Synthesis and properties of dinitrobenzamido-TEMPO derivatives

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Abstract

4-Chloro-3,5-dinitrobenzoic acid (**1a**) and 2-chloro-3,5-dinitrobenzoic acid (**1b**) were converted into the corresponding acid chlorides (**2a** and **2b**) and these were reacted first with an equimolar amount of 4-amino-2,2,6,6-tetramethylpiperidine-N-oxyl radical (4-amino-TEMPO) to afford monoradicals **3a**, **3b**, **5a**, and **5b** and then either (i) with methoxyamine to yield hetero-diradicals **6a** and **6b**, or (ii) with a second mole of 4-amino-TEMPO to afford homo-diradicals **4a** and **4b**. The reaction of **3a** with 1,3-bis(aminooxy)propane gave the homo-diradical **7a**. These reaction products are stable mono- or di-radicals as evidenced by their ESR spectra at various temperatures. The above reaction products can participate as oxidizers in redox reactions, and they afford deep-colored anions with inorganic or organic bases.

Keywords: Dinitrobenzamido-TEMPO derivatives, mono- and diradicals (homo- and hetero-diradicals), paramagnetic-chromogenic derivatives, RES, oxidizing properties

Introduction

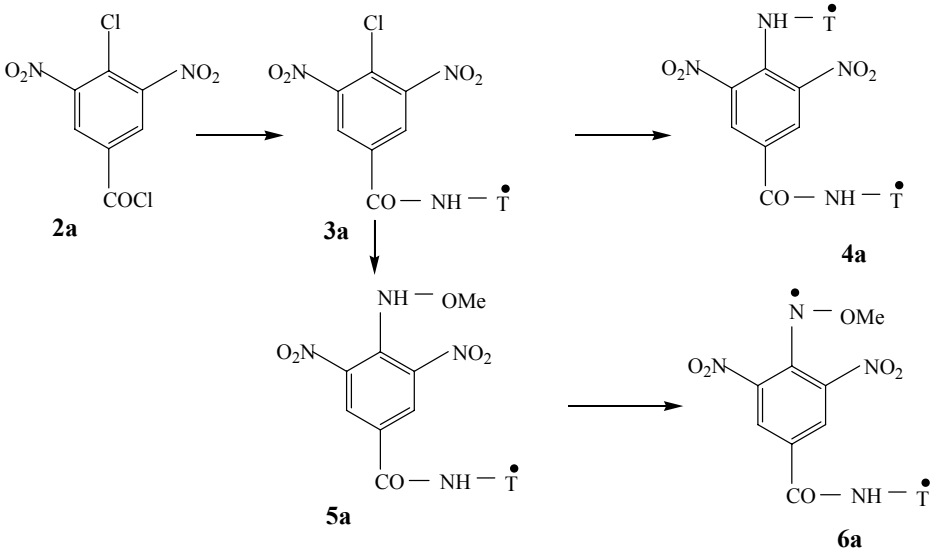
We designed a synthetic approach to stable monoradicals and diradicals starting from chlorodinitrobenzoic acid chlorides, which can undergo nucleophilic substitutions with markedly different rates allowing the selective preparation of target molecules.

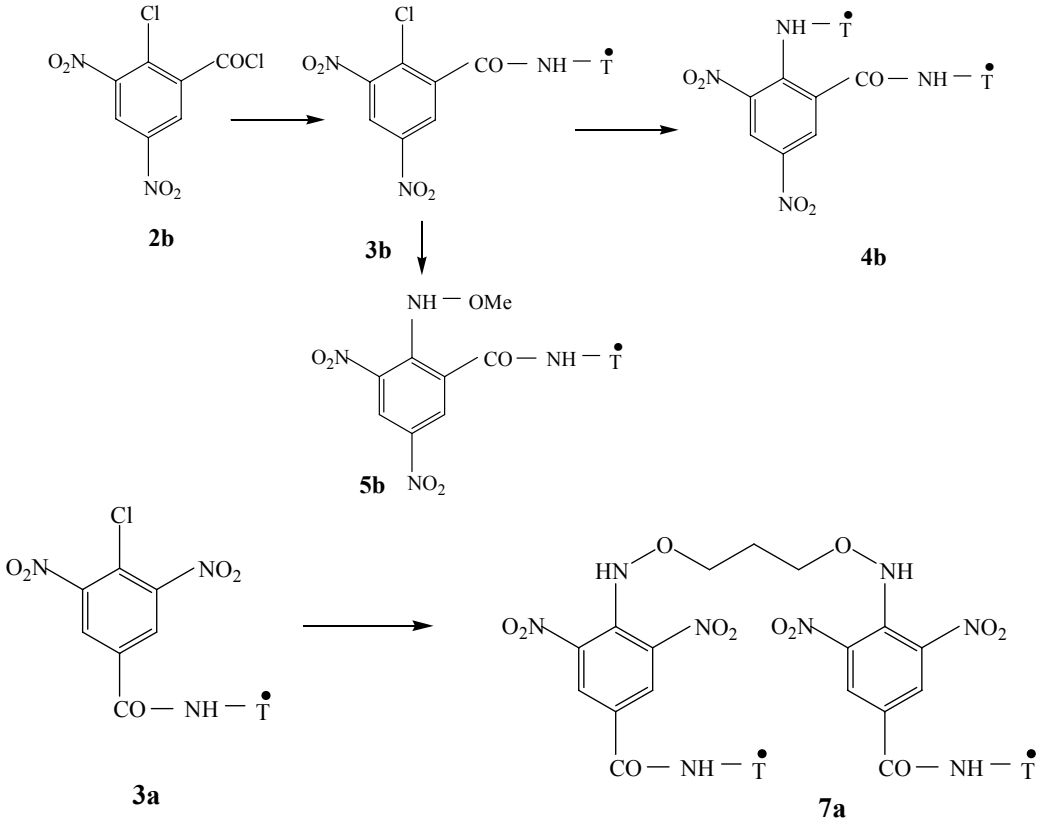
The notation used in the following will denote the series of 2,6-dinitrophenyl compounds with letter **a**, and the 2,4-dinitrophenyl-substituted compounds with letter **b**. A TEMPO radical (2,2,6,6-tetramethylpiperidine-N-oxyl) will be denoted by the letter T with a dot above it, representing the odd electron.

Starting with the commercially available 4-chloro-3,5-dinitrobenzoic acid (**1a**) and 2-chloro-3,5-dinitrobenzoic acid (**1b**), the corresponding acid chlorides (**2a** and **2b**) were prepared. Monoradicals (**3a** and **3b**) incorporating one TEMPO fragment (2,2,6,6-tetramethylpiperidine-N-oxyl) attached via an amidic bond were then obtained by reaction with an equimolar amount of the 4-amino-2,2,6,6-tetramethylpiperidine-N-oxyl radical (4-amino-TEMPO). Then, by an S_NAr reaction,[1,2] the aromatic-bonded chlorine atom was replaced by reaction with either methoxyamine yielding monoradicals **5a** and **5b**,[3-5] or with a second molecule of 4-amino-TEMPO affording homo-diradicals **4a** and **4b**. The latter compounds can also be obtained in one step from **3a** or **3b** with an excess of 4-amino-TEMPO.

A different type of homo-diradical (**7a**) was obtained from two moles of **3a** by reaction with one mole of 1,3-bis(aminooxy)propane.[5] In principle, this compound could be oxidized to a hetero-tetra-radical but this reaction has not yet been tried.

In turn, oxidation of the aryl-N-methoxyamino group [6-12] of **5a** with lead dioxide affords a persistent hetero-diradical **6a** free radical possessing an aminyl and a nitroxidic group. All these structures can be seen in Scheme 1. From them, only compound **3a** was reported earlier.[13]

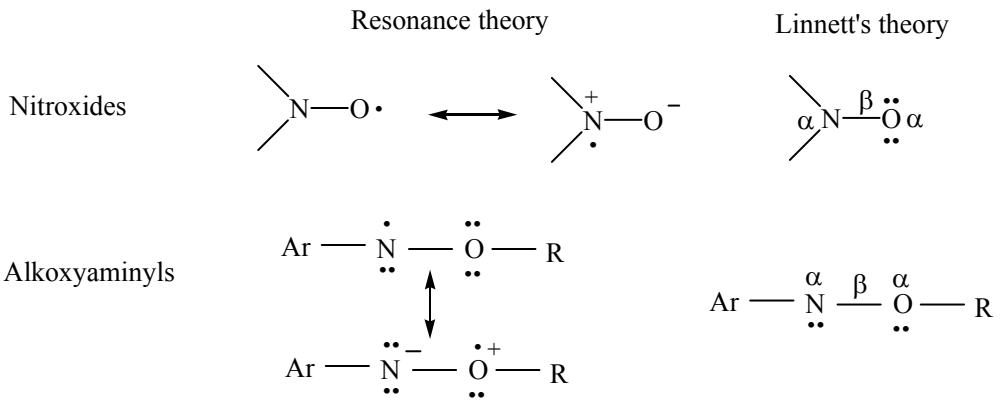




Scheme 1

Results and Discussion

The stability of nitroxides and of push-pull aminyls is nicely explained by Linnett's assumption [14,15] about a higher bond order than 1 between the two heteroatoms due to the presence of two opposite spins (α and β). As seen in Scheme 2, every atom has a closed electronic shell with opposite spins. Unlike the resonance-theoretical explanation, Linnett's theory implies a three-electron bond between the two heteroatoms. Evidence for such a higher bond order was obtained by variable temperature ESR spectroscopy of 1-arenesulfonyl-2,2-bis(3,5-di-tert-butylphenyl)hydrazyl: the rotation barrier between the hydrazinic nitrogens was found to be substantial, leading to magnetic non-equivalence between the two 3,5-di-tert-butylphenyl groups.[16] One should bear in mind that the polynitrophenyl–nitrogen bond in all neutral compounds (and even more in the corresponding anions, as will be discussed in one of the next sections) also has a partial double bond character.



Scheme 2

ESR Spectra

Figures 1 – 3 present room-temperature ESR spectra of some of the compounds discussed above, and Figure 4 shows one low-temperature ESR spectrum. Values of hyperfine coupling constants are presented in Table 1.

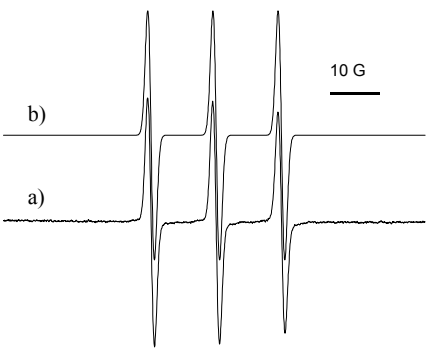


Figure 1. Experimental (a) and simulated (b) ESR spectra of compound **4a**, at room temperature.

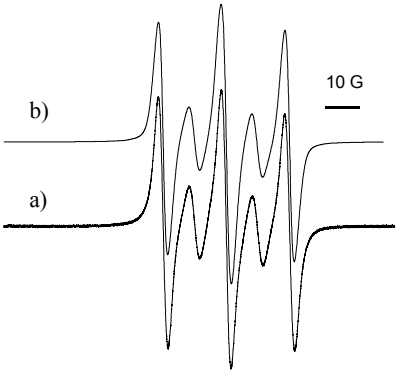


Figure 2. Experimental (a) and simulated (b) ESR spectra of compound **4b,** at room temperature.

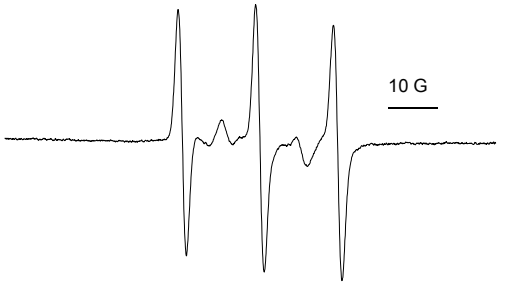


Figure 3. Experimental ESR spectrum of compound **6a**, at room temperature.

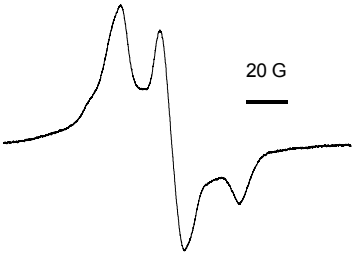


Figure 4. Low temperature experimental ESR spectra of compound **4b** at 120 K.

Table 1. Hyperfine coupling constants (a_N) for **3a,b**; **4a,b; 5a,b; 6a; 7a;** and **9**

Compound	Solvent [a]	a_N (Gauss)
Chloro-monoradical **3a**	Toluene	15.44
Chloro-monoradical **3b**	Methylene chloride	15.70
Methoxyamino-monoradical **5a**	Toluene	15.44
Methoxyamino-monoradical **5b**	Methylene chloride	8.19; 7.34
Homo-diradical **4a**	Toluene	15.46
Homo-diradical **4b**	Methylene chloride	15.72
Hetero-diradical **6a**	Toluene [c]	15.46; ~10
Homo-diradical **7a**	Methylene chloride	15.66
Homodiradical-anion **8a** (from **4a**)	Toluene [b]	15.46
Homodiradical-anion **8b** (from **4b**)	Methylene chloride [b]	15.75
Homodiradical-anion **9a** (from **7a**)	Methylene chloride [b]	15.72

[a] Deoxygenated, room temperature spectra.
[b] Compounds **4a** or **7a** in the presence of diethylamine.
[c] Compound **6a** in the presence of PbO_2.

Mono-radicals **3a, 3b**, **5a, 5b**, and **6a** present at room temperature the usual ESR triplet for TEMPO nitroxides as in Figure 1.[17] The homo-diradical **4b** with *ortho*-connected TEMPO residues is the only one to show a difference in ESR coupling constants indicating spin interaction (Figure 2).[17] At −153°C this frozen diradical shows line broadening (Figure 4), but no clear-cut evidence for a triplet state. The hetero-diradical **6a** (Figure 3) also presents signs of spin interaction, but at room temperature the ESR spectrum changes during a few minutes into a normal triplet, probably due to the lower stability of oxyaminyl free radicals. In the ESR spectrum of the homo-diradical **7a** at low temperature one observes a line broadening similar to that displayed in Figure 3.

One should note that we did not succeed to obtain ESR evidence for a hetero-diradical **6b**. One can conjecture that it would cyclize intramolecularly to a benzopyrazolone. An analogous

cyclization can be imagined for **6a** yielding a benzofuroxan, explaining perhaps the unusual aspects of its ESR spectrum (Figure 3).

Reactions with inorganic or organic bases

Methoxyamines **4a,b** and **7a** are acidic, like N-alkyl-polynitroanilines,[3-5] reacting instantaneously and reversibly with inorganic or organic bases when they afford coloured anions **8a,b** and **9a** having a more pronounced electronic delocalization (Scheme 3). The observed colours and the corresponding λ_{max} values are displayed in Table 2.

Table 2. Qualitative reactions of the acidic compounds **4a,b** and **7a** with bases and proteins (molar ratio: base:acidic compound = 3:1)

Bases and proteins	Colors of radical-anions 8a,b and 9a		
	4a→8a	**4b→8b**	**7a→9a**
Inorganic bases:[a] (LiOH, NaOH, KOH)	Blue [d]	Red [e]	Blue [f]
Organic bases:[b] (piperidine, pyrrolidine, morpholine, ethylenediamine, triethylamine, Kryptofix K22 [*] or K222 [**])	Blue [d]	Red [e]	Blue [f]
Basic amino acids:[a] (L-ornitine, L-lysine, arginine)	Blue [d]	Red [e]	Blue [f]
Proteins and enzimes:[c] Bovine serum albumin (Merck, fraction V) Peroxidase (Merck, 10000 U/mg) Lysozyme (Merck, 15000 E/mg)	Blue [d]	Red [e]	Blue [f]

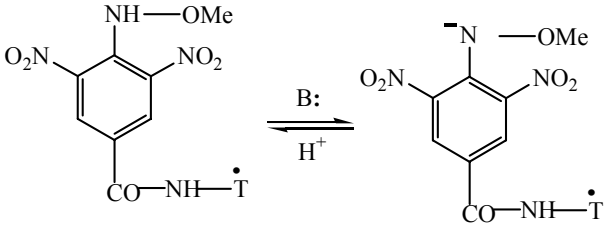
1,7,10,16-Tetraoxa-4,13-diazacyclooctadecane.
4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane.
L/L (water with base/methylene chloride with acidic compound).
In methylene chloride.
In water with 0.05–0.1 mL of ethanol solution with acidic compound.
λ_{max} = 561 nm.; [e] λ_{max} = 488 nm.; [f] λ_{max} = 573 nm.

The paramagnetic and chromogenic properties of compounds **4a, 4b** and **7a** make them possible candidates for applications in analytical and bioanalytical chemistry.

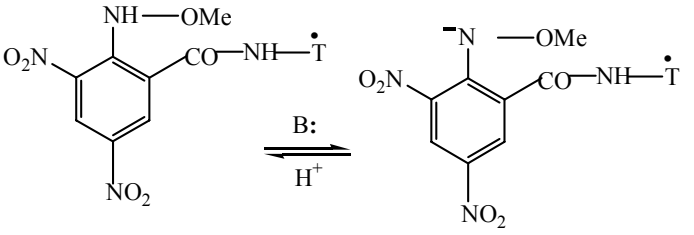
Mass spectra

In the ESI mass spectra of compounds **3–5** one observes always the molecular peak as the base peak. An interesting observation was made for compounds **3a** and **3b**, namely that in addition to the molecular peak one observes the peaks due to the hydrochloride (M + 36). In the mass

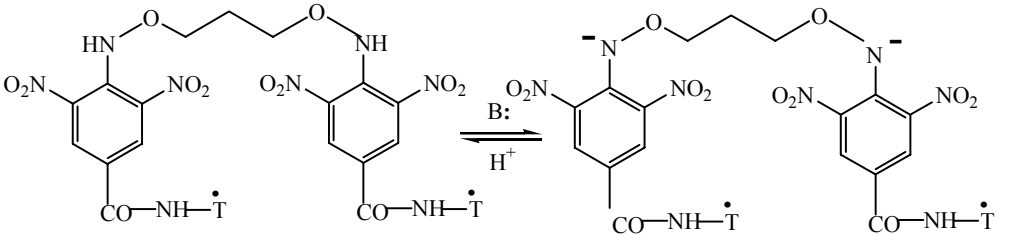
spectra of methoxyamino compounds **5a** and **5b** one observes low-intensity fragment peaks at m/z = M – 15 due to loss of the methyl group.



5a **8a**



5b **8b**



7a **9a**

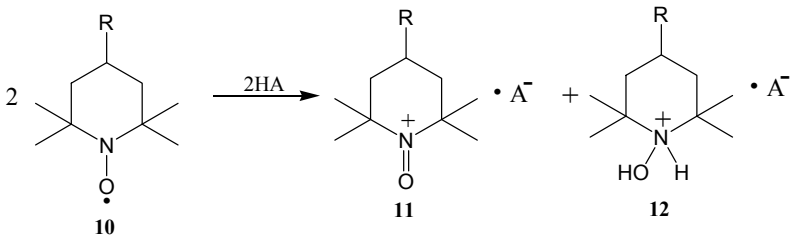
Scheme 3

Quenching effects and redox reactions

The substances described in this study (**3**–**7**) have a quenching effect on fluorescent compounds such as anthracene, carbazole, phenothiazine, tryptophan.[18,19] Again, possible applications may be envisaged.

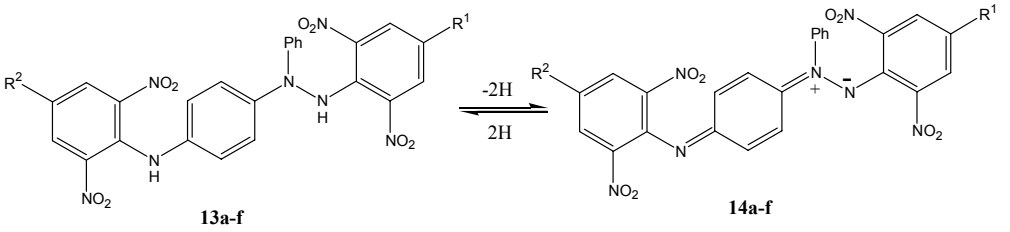
Oxidizing properties of TEMPO radicals are known,[20-22] and such compounds may be used for mild oxidations of thiols, amines, primary or secondary alcohols, It is also known that in

acidic medium TEMPO derivatives **10** undergo disproportionation yielding oxoammonium (**11**) and hydroxylamine salts (**12**), as indicated in Scheme 4.[21,22]



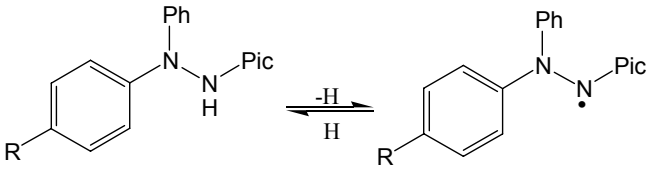
Scheme 4. Disproportionation of TEMPO derivatives **10**.

Compounds **3a,b**–**7a** were tested as oxidants for compounds **13a**–**13f** [23,24] in the absence (no reaction) and in the presence of *para*-toluenesulfonic acid [21] (when the blue-violet betainic structures **14a**–**14f** occurred).[23,24] In the reaction with 2,2-diphenyl-1-picrylhydrazine (DPPH-ine, **15**, R = H), compounds **3a,b** and **5a,b** afforded in the presence of *para*-toluenesulfonic acid the violet 2,2-diphenyl-1-picrylhydrazyl free radical (DPPH) (**16,** R = H), together with traces of its nitro-derivative (**16**, R = NO_2). This secondary product is formed by disproportionation [25-29] of DPPH (**16,** R = H) in methylene chloride in the presence of *para*-toluenesulfonic acid,[29,30] as checked by TLC.



a $R^1=R^2=NO_2$
b $R^1=NO_2$; $R^2=CN$
c $R^1=CN$; $R^2=NO_2$
d $R^1=R^2=CN$
e $R^1=NO_2$; $R^2=COOMe$
f $R^1=NO_2$; $R^2=CF_3$

Scheme 5. Redox reactions of compounds **13a**–**13f** and **14a**–**14f**.



15 **16**

Scheme 6. Redox reactions of DPPH and DPPH-ine (**15** and **16**, R = H).

The positive results on using compounds **3a** and **3b** as oxidizing agents prompted us to immobilize them by an S_NAr reaction on solid support (aminopropylsilica gel, Lichrospher^R, 100NH_2, 5μm, Merck). Working with solutions of **13a**–**13f** or **15** in the presence of *para*-toluenesulfonic acid, a suspension of our products on solid support afforded the same oxidation products.

Conclusions

The stable monoradicals **3a,b** formed from 4-amino-TEMPO and dinitrobenzoyl chlorides **2a,b** have a reactive chloro substituent that can be substituted by nucleophiles. Reaction of **3a** with methoxyamine yields the monoradical **4a** which can be oxidized to the hetero-diradical **6a.** Reaction of **3a,b** with 4-amino-TEMPO affords the homo-diradicals **4a,b**. Another homo-diradical, **7a**, was formed from **3a** and 1,3-bis(aminooxy)propane. Whereas most of the compounds described in the present study exhibit three lines in their ESR spectra, the homo-diradical **4b** with *ortho*-connected chains ending in TEMPO groups presents a 5-line ESR spectrum that broadens at low temperature.

Compounds **4a** and **7a** yield blue anions on treatment with inorganic or organic bases, whereas compound **4b** affords a red anion under the same conditions. Compounds **3**–**7** quench the fluorescence of aromatic compounds and oxidize push-pull hydrazinic derivatives such as 2,2-diphenyl-1-picrylhydrazine.

Experimental Section

General Procedures. NMR Spectra were recorded with a Varian Gemini 300 MHz instrument. Electronic absorption spectra were obtained with a UV-Vi Hitachi U-3000. IR spectra were obtained with a Paragon 1000 FT-IR and EPR spectra were recorded with a Jeol Jes-RE1X or Bruker ESP-300E instrument. Electrospray ionization mass spectra (ESI-MS) were recorded on a Finnigan LCQ mass spectrometer.

Commercially available starting materials were the two 4- and 2-chloro-3,5-dinitrobenzoic acids (**1a** and **1b,** respectively) from Aldrich, 4-amino-TEMPO (Aldrich), DPPH (Aldrich) and

N-methoxyamine or O-methylhydroxylamine (Merck). Silica gel glass plates $60F_{254}$ (Merck) were employed for TLC separations. The preparation of $DPPH_2$ (**15**, R= H), of compounds **13a**–**f**,[23,24] and of 1,3-bis(aminooxy)propane dihydrochloride was prepared as described earlier.[5]

4- and 2-Chloro-3,5-dinitrobenzoyl chloride (**2a** and **2b**, respectively) were prepared from the corresponding acids in benzene (5 mL/g of acid) with thionyl chloride (0.8 ml/g) and *N,N*-dimethylformamide (DMF, 2 drops/g). After refluxing for 1 h the volatile products were evaporated under reduced pressure leaving the crystalline products in quantitative yield: pale yellow solids, easily soluble in chloroform or dichloromethane, in which the acids are insoluble.
2a. ^{1}H-NMR ($CDCl_3$, ppm): 8.70 (s, 2H, H-2, H-6). ^{13}C-NMR ($CDCl_3$, ppm): 127.3 (C-4); 128.9 (C-2, C-6); 133.3 (C-1);149.8 (C-3, C-5); 164.3 (COCl).
2b. ^{1}H-NMR ($CDCl_3$, ppm, J, Hz): 8.80 (d, 1H, 2.5, H-6); 8.96 (d, 1H, 2.5, H-4). ^{13}C-NMR ($CDCl_3$, ppm): 123.2 (C-3); 129.1 (C-5); 131.6 (C-1); 137.6 (C-6); 145.6 (C-2); 149.8 (C-2); 149.8 (C-4); 162.8 (COCl).
4- and 2-Chloro-3,5-dinitro-*N*-(4-(2,2,6,6-tetramethyl-piperidine-1-oxyl)-benzamide)) (**3a** and **3b**, respectively). were obtained similarly to ref.[31] from an ice-cold solution of 4-amino-TEMPO (1g in 10 mL water) into which an ice-cold solution of acid chloride (1 g in 2.5 mL of acetone) was added in one portion under strong stirring in an ice-salt cooling bath. After 45 seconds, 50 mL of 1M hydrochloric acid was added in a single portion and the stirring was continued for 30min. keeping the cooling bath. The yellow-orange solid was filtered off through a G_3 sintered glass filter, washed with 1M cold hydrochloric acid and then with water, suspended in 30 mL of 10% aqueous sodium hydrogen carbonate, stirred for 30 min., filtered off and washed with water. After 24 h drying in a desiccator over anhydrous calcium chloride the crude product was dissolved in methylene chloride, alumina (Merck, Brockmann activity I) was added, the suspension was stirred for 30 min. and filtered. The solvent was removed under vacuum, and the purity (determined by TLC on silicxa gelGF254 glass plates with CH_2Cl_2–diethyl ether 8:2 v/v) was satisfactory for further use. For higher purity, preparative TLC was used under similar conditions, the product was extracted in a Soxhlet apparatus, and the solvent was removed under vacuum.
3a. yield 44%; mp.236-37ºC (lit.[13] 236-238ºC); ESI-MS m/z ($[M]^+$)=398. Elem. analysis: calcd. for $C_{16}H_{20}ClN_4O_6$: C, 48.07%; H, 5.04%; N, 14.01%; found: C, 47.93%; H, 5.08%; N, 13.87%. IR ($CHCl_3$), cm^{-1}: 3683 (NH-amide), 2975 (CH_3), 1675 (C=O), 1550 and 1520 (NO_2), 1319 (N-O^-); λ_{max} nm in CH_2Cl_2 (log ε): 424 (1.77); R_f = 0.72 (silica gel GF_{254} glass plates, methylene chloride-diethyl ether 8:2v/v).
3b. yield 42%; mp. 186-187ºC; ESI-MS m/z ($[M]^+$)=398 ; Elem. analysis: calcd. for $C_{16}H_{20}ClN_4O_6$: C, 48.07%; H, 5.04%; N, 14.01%; found: C, 47.98%; H, 5.06%; N, 13.91%; IR ($CHCl_3$), cm^{-1}: 3685 (NH-amide), 2928 (CH_3), 1681 (C=O), 1519 and 1500 (NO_2), 1346 (N-O^-); λ_{max} nm in CH_2Cl_2 (log ε):348 (2.50); R_f = 0.70 (silica gel GF_{254} glass plates, methylene chloride-diethyl ether 8:2v/v).

***N,N'*-Bis(4-(2,2,6,6-tetramethylpiperidine-1-oxyl))-3,5-dinitro-4- and -2-aminobenzamide** (**4a** and **4b**, respectively). were obtained in two variants as follows.

Variant A. To the acid chloride **3** in methylene chloride (5 mL/g), triethylamine and 4-amino-TEMPO (in methylene chloride, 5 mL/g) were added in molar ratios 1:3: 2. The mixture became red and was stirred at room temperature for 3 days. Then the mixture was shaken sequentially (three times each) in a separatory funnel with 1M hydrochloric acid, aqueous $NaHCO_3$, and water. After drying over anhydrous Na_2SO_4, the organic phase was evaporated under vacuum and the products were purified by preparative TLC as described above.

Variant B. The monoradicals **3a** or **3b** were converted into diradicals by treatment with with triethylamine and 4-amino-TEMPO (molar ratio 1:2.5:1.1) under the same conditions as described above.

4a. yield 65% for variant A and 57% for variant B; mp. 121-122ºC; ESI-MS m/z ($[M]^+$)=533; Elem. analysis: calcd. for $C_{25}H_{38}N_6O_7$: C, 56.17%; H, 7.16%; N, 15,72%; found: C, 56.12%; H, 7.11%; N ,15.67%; IR: ($CHCl_3$), cm^{-1}: 3682 (NH-amide), 2978 (CH_3), 1655 (C=O), 1531 and 1503 (NO_2), 1318 (N-O·); λ_{max} nm in CH_2Cl_2 (log ε): 424 (3.62); R_f = 0.50 (silica gel GF_{254} glass plates, methylene chloride-diethyl ether 8:2v/v).

4b. yield 61% for variant A and 53 % for variant B; mp. 179-180ºC; ESI-MS m/z ($[M^+]$=533; Elem. anal.: calcd. for $C_{25}H_{38}N_6O_7$:C, 56.17%; H, 7.16%; N, 15.72%; found: C, 56.14 %; H, 7.10%; N, 15.62 %; IR: ($CHCl_3$), cm^{-1}: 3685 (NH-amide), 3601 (NHamine), 2978 (CH_3), 1672 (C=O), 1508 and 1458 (NO_2), 1332 (N-O·); λ_{max} nm in CH_2Cl_2 (log ε):353 (3.88); R_f = 0.50 (silica gel GF_{254} glass plates, methylene chloride-diethyl ether 8:2v/v).

4- and 2-Methoxyamino-3,5-dinitro-*N*-(4-(2,2,6,6-tetramethyl-piperidine-1-oxyl)-benzamide)) (5a and **5b).** respectively, were obtained by stirring the monoradicals **3** in methylene chloride (25 mL/g) with triethylamine and solid methoxyamine hydrochloride in molar ratio 1:4:3 at room temperature for 5 days. The solution becomes rapidly blue for **5a** and red for **5b**. On washing twice with 1M hydrochloric acid the solutions became yellow. The product was extracted into aqueous sodium hydroxide which became colored as described above. Then the aqueous layer was acidified rapidly with 1M hydrochloric acid and the product was extracted into methylene chloride. After drying over anhydrous Na_2SO_4, the organic phase was evaporated under vacuum and the products were purified by preparative TLC as described above. Product detection can be performed either by detection with UV light at 254 nm, or by exposure to ammonia vapor when the two products become colored as indicated above.

5a. yield 63%; mp. 173-75ºC; ESI-MS m/z ($[M]^+$)=409 ; Elem. Analysis: calcd. for $C_{17}H_{24}N_5O_7$: C, 49.75%; H, 5.89%; N, 17.06%; found: C, 49.63%; H, 5.92%; N, 16.98%; IR ($CHCl_3$), cm^{-1}: 3684 (NH-amide), 3605 (NHOMe), 2926 (CH_3), 1655 (C=O), 1543 and 1510 (NO_2), 1320 (N-O·), 1064 (O-ether); λ_{max} nm in CH_2Cl_2 (log ε): 394 (3.47); R_f = 0.52 (silica gel GF_{254} glass plates, methylene chloride-diethyl ether 8:2v/v).

5b. yield 43%; mp. 90-91ºC; ESI-MS m/z ($[M]^+$)=409; Elem. analysis: calcd. for $C_{17}H_{24}N_5O_7$:C, 49.75%; H, 5.89%; N, 17.06%; found:C, 49.68%; H, 5.87%; N, 16.93%; IR ($CHCl_3$), cm^{-1}: 3685 (NH-amide), 3601 (NHOMe), 2979 (CH_3), 1671 (C=O), 1514 and 1455 (NO_2), 1336 (N-O·); λ_{max}

nm in CH_2Cl_2 (log ε): 342 (3.3443); R_f = 0.49 (silica gel GF_{254} glass plates, methylene chloride–diethyl ether 8:2v/v).

1,3-Bis(4-aminooxy-3,5-dinitro-*N*-(4-(2,2,6,6-tetramethyl-piperidine-1-oxyl)benzamide) propane) (7a). was prepared by stirring for 5 days an acetonitrile solution of compound **3a** with triethylamine and solid 1,3-bis(aminooxy)propane dihydrochloride in molar ratio 2:4:1. The color became yellow, green and then blue. Then a 1M solution was added to the resulting suspension till the color became yellow. After keeping in the refrigerator overnight, the precipitate was filtered off, washed on the filter with 1M hydrochloric acid, and dried over anh. $CaCl_2$. Purification was effected by preparative TLC (silica gel GF_{254} glass plates, methylene chloride–diethyl ether 8:2 v/v).

7a. yield 36%; mp. 135-36ºC; ESI-MS m/z ($[M-H]^+$)=831.1 and ($[M+Na]^+$)=855.1; Elem. analysis: calcd. for $C_{35}H_{48}N_{10}O_{14}$:C, 50.48%; H, 5.81%; N, 16.82%; found :C, 50.41%; H, 5.77%; N, 16.73%; IR ($CHCl_3$), cm^{-1}: 3693 (NH-amide), 3026 (CH_3), 1602 (C=O), 1545 and 1510 (NO_2), 1320 (N-O·); λ_{max} nm in CH_2Cl_2 (log ε):389 (4.79); R_f = 0.17 (silica gel GF_{254}, methylene chloride–diethyl ether 8:2v/v).

Visible absorption spectra for the colored anions 8a, 8b and 9a (Scheme 3) and for the hetero-diradical 6a (Scheme 1)

Weighed amounts of compounds **5a**, **5b** or**7a** were dissolved in dichloromethane in a graduated flask, with triethylamine (2 molar equivalents of amine for **5a,b** and 3molar equivalents for **7a**): λ_{max} nm (log ε) **8a**, 561 (3.58); **8b**, 488 (3.40); **9a**, 573 (3.68). For the hetero-diradical **6a**, a similar procedure was observed starting from **5a** and PbO_2: λ_{max} = 509nm.

Oxidizing properties of 3a,b, 4a,b, 5a,b, and 7a were investigated qualitatively as follows. Compounds **13a–f** and $DPPH_2$ (**15**, R = H) were dissolved in dichloromethane and stirred for 30 min. with stoichiometric amounts of *para*-toluenesulfonic acid. Then two molar equivalents of compounds **3a,b, 4a,b, 5a,b**, or **7a** (but 3 molar equivalents for $DPPH_2$) were added. After about 5 minutes the colour of the oxidation products started to appear, and these products were identified by TLC (silica gel GF_{254}, toluene, twice) relative to standards **14a–f** and DPPH, **16**, R = H prepared independently. Also, DPPH was identified by its ESR spectrum.

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