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Experimental and Theoretical Studies on Magnetic Exchange in Silole-Bridged Diradicals.

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Abstract: Five bis(*tert*-butylnitroxide) diradicals connected by a silole (**7a-d**) or a thiophene (**12**) ring as a coupler are presented. **12** crystallizes in orthorhombic space group $Pna2_1$ with $a = 20.752(5)$ Å, $b = 5.826(5)$ Å and $c = 34.309(5)$ Å. X-ray crystal structure determination, electronic spectroscopy, variable-temperature EPR spectroscopy, SQUID measurements and DFT computations (UB3LYP/6-31+G*) were used to study the molecular conformations and electronic spin coupling in this series of molecules. Whereas compounds **7b**, **7c** and **7d** are quite stable both in solution and in the solid state, **7a** and **12** partially undergo an electronic rearrangement to both a diamagnetic quinonoidal form and a monoradical specie due to the fact that they correspond to the open form of a π -conjugated Kekulé structure. In the solid state, the magnetic measurements indicate that the diradicals are all antiferromagnetically coupled as expected from their topology. These interactions are best reproduced using a “Bleaney-Bowers” model affording values of $J = -142.0$ cm⁻¹ for **7a**, -1.8 cm⁻¹ for **7b**, -1.3 cm⁻¹ for **7c**, -4.2 cm⁻¹ for **7d** and -248.0 cm⁻¹ for **12**. The temperature dependence of the EPR half-field transition in frozen dichloromethane solutions is consistent with singlet ground states and thermally accessible triplet states for diradicals **7b**, **7c** and **7d** with ΔE_{T-S} values of 3.48, 2.09 and 8 cm⁻¹, respectively. No evidence of populated triplet state was found for diradicals **7a** and **12**. Similarities between the ΔE_{T-S} and J values ($\Delta E_{T-S} = -2J$) clearly show the intramolecular origin of the observed antiferromagnetic interaction. Analyses of the data using a “Karplus-Conroy” type relation allowed us to establish that the silole ring, as a whole, allows for a more efficient magnetic coupling of the two nitroxide radicals attached to its 2,5-positions than the thiophene ring. This superiority likely originates from the non-aromaticity of the silole allowing for a better magnetic interaction through it. DFT calculations also support the experimental results, indicating that the magnetic exchange pathway preferentially involves the carbon π -system of the silole.

Keywords: silole • nitroxide diradicals • magnetic interactions • EPR spectroscopy • DFT calculations

Introduction

Organosilicon-based molecules have attracted much attention because of their unique optoelectronic properties and their importance in applications such as photoresists, photoconductors, nonlinear optical materials and light-emitting devices.^[1-4] Such interesting properties mainly originate from the unusual types of conjugation that are encountered in polysilanes ($\sigma(\text{SiSi})$ type)^[5], in compounds in which oligosilanylene units are alternating with carbon π systems ($\sigma(\text{SiSi})$ - π type - Figure 1b),^[6] and in compounds in which silanylene units are alternating with carbon π systems ($\sigma^*(\text{Si})$ - π^* type - Figure 1c).^[7] In general, the attachment of a silicon atom to a π system is not an innocent act since its presence induces appreciable electronic perturbations, which have been exploited by organic chemists for a long time. Among others, the Birch reduction of aromatic rings may be adequately directed by organosilicon substituents since they stabilize transient radical anions on the carbon atom to which they are bound.^[8]

Figure 1. Different types of conjugation between two aromatic rings through organosilicon units. a) Through-space overlap of the aromatic π -orbitals in the butterfly-shaped diarylsilane family. b) $\sigma(\text{SiSi})$ - π conjugation in the diaryldisilane family. c) $\sigma^*(\text{Si})$ - π^* conjugation in the planar diarylsilane family.

Another interesting example of the electronic perturbation induced by the presence of a silicon atom is found in five membered heteropentacycles: while furan ($X = \text{O}$), pyrrole ($X = \text{NR}$) and thiophene ($X = \text{S}$) derivatives are colorless, silacyclopentadiene or silole ($X = \text{SiR}_2$) derivatives are highly colored compounds because of the lowest HOMO-LUMO gap of the series. This characteristic originates from an unusual low-lying LUMO level associated with the σ^* - π^* conjugation (Figure 1c) arising from the interaction between the σ^* orbital of the two exocyclic σ -bonds on the silicon atom and the π^* orbital of the butadiene moiety, as exemplified in Figure 2 for 2,3,4,5-tetraphenyl-1,1-dimethylsilole **1**.^[7] Consequently, siloles have a high electron affinity and the fast electron mobility makes them molecules of choice to build highly efficient light-emitting layers for electro-luminescent devices.^[2, 9-12]

Figure 2. HOMO and LUMO orbitals (6-31G* level) of 2,3,4,5-tetraphenyl-1,1-dimethylsilole **1** showing the $\sigma^*-\pi^*$ conjugation in the excited state.

Keeping in mind the remarkable properties of silicon-containing molecules, several works in the field of molecular magnetism have been devoted to the syntheses and characterization of model compounds based on paramagnetic centers (organic radicals or paramagnetic metal ions) linked by organosilicon units.^[3, 9, 13-20] The connection of spin-bearing moieties through silicon-containing units was achieved in such a way that the magnetic interaction may take place through the molecular skeleton *via* the set of conjugated bonds available in such systems following two different approaches involving either the use of silanylene or disilanylene units as spin couplers. These studies revealed that i) the silicon atom, when it is part of a single pathway spacer, can act as a magnetic coupler; ii) as in other heteroatom containing couplers, the nature of the magnetic exchange depends on the connectivity of the paramagnetic centers; and finally that iii) the strength of the magnetic interaction strongly depends on the orbital overlap between the silanylene or disilanylene coupler and the spin bearing π -systems. However, while several studies of systems with paramagnetic centers connected through the 2,5-positions of heteropentacycles such as thiophene, pyrrole or furan have been reported, none of them were dedicated to siloles until we briefly described in a preliminary communication the synthesis and properties of the silole based diradical **7d** (see Scheme 1). Our objectives were: i) to study the silole as a magnetic coupler, to determine what kind of magnetic interaction is mediated through it and the role of the silicon atom in the magnetic exchange when it is incorporated in such a kind of ring; ii) to study the photo-excited state of the silole coupler and iii) to try to use it as an access to photo-excited high spin states following the strategy described by *Teki et al.* in the case of the anthracene coupler.^[21-23] Compound **7d**, which belongs to the pseudo-disjoint diradical class, allowed us to partially address the last two points: the silole coupler possess a photo-excited triplet state but the diradical did not show any high spin photo-excited state.^[24] However, the very weak intramolecular antiferromagnetic interaction observed in this compound, mainly originating from its doubly disjoint character, prevented us from clearly determining whether the silole ring mediates magnetic interactions and whether the magnetic exchange pathway involves the silicon atom or not since the spin density delocalization on the silole ring is very low in these systems.

In order to complete the study of the silole ring as a magnetic relay and to determine the role of the silicon atom in the magnetic exchange in such a five membered coupler, we

present herein a series of diradicals incorporating either the silole or the thiophene ring as a coupler, in which the relative position of the nitroxide radicals on the pendant aryl substituents (*para* vs *meta*, Scheme 1) has been changed to increase the spin density on the silole bridge. The synthesis, structural and electronic characterization of this series of diradicals is presented here in detail. Their magnetic behavior has been investigated both in the solid state and in dilute solutions, and the experimental data has been complemented by DFT calculations to shed some light on magnetic interactions mediated by this peculiar silicon containing organometallic unit.

Scheme 1. Silole- and thiophene-bridged diradicals.

Results and Discussion

Synthesis: 2,5-diaryl-3,4-diphenylsiloles were prepared as outlined in Scheme 2 by an adaptation of the general procedure described by Tamao and Yamaguchi.^[2, 25] It involves the intramolecular reductive cyclization of bis(phenylethynyl)dimethylsilane **2** followed by the Pd-catalyzed cross-coupling reaction^[26, 27] between organozinc derivative **3** and an adequately functionalized arylbromide. The arylhydroxylamines **4a-d** were synthesized by a stepwise procedure starting from aryldibromides that were first monolithiated with *n*-butyl lithium at low temperature and then treated with 2-methyl-2-nitrosopropane.^[28, 29] Since the following step involves reagent **3** that is sensitive to the slightly acidic NOH groups, all hydroxylamine derivatives had to be protected with trimethylsilyl (TMS) groups prior to afford compounds **5a-d** to be involved in the reaction. The TMS protecting group was chosen since it is easily removed during the hydrolysis step without the need to use a nucleophilic agent that might lead to unwanted ring-opening reactions of the silole ring. The subsequent Pd-catalyzed cross-coupling reaction between **3** and **5a-d** followed by hydrolysis afforded bishydroxylamines **6a,b** and **6d** in good yields. Unfortunately, due to its low stability, bishydroxylamine **6c** could not be obtained under such synthetic conditions. The silole derivatives **6a,b** and **6d** were further oxidized to the corresponding *tert*-butylnitroxide and nitronyl nitroxide diradicals using freshly prepared silver oxide as the oxidizing agent. As mentioned above, the low stability of **6c** forced us to synthesize diradical **7c** via a slightly different approach involving the coupling reaction of **3** with an excess of dibromonaphthalene (to avoid the formation of silole-naphthalene oligomers) to afford dibromosilole **6'**. A one-pot reaction including lithiation, intermediate formation of the bishydroxylamine and oxidation allowed us to obtain

compound **7c** in good yields. The crude nitroxides were all purified over aluminum oxide or silica gel.

Scheme 2. *i*) 4 eq. Np / Li, THF ; 4 eq. ZnCl₂-TMEDA ; *ii*) 3 eq. Me₃SiCl, 3 eq. Et₃N, THF ; *iii*) PdCl₂(PPh₃)₂, THF ; *iv*) 0.1M HCl; *v*) Ag₂O, CH₂Cl₂ ; *vi*) TMEDA, *n*-BuLi, *t*-BuNO, Et₂O ; *vii*) 0.1M HCl; *viii*) Ag₂O, CH₂Cl₂.

Compound **12** was synthesized and studied as a model compound for comparison. The synthesis of symmetrically disubstituted thiophene-bridged diradicals followed an adaptation of the procedure previously described by Takahashi *et al.* that involves the successive Pd-catalyzed cross-coupling reaction of arylbromides with thienylzinc chloride.^[30] As outlined in Scheme 3 for diradical **12**, the first step involves the cross-coupling reaction of thienylzinc chloride with the *tert*-butyldimethylsilyl- (TBDMS) -protected *N*-(4-Bromo-phenyl)-*N*-*tert*-butylhydroxylamine **4a-TBDMS** to afford **8** in 73% yield. Organozinc chloride **9** prepared from lithiated **8** and ZnCl₂ was allowed to react with **4a-TBDMS** as in the first step to give **10** in 33% yield. Removal of the protecting TBDMS with HF in THF/water solution quantitatively yielded the bishydroxylamine **11** that was subsequently oxidized with lead dioxide in dichloromethane to afford diradical **12** as black needle shaped crystals upon solvent evaporation (67%).

Scheme 3. *i*) *n*-BuLi, THF ; ZnCl₂ ; *ii*) **4a-TBDMS**, PdCl₂(PPh₃)₂, THF ; *iii*) *n*-BuLi, THF ; ZnCl₂(tmeda) ; *iv*) **4a-TBDMS**, PdCl₂(PPh₃)₂, THF ; *v*) HF aq., THF ; *vi*) PbO₂, CH₂Cl₂.

Geometries of the silole-bridged diradicals 7a-7d: The determination of the conformational preferences of these diradicals is of outmost importance for the understanding of their magnetic behavior. Since crystals suitable for a X-ray structure determination could only be obtained for **7d** (Figure 3a),^[19] we turned to density functional theory (DFT) calculations with the UB3LYP functional to obtain information about the molecular conformations for the rest of diradicals.^[31-33] Due to the size of the molecules, geometry optimizations without symmetry constraints were performed with the 6-31G basis set to the standard convergence criteria as implemented in Gaussian98.^[34] Such calculations were followed by single point runs using a 6-31+G* basis with tight convergence and the ultrafine integration grid in order to obtain accurate energies and spin densities. Structurally characterized silole-bridged diradical **7d** served as a benchmark to test how well the experimentally determined geometry

is reproduced by the calculations. Some relevant bond lengths, angles, and torsion angles are collected in Table 1 and also compared to the mean values for the core SiC₄ ring of other purely organic siloles obtained from the CSD database.^[35] Geometrical parameters of **7d**, obtained from X-ray analysis are in general very well reproduced, including the bond and torsion angles. The well-known over-estimation of bond lengths by density functional methods, especially manifest in the carbon-heteroatom bonds, does not exceed 3.3 % in any case.

Table 1. Selected bond lengths [Å], angles and torsion angles [°] for **7d**.

	X-ray structure	Optimized geometry	CSD data ^[a]
N-O	1.283	1.324	---
N-C(CH ₃) ₃	1.500	1.522	---
N-Ph ^A ^[b]	1.418	1.428	---
C-C in Ph ^A	1.366 to 1.397	1.392 to 1.412	---
Ph ^A -silole	1.480	1.480	---
C-C in Ph ^B	1.362 to 1.391	1.398 to 1.409	---
Ph ^B -silole	1.498	1.494	---
Si-CH ₃	1.854	1.916	1.869
Si-C2/C5	1.873	1.914	1.876
C=C	1.354	1.369	1.358
C-C	1.501	1.520	1.497
Ph ^B -C=C-Ph ^B	8.8	2.0	---
Ph ^A -C-C-Ph ^B	4.2	6.0	---
Ph ^A -C-Si-CH ₃	50.9 and -74.2	54.9 and -71.9	---
C-C=C	116.0	116.1	---
C=C-Si	107.9	108.4	---
CH ₃ -Si-CH ₃	108.4	109.8	---
CH ₃ -Si-C2/C5	109.7 and 118.4	109.8 and 111.5	---
Ph ^A -N-C(CH ₃) ₃	126.5	126.5	---
Ph ^A -N-O	116.2	116.7	---
C(CH ₃) ₃ -N-O	117.3	116.8	---
silole-Ph ^A	47.2	53.2	---
silole-Ph ^B	60.4	55.7	---
(CH ₃ -Si-CH ₃)-silole	82.5	85.9	---
Ph ^A -(CNO)	17.0	14.3	---

^[a]Average data for 14 independent molecules in 12 structures, only structures not containing coordinated transition metals were considered. ^[b] See Scheme 1 for labeling of the aromatic rings.

The bond distances and angles of the silole moiety and phenyl rings in the other diradicals are very similar to those of **7d**. Moreover, the geometrical parameters of the radical substituents are in the range of the data reported for other *tert*-butylnitroxide radicals. Therefore, the discussion will focus on the torsion angles between the aromatic spin-bearing units, the phenyl rings, and the central silole group, which are collected in Table 2. Coordinates of the minimum geometries for **7a** to **7d** are included in the Supporting Information (Tables S1 to S4). These torsion angles should determine the degree of delocalization/spin polarization of the unpaired electrons from the radical moieties onto the silole core of the molecule.

Table 2. Torsion angles [°] in diradicals **7**.^[a]

	7a	7b	7c	7d (opt.)	7d (X-ray)
silole-Ph ^A ^[b]	41.1	41.3	72.9/71.0	53.2	47.2
silole-Ph ^B	58.7	59.1	53.8/54.0	55.7	60.4
(CH ₃ -Si-CH ₃)-silole	85.2	85.5	87.7	85.9	82.5
Ph ^{A/C} -(CNO)	3.1/2.9	6.4/6.5	74.3/76.5	14.3	17.0
Ph ^A -C ₃ N ₂	---	---	---	---	---
Ph ^A -Ph ^C	---	33.6	---	---	---

^[a]Only one entry if both values are identical. ^[b] See Scheme 1 for labeling of the aromatic rings.

All compounds have a propeller-like arrangement of the four phenyl rings, as found in the crystal structure of **7d** (Figure 3a) and reported for other tetraphenyl-substituted siloles,^[2, 19] while the two methyl substituents on the silicon atom are nearly perpendicular to the mean plane of the SiC₄ ring. Therefore, the molecular geometries approach C₂ symmetry, even though the optimizations were done without any constraints. The torsion angles of the non-substituted phenyl rings at the 3- and 4-positions of the central silole ring are larger than those of the radical-bearing phenyl rings in 2- and 5-position due to the larger steric interactions with two neighboring rings in the former as compared with just one for the latter ring. An exception is found for diradical **7c**, in which the larger size of the aromatic groups, due to the additional fused rings D enforces a torsion angle between the naphthyl and silole ring which is 20 to 30 degree larger than in the others, leading to an almost perpendicular arrangement of the two rings (Figure 3b). The same degree of steric hindrance is also seen between the naphthyl and nitroxide groups in **7c**, leading to large torsion angles of 74.3° and 76.5°, while in the cases of **7a** and **7b**, the phenyl ring and radical-bearing units are almost coplanar, and only a slight deviation from planarity is found in **7d** with torsion angles of 17.0° and 14.3° for

the X-ray and optimized geometries, respectively. The torsion angle between both phenyl rings in the biphenyl unit of **7b** is 33.6°.^[35]

Figure 3. X-ray structure of **7d** (a). UB3LYP/6-31G-optimized geometry of **7c** (b).

Geometry of the thiophene-bridged diradical 12: Crystals of **12** obtained by slow evaporation of a dichloromethane solution were subjected to X-ray diffraction analysis at 150 K. Compound **12** crystallizes in the orthorhombic crystal system in the $Pna2_1$ space group (Figure 4). The crystal lattice structure is made up of pairs of independent molecules *A* and *B* forming an herringbone pattern along the *b* axis (see Figure S1 in Supporting Information). The examination of the molecular structure shows that the mean plane of the terminal phenyl rings is tilted relative to the central thiophene ring by 5.0° and 8.5° for molecule *A*, and 11.8° and 7.2° for molecule *B*, respectively. These values, as well as the bond lengths of the π -system, are in the range of those reported for the related 2,5-diarylthiophenes crystal structures SUSNEZ^[36] and FEJRUH.^[37] The torsion angles between the nitroxide moiety and the phenyl ring are 20.9° and 3.2° for molecule *A* and 23.1° and 1.8° for molecule *B*, respectively. While the first torsion angle values are not uncommon in phenyl-substituted nitroxide radicals (see above), the second ones are unusual,^[38, 39] and rather in the range of the values reported for benzoquinonimine-*N*-oxide derivatives (3.3°).^[40, 41] To check whether this structure reflects either a benzenoid or a quinonoid form in the crystal lattice, the 2,5-diphenylthienyl bond lengths for **12**, crystal structures SUSNEZ,^[36] FEJRUH (benzenoid forms),^[37] VIZBUB^[42] and QIPQAH (quinonoid forms)^[43] were compared (see Figure S2 and Table S5 in the Supporting Information). Interestingly, the bond lengths in the thiophene ring are not much affected by the structural modifications that accompany the transformation from a benzenoid form to a quinonoid form. More pronounced is the elongation of the C3-C4 and C4-C5 bonds in the adjacent phenyl rings that reaches *ca.* 10% and the concomitant shortening of the C2-C3 and C5-C6 bonds (*ca.* 5%). Therefore, since the bond lengths found for compound **12** are rather in the range of the values measured for benzenoid forms, we can assess that the diradical likely adopts this structure in the crystal.

Figure 4. ORTEP view of **12** (50% probability).

Electronic absorption spectra: The UV-visible spectra of freshly prepared diradicals and their parent hydroxylamines were measured in chloroform. The resulting data are summarized

in Table 3, which also contains the data on silole **1** for comparison. For all silole derivatives, the spectra are dominated by a broad absorption around 350-420 nm that is characteristic of the π - π^* transition originating from the silole ring.^[2] The diradicals are characterized by two additional absorption bands at *ca.* 300 nm and 450 nm ascribed to the Ar-NO π - π^* and N-O n - π^* transitions, respectively. From an examination of the peak positions of the π - π^* transitions (Table 3), it follows that these transitions are affected by three factors. First, by the nature of the aryl groups in the 2,5-positions (phenyl *vs* naphthyl), second, by the electron withdrawing effects induced by the substituents, and third, by the substituent position relative to the silole ring. Therefore, the conversion of the NOH groups to NO $\cdot$ leads to a bathochromic shift of the silole ring π - π^* transition in every case. A minor red-shift of 2 nm is also observed for diradicals **7d** with the nitroxide groups in *meta* orientation with respect of the silole ring. Although they are connected in a *para* orientation, which should promote larger electronic effects of the substituents, **7b** and **7c** only show a moderate red-shift of 9 and 12 nm, respectively, when compared to diradical **7a** which, with 54 nm, exhibits the largest shift in the series. Such differences might be ascribed to the different torsion angles as revealed by the molecular structures (Table 2). Thus, changing a biphenyl (**7b**) to a naphthyl (**7c**) ring does not seem to markedly affect the overall electronic effects induced by the oxidation of the hydroxyl groups since the combination of torsion angles and distances lowers the π -conjugation. Diradical **12**, with a lower steric hindrance and larger conjugation, however shows more drastic changes upon oxidation. The unique sharp absorption band observed at 344 nm for the bishydroxylamine, experiences a large red-shift to yield a very broad absorption at 391 nm whereas three new absorption bands appear at 444, 479 and 551 nm. These modifications strongly suggest that diradical **12** undergoes an electronic reorganization in solution (*vide infra*). The structural stability of the silole diradicals was also checked by UV-visible spectroscopy. With the exception of **7a**, the spectra of all the siloles remained identical for more than two weeks in solution and for several months in the solid state. By contrast, in the spectrum of **7a** four new absorption bands at 309, 364, 401, and 570 nm appear when the diradical remains in solution for one day. These new absorption bands are similar to those observed for **12**, indicating that both diradicals experience the same electronic reorganization. Actually, a similar behavior was observed for diradicals that correspond to an open-shell resonant form of a closed-shell structure.^[44] Basically, diradicals that are connected through the *para* position of a phenyl ring or of a more extended π -system quickly undergo an electronic rearrangement of their backbone leading to diamagnetic

quinonoidal structures.^[30, 40, 41, 45-48] From a spectroscopic point of view, quinonoidal structures are characterized by π - π^* transitions at *ca.* 320, 404 nm ($C=N^+-O^-$),^[41, 49] and 550 nm (terphenoquinone).^[30] The data strongly suggests that diradicals **7a** and **12** undergo an electronic rearrangement to adopt quinonoidal structures, as previously found in related systems.

Table 3. UV-visible absorption spectral data for dihydroxylamines **6** and diradicals **7**^[a].

Compound	1	6a	7a	6b	7b	6c	7c	6d	7d
π - π^* _{Ar-NO} ^[b]	-	-	300	-	323	-	296	-	285
π - π^* _{silole}	359	366	420	391	400	351	363	360	362
n - π^* _{NO}	-	-	448	-	451	-	450	-	450

^[a] 10⁻³ M solutions in CHCl₃. ^[b] transition $\lambda_{\max}$ values given in nm.

Electron Paramagnetic Resonance spectra: EPR spectra of the diradicals in degassed dichloromethane solutions were measured in the temperature range 4-298 K. At 298 K, the spectra of siloles **7a-d** and **12** (Figure 5a) show a well resolved symmetrical pattern consisting of five lines with intensities close to 1:2:3:2:1 due to hyperfine coupling between two equivalent nitrogen nuclei. The values found for the apparent hyperfine coupling constants with the N atom are (Table 4), as expected, one half of the related constant found for monoradical derivatives (see below). Moreover, the spectra of such bisnitroxide diradicals indicate that in each case, the exchange coupling parameter J is substantially larger than the nitrogen hyperfine coupling constant ($|J| \gg a_N$). In accordance with the UV-visible data (*vide supra*), the spectra of degassed solutions of diradicals **7b-d** remain unchanged for at least two weeks when stored in the dark, while the spectra of **7a** and **12** recorded after one day show several modifications indicative of a structural/electronic rearrangement in solution. Such modifications include an alteration of the relative peak intensities of the quintet and the appearance of a new hyperfine structure in the two outer and the central line that might be due to the concomitant presence of the diradical and a monoradical having similar chemical structures. As previously described by Forrester *et al.*^[46] the formation of monoradical species derived from bisnitroxides in solution might originate from the abstraction of a hydrogen atom from the solvent by the reactive bisnitrones that result from the quinonoidal

rearrangement of the parent diradicals (Scheme 4). As a result, a monoradical-hydroxylamine is generated, which gives rise to the additional structured signals that are observed in the EPR spectrum overlapped to the diradical signal. For **7a**, no further evolution is noticed in the EPR spectra after three days and the resulting pattern can be fully simulated as a mixture of 83% of diradical **7a** and 17% of a *para*-substituted phenyl-*tert*-butylnitroxide monoradical with the following hyperfine coupling constants: $a_N = 11.4$ G, $a_{\text{Hortho}} = 2.08$ G and $a_{\text{Hmeta}} = 0.85$ G (Figure 5b).^[50] Similar hyperfine coupling constants were found for diradical **12** after remaining three days in solution. From the simulated spectra, a mixture of *ca.* 25% of monoradical and 75% of diradical was obtained. Interestingly, this composition remains almost constant until the disappearance of the EPR signal is observed after a period of three weeks in solution.

Figure 5. Room-temperature EPR spectra (in CH₂Cl₂) of diradical **7a**. (a) Freshly dissolved and (b) after three days in solution.

Scheme 4. Quinonoidal rearrangement of diradical **7a**.

Table 4. Apparent hyperfine coupling constants [Gauss] and diradical purities [%] obtained by simulation of EPR spectra of freshly prepared dilute solutions.

Diradical	7a	7b	7c	7d	12
a_N	5.65	5.81	6.84	6.59	5.97
Diradical purity	90	95	97	97	89

Figure 6. Typical EPR spectrum obtained in frozen dichloromethane at 4K for diradicals **7a**, **c**, **d** and **12**.

EPR spectra of freshly prepared diradicals **7a-d** and **12** in glassy matrices at 100 K gave broad signals that show a fine structure. These signals correspond to the intermolecular $\Delta M_S = 1$ transition of diradicals and originate from the weak dipolar coupling of the two unpaired electrons (Figure 6). The determination of zero-field splitting (*zfs*) parameters from the

simulation of the $\Delta M_S = 1$ signals^[51] could only be carried out for diradicals **7a,c,d** and **12** (Table 5) since dipolar interactions in diradical **7b** are weak compared to the hyperfine coupling constants. The average interspin-distances were estimated to be 10 Å for diradicals **7a** and **12** and 13 Å for diradical **7c** using the point-dipole approximation.^[52] By comparing the average interspin-distances with the distance between the two NO groups obtained from the DFT-optimized geometries (NO...NO: 15.3 Å for **7a** and **12**, and 15.2 Å for **7c**), it is possible to conclude that the spin delocalization through the aromatic rings is much more effective in **7a** and **12** than in **7c** or **7d**. Moreover, the D parameter of **7c** is even smaller than that of **7d** in which the distance between the NO groups is slightly smaller.^[19] This result is in line with the large torsion angles that are found for **7c** (Table 2) that disrupts the π -conjugation and decreases the spin delocalization.

Table 5. EPR parameters used for the simulation of the $\Delta M_S = \pm 1$ signals of diradicals in frozen solution at 100 K.^[a]

Diradical	g_x	g_y	g_z	D (Gauss)	E (Gauss)
7a	2.005	2.005	2.005	30	0
7c	2.005	2.005	2.005	12.5	0
7d	2.008	2.005	2.002	16	0
12	2.005	2.005	2.005	31	0

^[a] In dichloromethane glass.

Decreasing the temperature below 80 K allows the observation of a signal at a field around 1715 G due to the $\Delta M_S = 2$ transition in the thermally populated triplet state of diradicals **7b-d**. This half-field signal is not observed for **7a** and **12** even when large signal amplification and high concentrations are used. On further lowering the temperature, a pronounced increase of the intensity of the $\Delta M_S = 1$ transition is noticed for diradicals **7b-d** whereas a different behavior is observed for **7a** and **12**. For the latter compounds, the signal intensity decreases to a minimum at 35 K for **7a** and at 50 K for **12**, and then slightly increases down to the lowest temperatures attainable. It is worth noting that the increase of the $\Delta M_S = 1$ signal at very low temperature is more pronounced with aged samples. Since the intensity of the $\Delta M_S = 1$ transition is proportional to the molar paramagnetic susceptibility of the sample, this behavior might originate from the simultaneous presence of either the diradical species, in which antiferromagnetic interactions take place between the unpaired

electrons, and the monoradical species; as suggested by the isotropic room temperature spectrum (*vide supra*).

To determine the nature and the strength of magnetic coupling between the spin-bearing moieties in diradicals **7b-d**, the intensity of the $\Delta M_S = 2$ transition was measured as a function of temperature between 4 and 30 K in frozen dichloromethane. In each case, as the temperature was decreased, the $\Delta M_S = 2$ signals, due to the triplet state, increased in intensity. The plot of the dependence of the intensity of this signal on the reciprocal of the absolute temperature (Curie plot) is given in Figure 7 for diradical **7b**. The observed deviation of the intensity from the Curie law strongly suggests that diradicals **7b-d** exist in a singlet ground state with an accessible thermally populated triplet state.

Figure 7. Temperature dependence of the EPR signal intensities of the $\Delta M_S = 2$ transition for diradical **7b** in frozen dichloromethane. The dashed curve shows the evolution of the signal using the spin-pair Bleaney-Bowers model (see text). The dotted line shows the variation of the signal expected for uncorrelated spins.

In order to evaluate the singlet-triplet energy gap, $\Delta E_{T-S}/k_B$, the Curie plots for diradicals **7b-d** were analyzed with the Bleaney-Bowers model (Eq. 1), which describes the magnetic behavior of isolated diradicals.^[53] The best fit of the experimental data to Eq.1, where C is a constant to fit the sample intensity, and ΔE_{T-S} is the singlet-triplet energy gap, indicates that the energy separation between the accessible thermally populated triplet state and the singlet ground state are 3.5, 2.1 and 5.6 cm^{-1} for diradicals **7b**, **7c** and **7d**, respectively.

$$I_{\text{ESR}} = \frac{C}{T} \left[\frac{1}{3 + \exp\left(\frac{\Delta E_{T-S}}{k_B T}\right)} \right] \quad (1)$$

Magnetic susceptibility measurements:^[54] The magnetic properties of diradicals **7a-d** and **12** were also investigated on polycrystalline samples in the temperature domain of 2 to 300 K. The temperature dependence of the molar magnetic susceptibility, χ_M , for compounds **7a**, **7c** and **12** is given in Figure 8 in the form of a plot of $\chi_M T$ versus T since they are representative of the two types of magnetic behavior that are observed for this series of diradicals. For

diradicals **7b-d**, the $\chi_M T$ value of *ca.* $0.63 \text{ cm}^3 \text{Kmol}^{-1}$ remains constant from 300 K down to *ca.* 20 K and a slight decrease at lower temperatures is observed. Such a behavior is indicative of very weak antiferromagnetic interactions between the spin carriers. In contrast, $\chi_M T$ values of $0.33 \text{ cm}^3 \text{Kmol}^{-1}$ and $0.28 \text{ cm}^3 \text{Kmol}^{-1}$ were found at 300 K for compounds **7a** and **12**, respectively. Such values are well below the expected contribution of two non-correlated $S = \frac{1}{2}$ spins ($0.75 \text{ cm}^3 \text{Kmol}^{-1}$). Moreover, the $\chi_M T$ values rapidly decrease as the temperature is lowered, finally reaching a plateau value of $0.06 \text{ cm}^3 \text{Kmol}^{-1}$ below 28 K for **7a** and $0.10 \text{ cm}^3 \text{Kmol}^{-1}$ below 55 K for **12**. For these two compounds rather strong antiferromagnetic interactions are operative between the two radical units. In the lower temperature domain, the observation of $\chi_M T$ values different from zero is ascribed to the presence of a minor fraction of mono-radical species in the samples, resulting from the structural/electronic rearrangement and hydrogen abstraction of **7a** and **12**, as shown by the EPR and the UV-visible studies described above.

The magnetic behavior of compounds **7b-d** has been analyzed by a modified dimer model, using the spin Hamiltonian $\hat{H} = -2JS_1\hat{S}_2$.^[53, 55] The corresponding expression for $\chi_M T$ is given by Eq. 2 where J stands for the exchange parameter, g is the isotropic Landé constant, β is the Bohr magneton, and k_B is the Boltzmann's constant. A purity factor, f , was introduced to account for the possible presence of diamagnetic fractions due to the instability of these diradicals.^[56] The best fit to the experimental data yielded $J = -1.8 \text{ cm}^{-1}$ with $f = 0.84$ for **7b**, $J = -1.3 \text{ cm}^{-1}$ with $f = 0.81$ for **7c** and $J = -4.2 \text{ cm}^{-1}$ and $f = 0.96$ for **7d**. The introduction of a Weiss constant, θ , in the analytical expression did not significantly modify the resulting parameters. These exchange parameters are very similar to the singlet-triplet gaps ($\Delta E_{T-S} = -2J$) obtained from the glassy matrix EPR studies and, therefore, they can be attributed to intramolecular interaction taking place between the two radical units.

$$\chi_M T = f \left[\frac{2Ng^2\beta^2}{k_B} \cdot \frac{1}{3 + \exp(-2J / k_B T)} \right] \quad (2)$$

The magnetic behavior for compounds **7a** and **12** has also been analyzed by a dimer model but including a paramagnetic contribution arising from monoradical $S = 1/2$ species. The rather low values observed for $\chi_M T$ at 300 K suggested the presence of a non-magnetic fraction and, therefore, the ratios of di- and mono-radicals have been taken as relative to the whole sample. The expression used to analyze the experimental data is given Eq. 3 where a and b refer to the molar fraction of di- and mono-radical species, respectively. The best fit of the experimental data, taking $g = 2$, for **7a** yielded an exchange parameter $J = -142 \pm 0.3 \text{ cm}^{-1}$

with a sample composition in magnetic species of 51% of diradical and 15 % of mono-radical. For compound **12** the resulting parameter was: $J = -248 \pm 1 \text{ cm}^{-1}$ with a sample composition of 39 % of diradical and 25 % of mono-radical.

$$\chi_{\text{M}}T = a \left[\frac{2Ng^2\beta^2}{k_B[3 + \exp(-2J/k_B T)]} \right] + b \left[\frac{Ng^2\beta^2}{2k_B} \right] \quad (3)$$

Figure 8. Temperature dependence of the experimental ($\square$) and calculated (—) $\chi_{\text{M}}T$ behavior for (from top down) compounds **7a**, **7c**, and **12**.

Theoretical calculation of spin densities and exchange parameters: The atomic spin densities calculated in single point runs at the UB3LYP/6-31+G* level are collected in Table 6 for *tert*-butylnitroxides **7a-d**. Spin densities on the *tert*-butyl group are not included since they are very small and comparable to values observed both experimentally or deduced by calculation for other radicals of the same kind.^[38, 57-59]

Table 6. Mullikan atomic spin densities for **7a-d** calculated at the UB3LYP/6-31+G* level.

Atom ^[a]	7a	7b	7c	7d ^[b]	7d ^[b]
	Optimized geometry	Optimized geometry	Optimized geometry	X-ray structure	Optimized geometry
N	0.3757/0.3747	0.3719/0.3785	0.4304/0.4326	0.4017	0.4020
O	0.4714/0.4728	0.4809/0.4765	0.5206/0.5235	0.4764	0.4789
C4 Ph ^C		-0.1200/-0.1185			
C3/C5 Ph ^C		0.1352/0.1320			
		0.1264/0.1285			
C2/C6 Ph ^C		-0.0631/-0.0687			
		-0.0712/-0.0671			
C1 Ph ^C		0.1175/0.1177			
C4 Ph ^A	-0.1306/-0.1293	-0.0240/-0.0226	-0.0233/-0.0320	0.1461	0.1634
C3/C5 Ph ^A	0.1257/0.1261	0.0226/0.0220	0.0349/0.0307	-0.0588	-0.0652
	0.1306/0.1325	0.0222/0.0220	0.0165/0.0307	-0.1351	-0.1487
C2/C6 Ph ^A	-0.0679/-0.0687	-0.0127/-0.0138	-0.0111/-0.0085	0.1196	0.1238
	-0.0653/-0.0650	-0.0123/-0.0121	-0.0070/-0.0063	0.1270	0.1346
C1 Ph ^A	0.1228/0.1181	0.0232/0.0219	0.0204/0.0152	-0.0607	-0.0696
C7 Ph ^D			0.0073/0.0059		
C8 Ph ^D			-0.0053/-0.0041		
C9 Ph ^D			0.0073/0.0057		

C10 Ph ^D			-0.0026/-0.0021		
Si	0.0054	0.0012	0.0017	-0.0051	-0.0061
Si-CH ₃	-0.0013/-0.0001	-0.0001/0.0000	-0.0001/0.0000	0.0008	0.0005
silole-C2/C5	0.0277/-0.0062	-0.0025/-0.0003	-0.0001/0.0146	0.0069	0.0093
silole-C3/C4	0.0125/0.0395	0.0045/0.0062	0.0084/-0.0218	-0.0085	-0.0081
C1 Ph ^B	-0.0060/-0.0062	-0.0009/0.0016	0.0001/0.0008	0.0003	-0.0010
C2/C6 Ph ^B	0.0044/0.0042	0.0008/0.0007	0.0000/0.0000	-0.0001	0.0002
	0.0039/0.0038	0.0007/0.0007	-0.0002/0.0001	-0.0043	-0.0059
C3/C5 Ph ^B	-0.0019/-0.0018	-0.0004/-0.0003	0.0001/0.0000	-0.0006/	0.0035/
	-0.0013/-0.0012	-0.0002/-0.0001	0.0002/0.0000	0.0028	-0.0002
C4 Ph ^B	0.0032/0.0033	0.0007/0.0006	-0.0001/0.0001	0.0004	-0.0002

^[a]See Scheme 1 for labeling scheme. ^[b]Only one value is reported since the two halves of the molecule are identical due to its C₂ symmetry.

The spin density on the spin-bearing units is as expected, with a large positive spin density on the NO groups. The spin density then spreads out onto the adjacent phenyl ring *A* (see Scheme 1), due to the direct delocalization of the unpaired electron onto the phenyl ring in the latter, and follows the sign alternation principle.^[57, 58] The only exception is found for naphthyl-substituted **7c**, in which the large NO-naphthyl torsion angles of 74.3° and 76.5° prevents delocalization of the unpaired electron from the NO group, therefore leading to spin densities on the *A* ring of the naphthyl group that are one order of magnitude smaller than in the other *tert*-butylnitroxides **7a**, **7b**, and **7d**, while the fused ring *D* carries an even smaller spin density. Furthermore, in the biphenyl-substituted compound **7b**, only the ring *C*, directly connected to the NO group, carries a spin density comparable to **7a** and **7d**, while on ring *A*, the spin density is smaller by a factor of about five due to the Ph-Ph torsion angle of 33.6°, which prevents further delocalization of the unpaired electron from ring *C* to ring *A*. This diradical is another example of conformational effects modulating the spin density distribution in this series of compounds.

The spin density on the silicon atom is small (< 0.01) in all cases and the sign systematically depends on the position (*meta* vs. *para*) where the spin-bearing moiety is attached to the aromatic ring. It also correlates with the amount of spin density on the phenyl ring *A* attached to the central silole ring. In cases with little spin density on ring *A*, either because it only originates from spin polarization or due to conformational constraints that prevent efficient delocalization of the unpaired electron (**7b** and **7c**), the spin density on the silicon atom is very small (< 0.002). In contrast, in radicals **7a** and **7d** with larger spin

densities on phenyl ring *A*, the spin density on the Si atom is larger by a factor of three to five (**7a**: 0.0054, **7d**: -0.0051 (X-ray), -0.0061 (optimized)). The spin density on the methyl substituents on the silicon atom and the 3- and 4-phenyl rings *B* is very small and approaches zero in all compounds. Interestingly, no clear correlation between the sign and magnitude of the spin density and conformational preference can be drawn for the carbon atoms of the silole ring, especially in the cases with no imposed symmetry (**7a-d**). In general, there is little unpaired spin on the carbon atoms (< 0.01 in almost all cases), but the magnitude and sign are in some cases different for the C2/C5 and C3/C4 atoms, even though all molecules possess near- C_2 symmetry. This might be either due to subtle differences in the conformations of the two halves of the molecules or a slight contamination of the triplet states by close-lying higher spin states, as is apparent in the deviation of $\hat{S}^2$ from the expected value of 2.0 (**7a**: 2.0292, **7b**: 2.0284, **7c**: 2.0100, **7d**: 2.0211 (x-ray), 2.0215 (optimized)).

In order to test if the computational methods used are able to correctly reproduce both the sign and magnitude of the exchange parameter J experimentally determined for **7d**, the energies of the broken-symmetry singlet and high-spin triplet states of **7d** were determined at the X-ray structure coordinates and optimized geometry with high accuracy (UB3LYP, 6-31+G* basis set, tight convergence, ultrafine grid). The values calculated for J of -0.55 cm⁻¹ (x-ray) and -0.39 cm⁻¹ (optimized) from the S-T gap without spin projection using a Hamiltonian of $\hat{H} = -2J\hat{S}_1\hat{S}_2$ are somewhat smaller than the experimental ones ($J = -4.2$ cm⁻¹, SQUID, microcrystalline powdered sample and -5.6 cm⁻¹, EPR, frozen solution), but nevertheless confirm the weak antiferromagnetic coupling mediated by the silole ring in **7d**.

Magnetic coupling mechanism in silole-bridged diradicals: There are two main issues associated with the experimental results here described. First, how do nitroxide radicals interact magnetically when linked by a silole ring? And, second, what is the role of the silicon atom in mediating the magnetic interaction when incorporated in the silole ring? Concerning the first issue, some work has recently been dedicated to the study of systems with paramagnetic centers connected through the 2,5-positions of heteropentacycles such as furans, pyrroles and thiophenes, since these non-alternant conjugated systems may open a large number of intramolecular magnetic exchange possibilities.^[48, 60-62] Among them, the thiophene ring has been shown to act more efficiently than the benzene ring itself since it is more electron-rich and it is sterically less demanding than the latter.^[61] The influence of the spin-bearing sites connected to five membered rings has also been extensively studied. For

instance, the connection of two *meta*-phenylnitrene units leads to systems termed as pseudo-disjoint since spin-bearing units are connected to the central ring through sites bearing minimal spin density (Scheme 5a). These systems usually display singlet ground states with low-lying excited multiplet states. On the other hand, the attachment of two *para*-phenylnitrene units allows the connection through spin-bearing sites that leads to localized quinonoidal diradical systems since they actually correspond to an open-shell form of a Kekulé π -conjugated molecule (Scheme 5b).

Scheme 5.

With respect to this classification, we will divide the molecules described herein in two main categories. Diradical **7d** will be classified in the pseudo-disjoint category whereas the others will be classified in the non-pseudo-disjoint one. Obviously, in all cases antiferromagnetic interactions between the paramagnetic centers are expected both from a valence bond and spin polarization point of view (Scheme 6). However, a careful examination of their magnetic properties will be useful to address the second question concerning the role of silicon in the mediation of magnetic interactions in the silole coupler.

Scheme 6. Expected magnetic interaction in silole-bridged diradicals using the spin-polarization mechanism. Grey circles depict positive spin density regions.

As mentioned above, the pseudo-disjoint category only includes diradical **7d**, which displays weak intramolecular antiferromagnetic interactions in the solid state as well in frozen solution.^[19] At first glance, the nearly planar conformation around the silicon atom in the silole linker accounts for the different behavior with respect to the flexible dinitrene **13** (see scheme 7) for which no magnetic interaction was observed.^[63] Though the spin density on the silicon atom is quite low in all cases (see Table 6), this observation suggests that it might be involved in the exchange interaction pathway. Since the exchange interaction can either be mediated by the π -system of the silole ring or by a σ -pathway involving the silicon atom, the calculations were repeated for the singlet and triplet state of model compound **14** in which the silicon atom was replaced by a sp^3 hybridized carbon atom while otherwise retaining the X-ray structure without geometry relaxation. A value of $J = -0.54 \text{ cm}^{-1}$ was obtained, which is almost identical to the one calculated for the parent compound. Though the energy differences

are very small, we feel that they can accurately be reproduced within a series of compounds and give some evidence that the exchange interaction is mainly mediated by the π -system of the silole ring.^[57, 64, 65]

Scheme 7.

Concerning the second category (non-pseudo-disjoint), two classes of molecules, named here as Class A and Class B, can be distinguished both from magnetic measurements and bonding considerations.

Class A diradicals: The first class of compounds includes diradicals **7a** and **12** that correspond to the open-shell resonant form of a classical Kekulé π -conjugated molecules.^[66] In such systems, the spin coupling is often sufficient to induce a pairing of the single electrons leading to closed-shell structures. This is indeed the case with **7a** and **12**, which exhibit rather strong antiferromagnetic interactions and experience a structural/electronic rearrangement to the corresponding quinonoidal structure. The experimental exchange parameter for these diradicals is very large ($J = -142 \text{ cm}^{-1}$ for **7a** and $J = -248 \text{ cm}^{-1}$ for **12**), thus underlining a strong dependence of the exchange interactions on the nature of the central heterocycle. At least three factors may be invoked to explain such a difference: conformation, spin density and heteroatom effect. Conformational and spin density effects are already known to play an important role in the magnetic exchange modulation for TMM-type diradicals.^[64, 67] It has been shown that the exchange coupling parameter can be closely correlated to the average side-ring torsion angles (ϕ_{av}) via a “Karplus-Conroy type” relation (Eq. 4) where the A term is related to the coupler and the spin density on the spin-containing group and the B term corresponds to the through-space antiferromagnetic interaction.

$$J = A \cos^2 [\phi_{av}] + B \quad (4)$$

If we assume that the through-space antiferromagnetic interaction is negligible (*vide supra*), and that the spin density carried by the side groups is similar for both compounds (see magnetic measurements above), then the ratio $A(\mathbf{7a})/A(\mathbf{12})$ should give an estimate of the ability of the central heterocycle to mediate antiferromagnetic interactions.

$$A(\mathbf{7a})/A(\mathbf{12}) = \{J(\mathbf{12}) \cos^2 [\phi_{av}(\mathbf{7a})]\} / \{J(\mathbf{7a}) \cos^2 [\phi_{av}(\mathbf{12})]\} \quad (5)$$

Taking average torsion angles of 41.1° for **7a** and 12.3° for **12**, we find a value of 0.96 for the $A(\mathbf{7a})/A(\mathbf{12})$ ratio whereas the $J(\mathbf{7a})/J(\mathbf{12})$ ratio is 0.57. This result indicates that both the silole ring and the thiophene ring intrinsically act as antiferromagnetic couplers with the same efficiency. The presence of the additional phenyl rings at the 3,4-positions of the silole ring for **7a** induces torsion angles for the spin-bearing units that are responsible for the low value of the exchange parameter compared to **12**. On the other hand, the increased stability of **12** likely originates from the aromatic character of the thiophene compared to the silole unit. Indeed, as shown for phenyl-conjugated Kekulé-type dinitrenes,^[65] the tendency to maintain the aromaticity tends to favor the diradical structure over the quinonoidal one.

Class B diradicals: The second class of compounds, which includes diradicals **7b** and **7c**, also corresponds to the open-shell resonant form of Kekulé π -conjugated molecules. The main difference between these siloles and **7a** is that they have been designed to disfavor a quinonoidal rearrangement, either by inserting or by fusing an additional phenyl ring to the structure. The Magnetic studies revealed weak antiferromagnetic interactions for this class of diradicals with exchange parameter of $J = -1.8 \text{ cm}^{-1}$ and $J = -1.3 \text{ cm}^{-1}$ for **7b** and **7c**, respectively. This can be attributed to both the large separation (**7b**) and the large torsion angles (**7c**) between the spin bearing units. It is therefore not surprising to find very small values of spin density on the silicon atom by DFT calculations.

$$J = A \cos^2 [\phi_{av}].\cos^2 [\phi'_{av}] + B \quad (6)$$

Since the distance between the radical centers is very similar in diradicals **7a** and **7c**, we have checked if the exchange modulation observed for these diradicals is governed by conformational considerations. Modifying Eq. 4 to take into account the average torsion angle between the phenyl ring and the *tert*-BuNO group (ϕ'_{av}) (Eq. 6) and the $A(\mathbf{7a})/A(\mathbf{7c})$ ratio can be determined. Using the torsion angles from Table 2, and setting B to zero we find that the $A(\mathbf{7a})/A(\mathbf{7c})$ ratio, which reflects the magnetic coupling ability of the silole, is equal to 1.05 whereas the $J(\mathbf{7a})/J(\mathbf{7c})$ ratio is equal to 94.7. For this class of diradical, too, the exchange mechanism appears to mainly involve the π -system of the silole ring.

Conclusion

In order to study the ability of the silole ring to act as a magnetic coupler and to determine the role of the silicon atom in the magnetic exchange in such molecules, we have synthesized and investigated the magnetic properties of a series of diradicals where the two spin-bearing units are linked by a non-alternant silole ring. The thiophene-coupled diradical **12** was also synthesized to allow for the comparison with this well-known heteropentacycle. While compounds **7b**, **7c** and **7d** are quite stable either in solution or in the solid state, **7a** and **12** partially undergo an electronic rearrangement to both a diamagnetic quinonoidal form and a monoradical specie due to the fact that they correspond to the open-shell form of a π -conjugated Kekulé structure. Geometry optimizations on silole-bridged diradicals, at the UB3LYP/6-31G level, accurately reproduce the experimental geometry available for comparison. Spin densities calculated with the larger 6-31+G* basis set and the same functional compare quite well with other reported calculations. Such spin densities along with the structural data obtained from the geometry optimizations, show how different mechanisms giving rise to the spin density distribution (direct delocalization vs. spin polarization) combined with conformational constraints determine the spin density at the core of the molecules. Thus, the connection across the 2,5-positions of spin-bearing units leads to intramolecular antiferromagnetic interactions that are modulated by the conformation of the molecules leading to singlet ground states. The weak antiferromagnetic exchange interaction between the two radical moieties that is experimentally found in compound **7d** could also be confirmed by theoretical calculations and an exchange parameter unaltered by substitution of silicon by carbon in a model compound suggests the interaction to proceed mainly via the π -system of the silole ring. Finally, analyses of the data using a “Karplus-Conroy” type relation allowed us to establish that the silole ring, as a whole, leads to a stronger exchange interaction between the two nitroxide radicals attached to its 2,5-positions than the thiophene ring. This increased efficiency likely originates from the non-aromaticity of the silole allowing for a better magnetic interaction through it.

Experimental Section

Materials and methods: All reactions were routinely carried out under argon using standard Schlenck techniques. Solvents were distilled prior to use. THF was dried over sodium/benzophenone and distilled under Argon. All commercial reagents were used as received. Bis(phenylethynyl)dimethylsilane^[68] was obtained by the reaction of

dimethyldichlorosilane and phenylethynyllithium, which was prepared from *n*BuLi and phenylacetylene in ether. ^1H , ^{13}C and ^{29}Si NMR spectra were recorded on a Bruker Advance 200 DPX spectrometer, the FT-IR spectra on a Thermo Nicolet Avatar 320 spectrometer, the UV-visible spectra on a Secomam Anthelie instrument and the MS spectra on a Jeol JMS-DX 300 spectrometer. Elemental analyses were performed at the Service Central de Microanalyse of the CNRS, Vernaison, France. The ESR spectra were recorded on X-band Bruker Elecsys spectrometer. Magnetic measurements down to 2 K were carried out in a Quantum Design MPMS-5S SQUID susceptometer. All magnetic investigations were performed on polycrystalline samples. The molar susceptibility was corrected for the sample holder and for the diamagnetic contribution of all atoms by using Pascal's tables.^[55, 69]

1-[*N*-*tert*-butyl-*N*-(trimethylsiloxy)amino]-4-bromobenzene **5a:** To a solution of 1-[*N*-*tert*-butyl-*N*-(hydroxylamino)-4-bromobenzene **4a**^[29] (12.2 g, 50 mmol) in THF (100 mL) was added an excess of triethylamine (21 mL, 150 mmol). To the reaction mixture was added chlorotrimethylsilane (19 mL, 150 mmol) in THF (50 mL). After stirring at 45 °C for 20 h, the solvents were evaporated to yield a residue that was treated with 200 mL of pentane and filtered. The filtrate was evaporated in vacuum to yield **5a** as an orange oil (14.1 g, 89%). ^1H NMR (CDCl_3 , 298 K) : δ = 0.01 (s, 9 H), 1.10 (s, 9 H), 7.16 (d, $J(\text{H,H})$ = 8 Hz, 2 H), 7.37 ppm (d, $J(\text{H,H})$ = 8 Hz, 2 H) ; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 298 K) : δ = 0.20, 26.48, 61.06, 118.11, 127.11, 130.76, 150.68 ppm; ^{29}Si NMR (CDCl_3 , 298 K) : δ = 22.23 ppm; IR (CHCl_3) : $\bar{\nu}$ = 1360 cm^{-1} (N–O) ; MS (FAB+, *m*-nitrobenzyl alcohol matrix) : m/z : 316 [M^+ + H].

1-[*N*-*tert*-butyl-*N*-(trimethylsilyloxy)amino]-4-bromobiphenyl **5b:** This compound was prepared starting from 1-[*N*-*tert*-butyl-*N*-(hydroxylamino)-4-bromobiphenyl **4b**^[28] in a manner similar to the synthesis of compound **5a** (90%). ^1H NMR (CDCl_3 , 298 K): δ = 0.03 (s, 9 H), 1.16 (s, 9 H), 7.30 (d, $J(\text{H,H})$ = 8 Hz, 2 H), 7.56-7.60 ppm (m, 6 H) ; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 298 K) : δ = 0.25, 26.63, 61.25, 121.44, 125.86, 128.84, 132.17, 136.46, 140.32, 151.29 ppm; ^{29}Si NMR (CDCl_3 , 298 K) : δ = 21.85 ppm; IR (CHCl_3) : $\bar{\nu}$ = 1361 cm^{-1} (N–O) ; MS (FAB+, *m*-nitrobenzyl alcohol matrix) : m/z : 392 [M^+ + H].

1-[*N*-*tert*-butyl-*N*-(trimethylsilyloxy)amino]-4-bromonaphthalene **5c:** This compound was prepared starting from 1-[*N*-*tert*-butyl-*N*-(hydroxylamino)-4-bromonaphthalene **4c** in a manner similar to the synthesis of compound **5a** (95%). ^1H NMR (CDCl_3 , 298 K): δ = 0.04 (s,

9 H), 1.10 (s, 9 H), 5.46 (s, 1 H), 7.79 (d, $J(\text{H,H}) = 8 \text{ Hz}$, 1 H), 8.18 (d, $J(\text{H,H}) = 8 \text{ Hz}$, 1 H), 8.53-8.56 ppm (m, 1 H); ^{29}Si NMR (CDCl_3 , 298 K): $\delta = 21.94 \text{ ppm}$; IR (CHCl_3): $\bar{\nu} = 1361$ (N–O); MS (FAB⁺, m-nitrobenzyl alcohol matrix): m/z : 366 [$\text{M}^+ + \text{H}$].

1-[N-tert-butyl-N-(trimethylsiloxy)amino]-3-bromobenzene 5d: This compound was prepared starting from 1-[N-tert-butyl-N-(hydroxylamino)-3-bromobenzene **4d** in a manner similar to the synthesis of compound **5a** (89%). ^1H NMR (CDCl_3 , 298 K): $\delta = 0.02$ (s, 9 H), 1.13 (s, 9 H), 7.49-7.12 ppm (m, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 298 K): $\delta = 0.19, 26.54, 61.31, 121.47, 124.17, 128.07, 127.93, 128.95, 153.18 \text{ ppm}$; ^{29}Si NMR (CDCl_3 , 293 K): $\delta = 22.51 \text{ ppm}$; IR (CHCl_3): $\bar{\nu} = 1361$ (N–O); MS (FAB⁺, m-nitrobenzyl alcohol matrix): m/z : 316 [$\text{M}^+ + \text{H}$].

Silole 6a: A mixture of lithium (0.2 g, 29 mmol) and naphthalene (3.71 g, 29 mmol) in THF (30 mL) was stirred at room temperature under argon for 5 h to form a deep green solution of lithiumnaphthalenide. To the mixture was added bis(phenylethynyl)dimethylsilane **2** (2 g, 7.7 mmol) in THF (20 mL). After stirring for 10 min, the reaction mixture was cooled to 0 °C and $[\text{ZnCl}_2(\text{tmen})]$ (tmen = *N,N,N',N'*-tetramethylenediamine) (7.82 g, 29 mmol) was added as a solid to form organozinc derivative **3**. After stirring for an hour at room temperature, a solution of **5a** (4.82 g, 15.3 mmol) in THF (20 mL) and $[\text{PdCl}_2(\text{PPh}_3)_2]$ (0.28 g, 0.4 mmol) were successively added. The mixture was heated under reflux and stirred for 24 h. After hydrolysis by HCl (1 *M*), the mixture was extracted with Et_2O . The combined organic layers were washed with brine, dried over MgSO_4 and concentrated. The resulting residue was subjected to a column chromatography (neutral aluminum oxide, pentane:dichloromethane 80:20) to give 2.68 g (4.57 mmol) of **6a** (56 %). M.p. 198°C (decomp.); ^1H NMR ($[\text{D}_6]\text{DMSO}$, 298 K): $\delta = 0.51$ (s, 6 H), 1.13 (s, 18 H), 5.37 (s, 2H), 6.81-6.87 (m, 8H), 7.00-7.05 ppm (m, 10H); $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_6]\text{DMSO}$, 298 K): $\delta = -2.67, 26.83, 60.18, 124.60, 127.14, 128.33, 128.41, 130.22, 135.48, 139.84, 141.02, 149.29, 153.81 \text{ ppm}$; ^{29}Si NMR ($[\text{D}_6]\text{DMSO}$, 298 K): $\delta = 7.46 \text{ ppm}$; IR (CCl_4): $\bar{\nu} = 3589$ (O–H), 1359 cm^{-1} (N–O); UV/Vis (CCl_4): λ_{max} (log ϵ) : 366 nm (1,347, $\pi \rightarrow \pi^*$ silole); HRMS (FAB⁺, m-nitrobenzyl alcohol matrix): m/z : calcd for $\text{C}_{38}\text{H}_{45}\text{N}_2\text{O}_2\text{Si}$ [$\text{M}^+ + \text{H}$]: 589.3250; found 589.3198; anal. calcd for $\text{C}_{38}\text{H}_{44}\text{N}_2\text{O}_2\text{Si}$: C, 77.51; H, 7.53; N, 4.76; Si, 4.77; found: C, 77.55; H, 7.59; N, 4.82; Si, 4.51.

Silole 6b: This compound was prepared starting from compound **5b** in a manner similar to the synthesis of compound **6a** (78 %). M.p. 172°C (decomp.); ^1H NMR ($[\text{D}_6]$ DMSO, 298 K): δ = 0.53 (s, 6 H), 1.16 (s, 18 H), 6.88-6.98 (m, 4H), 6.99-7.08 (m, 8H), 7.20-7.42 (m, 10H), 7.52-7.58 ppm (m, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_6]$ DMSO, 298 K): δ = -2.86, 26.43, 61.15, 125.25, 125.26, 126.30, 126.82, 127.37, 128.56, 129.90, 130.24, 132.27, 132.37, 132.61, 137.54, 138.88, 139.47, 141.51, 154.69 ppm; ^{29}Si NMR ($[\text{D}_6]$ DMSO, 298 K): δ = 8.18 ppm; IR (CCl_4): $\bar{\nu}$ = 3590 (O–H), 1359 cm^{-1} (N–O); UV/Vis (CCl_4): λ_{max} (log ϵ): 391 nm (2.106, $\pi \rightarrow \pi^*$ silole); HRMS (FAB+, m-nitrobenzyl alcohol matrix): m/z : calcd for $\text{C}_{50}\text{H}_{53}\text{N}_2\text{O}_2\text{Si}$ [$\text{M}^+ + \text{H}$]: 741.3877; found 741.3875; anal. calcd for $\text{C}_{50}\text{H}_{52}\text{N}_2\text{O}_2\text{Si}$: C, 81.04; H, 7.07; N, 3.78; Si, 3.79. found: C, 80.95; H, 7.09; N, 3.85; Si, 3.67.

Silole 6d: This compound was prepared starting from compound **5d** in a manner similar to the synthesis of compound **6a** (63 %). M. p. 130°C (decomp.); ^1H NMR ($[\text{D}_6]$ DMSO, 298 K): δ = 0.48 (s, 6 H), 0.97 (s, 18 H), 5.20 (s, 2H), 6.76-6.83 (m, 8H), 7.00-7.14 ppm (m, 10H); $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_6]$ DMSO, 298 K): δ = -3.21, 26.72, 59.92, 80.03, 122.57, 124.94, 125.49, 127.06, 127.315, 127.93, 128.35, 129.07, 130.18, 135.38, 139.04, 139.39, 141.99, 151.29, 154.30 ppm; ^{29}Si NMR ($[\text{D}_6]$ DMSO, 298 K): δ = 7.82 ppm; IR (CCl_4): $\bar{\nu}$ = 3589.7 (O–H), 1363.2 cm^{-1} (N–O); UV/Vis (CHCl_3): λ_{max} (log ϵ): 360 nm (4.83, $\pi \rightarrow \pi^*$ silole); HRMS (FAB+, m-nitrobenzyl alcohol matrix): m/z : calcd for $\text{C}_{38}\text{H}_{45}\text{N}_2\text{O}_2\text{Si}$ [$\text{M}^+ + \text{H}$]: 589.3250; found 589.3243; anal. calcd for $\text{C}_{38}\text{H}_{44}\text{N}_2\text{O}_2\text{Si}$: C, 77.51; H, 7.53; N, 4.76; Si, 4.77; found: C, 77.47; H, 7.58; N, 4.74; Si, 4.56.

Silole 6': This compound was prepared by Pd^0 -catalyzed cross-coupling reaction between 1,4-dibromonaphthalene (6 equivalents) and organozinc derivative **3** in a manner similar to the synthesis of compound **6a** (40 %). M.p. 228-230°C; ^1H NMR ($[\text{D}_6]$ DMSO, 298 K): δ = 0.30 (s, 6 H), 6.78-6.94 (m, 10 H), 7.54-7.68 (m, 8H), 8.08-8.12 (m, 2H), 8.23-8.28 ppm (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_6]$ DMSO, 298 K): δ = -3.66, 126.05, 126.59, 126.83, 127.40, 127.49, 127.52, 127.84, 129.62, 130.11, 130.50, 132.35, 134.31, 138.42, 139.58, 143.41, 155.90 ppm; ^{29}Si NMR ($[\text{D}_6]$ DMSO, 298 K): δ = 11.63 ppm; UV/Vis (CHCl_3): λ_{max} (log ϵ): 351 nm (4.975, $\pi \rightarrow \pi^*$ silole); HRMS (FAB+, m-nitrobenzyl alcohol matrix): m/z : calcd for $\text{C}_{38}\text{H}_{28}\text{Br}_2\text{Si}$ [M^+]: 670.0327; found 670.0349; anal. calcd for $\text{C}_{38}\text{H}_{28}\text{Br}_2\text{Si}$: C, 67.87; H, 4.20; Si, 4.18; found: C, 67.98; H, 4.09; Si, 4.03.

Silole diradical 7a: To a solution of **6a** (0.77g, 1.31 mmol) in CH₂Cl₂ (40mL) was added freshly prepared Ag₂O (0.64g, 2.73mmol). The mixture was stirred for 45 min at 0 °C and filtered. The solvent was removed under vacuum and the resulting deep red solid was purified by column chromatography (neutral aluminum oxide, pentane:dichloromethane 80:20) to give 0.6g (1.01 mmol) of **7a** (78%). M.p. 151°C; IR (CCl₄): 1359 cm⁻¹ (N–O); UV/Vis (CHCl₃): λ_{max} (log ϵ): 300 (4.28, $\pi \rightarrow \pi^*$ aryl nitroxide), 420 (1.365, $\pi \rightarrow \pi^*$ silole), 448 nm ($n \rightarrow \pi^*$ N–O); HRMS (fab+, m-nitrobenzyl alcohol matrix): m/z : calcd for C₃₈H₄₄N₂O₂Si [M⁺ + 2 H]: 588.3172; found 588.3168.

Silole diradical 7b: This compound was prepared starting from compound **6b** in a manner similar to the synthesis of compound **7a** (78%). M.p. 211-213°C; IR (CCl₄): 1354 cm⁻¹ (N–O); UV/Vis (CHCl₃): λ_{max} (log ϵ): 323 (5.351, $\pi \rightarrow \pi^*$ aryl nitroxide), 400 (5.412, $\pi \rightarrow \pi^*$ silole), 451 nm ($n \rightarrow \pi^*$ N–O); HRMS (fab+, m-nitrobenzyl alcohol matrix): m/z : calcd for C₅₀H₅₂N₂O₂Si [M⁺ + 2 H]: 740.3798; found 740.3787.

Silole diradical 7c: To a suspension of silole **6'** (0.37 g, 0.55 mmol) in 100 mL of diethyl ether was added 0.41 mL (2.57 mmol) of *N,N,N',N'*-tetramethylethylenediamine. The mixture was cooled to –78 °C, and then added 1.3 mL (2.57mmol) of a 2 *M* solution of *n*-butyl lithium in hexane under argon. After being stirred for 90 min, the mixture was warmed up to room temperature and stirred for another 90 min. The mixture was cooled to 0 °C. Then a solution of 2-methyl-2-nitrosopropane (340 mg, 3.8 mmol) in 10 mL of diethyl ether was added; the mixture was stirred overnight at ambient temperature under argon, and then treated with 10 mL of saturated aqueous ammonium chloride solution. The organic layers were combined and concentrated under reduced pressure. Addition of pentane yielded a white precipitate of hydroxylamine that was washed several times with pentane to yield the crude. The hydroxylamine was both moisture and air sensitive, so it was used directly to prepare the nitroxide. The white solid was dissolved in 10 mL of freshly distilled dichloromethane and freshly prepared Ag₂O (700 mg, 3 mmol) was added. The mixture was stirred for 60 min at 0°C and the solid Ag₂O was removed by filtration. The filtrate was concentrated under reduced pressure and chromatographed through a silica gel column with 3:2 ethyl acetate:pentane to yield silole **7c** as a reddish orange solid (37%). M.p. 129-132°C; IR (CCl₄): 1357 cm⁻¹ (N–O); UV/Vis (CHCl₃): λ_{max} (log ϵ): 293 (5.304, $\pi \rightarrow \pi^*$ aryl nitroxide), 363

(5.096, $\pi \rightarrow \pi^*$ silole), 456 nm ($n \rightarrow \pi^*$ N–O); HRMS (fab+, m-nitrobenzyl alcohol matrix): m/z : calcd for $C_{46}H_{48}N_2O_2Si$ [$M^+ + 2 H$]: 688.3485; found 688.3476.

Silole diradical 7d: This compound was prepared starting from compound **6d** in a manner similar to the synthesis of compound **7a** (78%). M.p. 124–127°C; IR (CCl_4): 1363.2 cm^{-1} (N–O); UV/Vis ($CHCl_3$): λ_{max} (log ϵ): 283 (5.31, $\pi \rightarrow \pi^*$ arylaminoxide), 361 nm (5.01, $\pi \rightarrow \pi^*$ silole); HRMS (fab+, m-nitrobenzyl alcohol matrix): m/z : calcd for $C_{38}H_{45}N_2O_2Si$ [$M^+ + 3 H$]: 589.3250; found 589.3251.

***N*-tert-butyl-*N*-(tert-butyl-dimethylsilyloxy)amino-4-phenyl-2-thiophene 8:** To a solution of thienylzinc chloride^[30] (0.01 mol) in dry ether (20 ml) was added a solution **4a-TBDMS**^[29] (3.58 g, 0.01 mol) in THF (20 ml) and $Pd(PPh_3)_4$ (0.058 g). The mixture was then stirred at 50 °C for 16 h, quenched with a saturated NH_4Cl solution and extracted with ether. The combined extracts were dried over $MgSO_4$. Evaporation of the solvents and chromatography of the residue on silica gel by eluting with pentane afforded **8** as a white waxy solid (73%). M.p. 56°C; 1H NMR (CD_2Cl_2 , 298 K): δ = -0.02 (s, b, 6 H), 0.97 (s, 9 H), 1.18 (s, 9 H), 7.10 (dd, $J_1(H,H) = 3.4$ Hz, $J_2(H,H) = 3.6$ Hz, 1 H), 7.25 – 7.47 (m, 4 H), 7.53 ppm (d, $J(H,H) = 8.6$ Hz, 2 H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2 , 298 K): δ = -4.50, 18.25, 26.38, 61.31, 122.52, 124.41, 125.96, 131.20, 143.29, 152.18 ppm; ^{29}Si NMR ($CDCl_3$, 298 K): δ = 23.95 ppm; IR (KBr): 3103, 3070 (aromatic C–H), 2990 – 2852 (aliphatic C–H), 1600, 1575 (C=C), 1387 cm^{-1} (N–O); HRMS (FAB+, m-nitrobenzyl alcohol matrix): m/z : calcd for $C_{20}H_{31}NOSSi$ [M^+]: 361.1896; found 361.1904.

Bis[*N*-tert-butyl-*N*-(tert-butyl-dimethylsilyloxy)amino-4-phenyl]-2,5-thiophene 9: To a stirred solution of **8** (2.48 g, 6.86 mmol) in ether (25 ml), was added dropwise a 1.33 *M* solution of *n*-BuLi in hexanes (5.3 ml, 7.03 mmol) at 0 °C. After being stirred for 1 h, the resulting solution was added to $ZnCl_2(tmeda)$ (1.766 g, 6.99 mmol) dissolved in THF (10 ml) at 0 °C, and the mixture is allowed to warm up gradually to room temperature to afford the zinc derivative **9** as light yellow solution. A solution of **4a-TBDMS** (2.45 g, 6.86 mmol) and $Pd(PPh_3)_4$ (0.040 g, 35 μ mol) in THF (30 ml) was added to the zinc derivative **9** and the reaction mixture was stirred for 18 h at 50 °C. After usual work up and silica gel chromatography (pentane), **10** is recovered as a white solid (33%). M.p. 130 – 131°C; 1H NMR (CD_2Cl_2 , 298 K): δ = -0.03 (s, b, 12 H), 0.98 (s, 18 H), 1.17 (s, 18 H), 7.31 (s, 2H), 7.57

(d, $J(\text{H,H}) = 8.5$ Hz, 4 H), 7.37 ppm (d, $J(\text{H,H}) = 8.5$ Hz, 4 H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 298 K): $\delta = -4.49, 18.24, 26.30, 26.35, 61.43, 123.83, 124.67, 126.01, 131.09, 143.29, 151.11$ ppm; ^{29}Si NMR (CD_2Cl_2 , 298 K): $\delta = 23.95$ ppm; IR (KBr): 3071, 3028 (aromatic C–H), 2980 – 2856 (aliphatic C–H), 1600, 1575 (C=C), 1387 cm^{-1} (N–O); UV/Vis (CHCl_3): λ_{max} (log ϵ): 348 nm (4.519, $\pi \rightarrow \pi^*$ thiophene); HRMS (FAB+, m-nitrobenzyl alcohol matrix): m/z : calcd for $\text{C}_{36}\text{H}_{58}\text{N}_2\text{O}_2\text{SSi}_2$ [M^+]: 638.3758; found 638.3760.

Bis[*N-tert*-butyl-4-phenylhydroxylamine]-2,5-thiophene 11: To a stirred solution of **10** (0.798 g, 1.25 mmol) in THF (10 ml) was added a 22.6 M aqueous solution of HF (0.13 ml, 3 mmol) at room temperature. After 1 h, the reaction mixture is evaporated under vacuum to yield the bishydroxylamine as a white solid (99%). M.p. 104°C (decomp.); ^1H NMR ($[\text{D}_6]\text{DMSO}$, 298 K): $\delta = 1.14$ (s, 18 H), 7.29 (d, $J(\text{H,H}) = 8.5$ Hz, 4 H), 7.47 (s, 2 H), 7.61 (d, $J(\text{H,H}) = 8.5$ Hz, 4 H), 8.50 ppm (s, b, 2 H); $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_6]\text{DMSO}$, 298 K): $\delta = 26.82, 60.91, 125.06, 125.14, 125.47, 130.43, 142.81, 150.76$ ppm; IR (KBr): 3230 (O–H), 3029 (aromatic C–H), 2971 – 2870 (aliphatic C–H), 1600, 1542 (C=C), 1387 cm^{-1} (N–O); UV/Vis (CHCl_3): λ_{max} (log ϵ): 348 nm (4.519, $\pi \rightarrow \pi^*$ thiophene); HRMS (FAB+, m-nitrobenzyl alcohol matrix): m/z : calcd for $\text{C}_{24}\text{H}_{30}\text{N}_2\text{O}_2\text{S}$ [M^+]: 410.2028; found 410.1965; anal. calcd for $\text{C}_{24}\text{H}_{30}\text{N}_2\text{O}_2\text{S}$: C, 70.21; H, 7.36; N, 6.82; S, 7.81; found: C, 70.25; H, 7.40; N, 6.79; S, 7.80.

Bis[*N-tert*-butylaminoxyl-4-phenyl]-2,5-thiophene 12: The further oxidation with PbO_2 (2-fold excess) in dichloromethane at room temperature for 2 h gives a deep red solution which was filtered and evaporated under vacuum. The deep red resulting solid was crystallized by diffusion of hexane in dichloromethane to give **12** as black needle-shaped crystals (45%). M.p. 104°C (decomp.); IR (KBr): 3069, 3028 (aromatic C–H), 2997 – 2853 (aliphatic C–H), 1601, 1580 (C=C), 1349 cm^{-1} (N–O); λ_{max} (log ϵ): 322 (4.167, $\pi \rightarrow \pi^*$ aryl nitroxide, terphenoquinone), 391 (4.477, $\pi \rightarrow \pi^*$ thiophene), 444 (4.167), 479 (4.072), 551 nm (3.875, $\pi \rightarrow \pi^*$ terphenoquinone); anal. calcd for $\text{C}_{24}\text{H}_{28}\text{N}_2\text{O}_2\text{S}$: C, 70.56%; H, 6.91%; N, 6.86%; S, 7.85%; found: C, 70.13 6%; H, 7.11%; N, 6.81%; S, 7.88%. A single crystal of approximate dimensions 0.40 x 0.03 x 0.03 mm^3 was mounted on a Nonius κ -CCD diffractometer with $\text{MoK}\alpha$ radiation (0.71069 Å) and cooled to 150 K. The diffracted intensities were collected within the range $3.55^\circ < \theta < 24.71^\circ$. The structural determination by direct methods and the refinement of atomic parameters based on full-matrix least squares on F^2 were performed using the SHELX-97 programs.^[70] Hydrogen atoms positions were all calculated. Results:

2[C₂₄H₂₈N₂O₂S₁] a = 20.752(5) Å, b = 5.826(5) Å, c = 34.309(5) Å, V = 4148(4) Å³, density(calc.)= 1.308, system orthorhombic, space group Pna2₁, 99.8% completeness to theta=24.70°, 24363 collected reflections of which 7020 unique (R_{int} = 0.15) for 523 refined parameters, R_{obs} = 0.056, wR2_{obs} = 0.091, (Δ/σ)_{max} = 0.002, largest difference peak and hole 0.40 / -0.256 e.Å⁻³, max.

Theoretical Calculations: All calculations were done with the Gaussian98 package on a Compaq ES40 parallel computer at the Max-Planck-Institut für Bioanorganische Chemie.^[34] The UB3LYP exchange-correlation functional and a 6-31G basis set were used for the geometry optimizations due to the size of the molecules. To obtain accurate spin densities and energies for the calculation of the exchange coupling constant, calculations were then repeated at the minimum geometries with a 6-31+G* basis set, a tight convergence criterion with the limit set to 10⁻⁸ and the ultrafine integration grid. No spin projection was used in the calculation of the exchange parameter as advocated by Ruiz et al.^[71] The spin-Hamiltonian used to calculate the energy differences was $\hat{H} = -2J\hat{S}_1\hat{S}_2$. The exchange parameter is then obtained as $J = 1/2(E_S - E_T)$.

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Supporting Information Available

UB3LYP/6-31G optimized geometries for radicals **7a–7d**. CIF file and crystal packing of **12** in the *ac*-plane. Selected bond lengths for selected benzenoid and quinonoid structures. Bond

distance variations in 2,5-diphenylthiophenes and *p*-terphenoquinones for the adjacent phenyl ring and the central thiophene ring. CCDC-286386 contains the supplementary crystallographic data for the molecule **12**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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