II** was obtained and fully characterized using spectral (ESR, HRMS, UV-Vis) and electrochemical methods. It is stable in solution and exhibits completely

reversible oxidation at 1.33 V (vs. Ag/AgCl, KCl). This is the maximal anodic potential value achieved for reversibly oxidized nitroxides to date.

One can expect that new compound might be of interest as cathodic redox material providing much higher potential gap as compared to the previously reported compounds.

Experimental Section

Mass spectra were measured with a high resolution time-of-flight instrument by using electrospray ionization (ESI-MS). Measurements were performed in positive and negative ion modes with an interface capillary voltage at 4.5 kV, an effective scan range at m/z 100–1200, external calibration (0.016 M sodium formate in MeCN/water, 1:1 mixture or ESI-L Low Concentration Tuning Mix, Agilent Technologies), direct syringe injection at flow rate of 3 μL/min, nitrogen as dry gas at 4 L/min, and interface temperature at 180 °C.

ESR spectrum was recorded in toluene solution (containing approximately 1×10¹⁷ radical species), deaerated by using standard freeze-pump-thaw techniques, using Bruker EMX-plus instrument.

UV/Vis spectra were recorded from solutions in dry acetonitrile (1×10⁻² - 5×10⁻⁵ M).

¹H (400 MHz) and ¹³C (100 MHz) *NMR spectra* were recorded in CDCl₃. Chemical shifts were referenced to signals from residual non-deuterated solvents.

Voltammetric experiments were performed with AutoLab PGSTAT100 N potentiostat, in a home-made three-electrode cell of 10 ml with a platinum wire counter electrode (CE) and Ag/AgCl, KCl (sat.) reference electrode (RE). All potentials below refer to this reference electrode. The half-wave potential of the ferrocene couple (Fc⁺/Fc) versus our reference electrode is about 0.48 V in 0.05 M Bu₄NBF₄ in acetonitrile. The reference electrode was connected to the electrolyte solution via a salt bridge containing 0.05 M n-Bu₄NBF₄ solution in acetonitrile. A Pt disk electrode with active surface area of 0.045 cm² was used as the working electrode (WE). The Pt electrode was polished with Al₂O₃ suspension SPA 0.3 mm on a polishing pad (Metrohm, Germany), washed with sulfuric acid and rinsed with water and acetone. Ohmic drops corrections were performed using convolution approach.

All solutions were thoroughly deaerated by passing an argon flow through the solution prior to the CV experiments and above the solution during the measurements, the supporting electrolyte in all experiments was 0.05 M n-Bu₄NBF₄ (Aldrich, purity >99%), which has been recrystallized from water and dried by gentle heating at 100 °C under reduced pressure (0.05 Torr) prior to use.

Acetonitrile (AN, Aldrich spectroscopic quality, <0.02% water content) was distilled over P₂O₅. In each case, a freshly distilled portion of the solvent was used.

Computational Details: Gas phase optimizations for all the radicals **1 - 4** as well as vibrational analysis for the structures obtained was performed in PRIRODA quantum-chemistry program [33,34]. The gradient-corrected exchange-correlation Perdew, Burke, and Ernzerhof (PBE) functional [35] and basis sets L1 were used for calculations [36]. The 10⁻⁶ threshold on the molecular gradient at the geometry optimization procedure was

employed. A method suggested in ref. [20] was used for calculation of oxidation potential values.

Gas phase optimizations and spin density distributions in radical **II** were calculated in ORCA 4.1.1 quantum chemistry package [37] using PBE functional and cc-pVDZ basis set. A threshold of $1 \cdot 10^{-8}$ Hartree was used for SCF convergence; thresholds of $1 \cdot 10^{-6}$ Hartree and $3 \cdot 10^{-5}$ Hartree Bohr⁻¹ on energy and RMS gradient, respectively, were employed in optimization procedures.

Phenothiazine and 3,7-di-tert-butyl-phenothiazine were synthesized as described in refs. [38] and [25], respectively.

Synthesis of 3,7-di-tert-butyl-10H-phenothiazine 5,5-dioxide (I): To a solution of 5 g (25 mmol) of 3,7-di-tert-butyl-phenothiazine in 50 ml of glacial acetic acid and 10 ml of CH₂Cl₂, 6.1 mL of 37% hydrogen peroxide solution (75 mmol) was added. The mixture was kept at 80–85°C for 5 h. After it returned to room temperature, it was diluted with 50 mL of distilled water and the resulting mixture was stirred for 5 h. Then it was filtered and the resulting brown precipitate was recrystallized from a minimal amount of methanol (about 15 ml). The methanol filtrate was evaporated under reduced pressure and the solid residue was recrystallized from a minimal amount of toluene (about 15 ml). The combined fractions were dried under reduced pressure yielding 2.6 g (50%) of orange crystals.

ESI-(+)MS: *m/z* = 344.1678 ([M+H]⁺, 344.1684 calculated for C₂₀H₂₆NO₂S), 366.1499 ([M+Na]⁺, 366.1504 calculated for C₂₀H₂₅NNaO₂S).

¹H NMR (400 MHz, CDCl₃) δ, ppm: 8.00 (br. s, 1H, NH), 7.97 (d, ⁴J = 2.2 Hz, 2H-5), 7.34 (dd, ³J = 8.7, ⁴J = 2.2 Hz, 2H-3), 6.78 (d, ³J = 8.7 Hz, 2H-2), 1.29 (s, 18H, t-Bu).

¹³C NMR (100 MHz, CDCl₃) δ, ppm: 145.08 (C-4), 135.83 (C-1), 130.90 (C-3), 120.24 (C-6), 118.69 (C-5), 116.34 (C-2), 34.78 (C-7), 31.31 (CH₃).

For atoms numeration, see SI.

IR (KBr, cm⁻¹): 3307, 3188, 3089, 2962, 2868, 1678, 1616, 1576, 1522, 1495, 1400, 1363, 1342, 1265, 1240, 1203, 1130, 1059, 955, 910, 885, 822, 783, 729, 685, 636, 577.

Synthesis of 3,7-di-tert-butyl-10H-phenothiazine-N-oxyl 5,5-dioxide (II): 200 mg (0.58 mmol) of **I** was dissolved in 10 ml of benzene and the mixture was heated to 80°C. Then 18 mg (0.03 mmol) of cobalt(II) stearate was added. The color of the solution immediately changed to dark blue. Afterwards, t-BuOOH (120 μL, 1.25 mmol) was dissolved in 2.9 ml of heated benzene and the resulted solution was added to the reaction mixture successively in 3 portions each 20 min. The color of the solution immediately changed to dark brown. The reaction mixture was stirred at 80°C for 30 min, cooled to room temperature and the solvent was evaporated under reduced pressure. The residue was dissolved in minimal amount of eluent (CH₂Cl₂/hexane 7:6) and the resulted solution was fractionated using column chromatography (Silica gel 40–63 μm, Merk). The first colored fraction (red) was collected and evaporated yielding 50 mg (24%) of the nitroxide **II** as a yellow- brownish solid.

ESI(-)MS: *m/z* = 358.1481 (M⁻, 358.1477 calculated for C₂₀H₂₄NO₃S)

ESR (toluene solution): *g* = 2.0056; *a_N* = 7.95 G (2N), *a_H* = 2.16 G (2H), *a_H* = 0.78 G (2H), *a_H* = 0.59 G (2H).

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Keywords: stable nitroxide • radicals, • oxidation potentials, • density functional calculations, • cathodic materials

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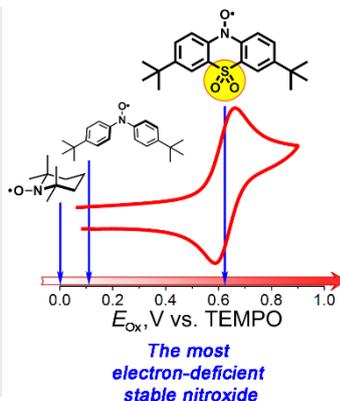
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Layout 1:

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Targeted molecular design of bridged diarylnitroxides with increased kinetic stability of redox forms allowed suggesting new SO₂-locked diarylnitroxide which was synthesized and fully characterized. It is stable in solution, exhibits the maximal anodic potential value achieved for reversibly oxidized nitroxides to date and might be of interest as cathodic redox active material.



Oleg A. Levitskiy, Dmitry A. Dulov,
Alexey V. Bogdanov and Tatiana V.
Magdesieva*

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**Carbon- and SO₂-locked
diarylnitroxides: quantum chemical
consideration, synthesis and
electrochemistry**

Layout 2:

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