

Article

Diazenium Betaines Derived from the Stable Free Radical DPPH with Diradicaloid Behavior

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Abstract: Starting from the well known stable free radical DPPH (or its reduced counterpart, 2,2-diphenyl-1-picryl-hydrazine) and several amino derivatives, novel zwitterionic compounds (diazenium betaines) were obtained and characterized by different means, like NMR, IR, MS, and UV–Vis. These betaines are highly intense blue-colored compounds that can be easily reduced by ascorbic acid (vitamin C) or sodium ascorbate to their corresponding *para*-phenyl substituted derivatives of DPPH, which have a yellow color. Most of such redox processes were found to be reversible. However, the oxidation of 2-*p*-aminophenyl-2-phenyl-1-picryl-hydrazine led to an azo-derivative of DPPH diradical, and its structure was unveiled by X-ray monocrystal diffraction. Possible diradicaloid behavior is also discussed.

Keywords: free radical; DPPH; betaine; synthesis; structural characterization; ESR



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1. Introduction

The stable free radical DPPH (2,2-diphenyl-1-picrylhydrazyl) is well known for its indefinite stability, which is due to a blend of steric and electronic factors [1,2]. The two ortho-nitro groups have a major influence on its stability, preventing dimerization [2]. Meanwhile, the presence of the diarylamino group, having electron-donor behavior, together with the 2,4,6-trinitrophenyl group (picryl), which has electron-acceptor behavior, provide a unique electronic assembly, usually called ‘push-pull’, ‘capto-dative’, or ‘mero-stabilization’ [3]. In addition, the DPPH free radical has an intense violet color that fades in the presence of an antioxidant, and this property is frequently employed in many acid–base or redox processes [4,5]. As well, DPPH is used as a reagent in analytical chemistry, in total antioxidant measurements [6–9] or as a standard for electron spin resonance (ESR) spectroscopy [10]. The synthetic precursor of DPPH is its corresponding hydrazine, namely, 2,2-diphenyl-1-picryl-hydrazine, usually denoted as DPPH-H. The conversion of DPPH-H into DPPH is achieved by simple oxidation with lead dioxide or potassium permanganate [11], while the reduction of DPPH to DPPH-H is performed with a reducing agent, the most employed being ascorbic acid (vitamin C) [12]. This redox process is perfectly reversible, as demonstrated by cyclic voltammetry [12,13].

Although DPPH is regarded as a stable compound, it can be used in a variety of reactions; the literature shows that it captures unstable radicals with the formation of a *para*-phenyl derivative; and, in this way, a wide range of congeners can be obtained [1]. One of the most peculiar reactions of DPPH was noticed in the presence of methoxy-picramide, where a diazenium betaine was obtained (for such compounds, their betainic structures were confirmed by X-ray single-crystal measurements) [14,15]. Such compounds were proved to be stable and have quite interesting redox properties; additionally, their structure allows for diradicaloid behavior [16]. The extremely intense color of betaines is well known [17].

Some diazenium betaines seem to have unusual properties; for example, they can behave as diradicaloids, in which the two unpaired electrons might or not interact, leading, depending on the case, to a closed- or open-shell structure [18–20]. Such properties are of high interest due to their unique optical, electronic, and magnetic performance and adaptive aromaticity, which can be tailored by changing the substituents of the core structure, the distance between spins, or by changing the molecular isomerism. The potential applications for multiple functional organic materials include solar cells (including those based on singlet fission (conversion of one excited singlet state to two triplet states)), new generation of photovoltaics, spintronics, nonlinear optics and energy storage, organic batteries, dye and diode lasers, semiconductors, etc., as often discussed in the literature [21–24].

In this work, we extended the scope of the chemical synthesis of such diazenium betaines derived from DPPH, enlarging the substrates that can react with this stable free radical and thus forming novel diazenium betaines with very interesting and often peculiar properties.

2. Results and Discussion

2.1. Synthesis and General Characterization of the Betaines 3, 8, 14, and 15

Our previous results [25] showed that 5-(dimethylamino)-N-methoxy-naphtalene-1-sulfonamide (**1**) can generate the corresponding short-lived free radical **2** by oxidation, which eventually decomposes to a methoxy free radical, proved by the electron spin resonance (ESR) spin-trapping technique. However, in the presence of the DPPH free radical, a diazenium betaine was obtained, denoted here as **3** (Figure 1). Assignment of this structure was mainly achieved by ^1H -, ^{13}C -NMR, UV-Vis, IR, and HR-MS spectra.

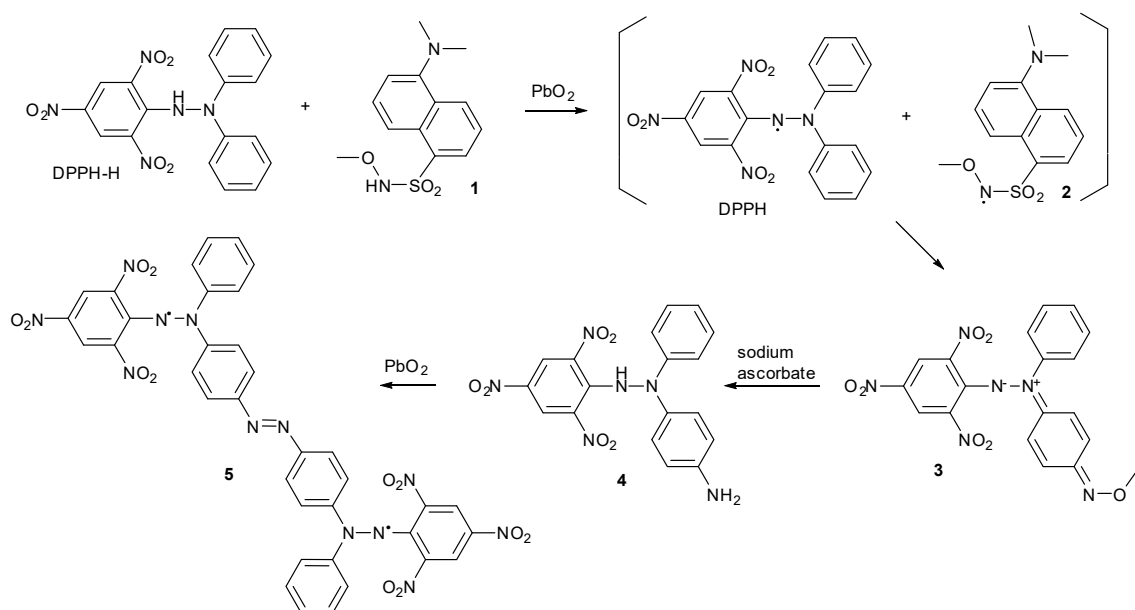


Figure 1. Synthesis of betaine **3**, *p*-amino-DPPH-H (**4**), and azo-derivative **5**.

Thus, for betaine **3**, the ^1H -NMR spectrum showed the presence of all H nuclei with their corresponding δ values, as well as their integrals (see the Materials and Methods Section for details). The picryl H atoms are equivalent and appear as singlets around 8.5 ppm, while the H-methoxy atoms are present as singlets at about 4.24 ppm. Moreover, HR-MS showed the molecular peak with an intensity of 100%. Additional evidence confirming the structure was obtained by IR and UV-Vis spectroscopy. In the IR spectrum, the nitro groups were present at about 1550 and 1350 cm^{-1} , while the aromatic moieties at around 3100 cm^{-1} . The UV-Vis spectrum recorded in dichloromethane (DCM) showed a major band at 602 nm, which is common for such diazenium betaines [1,14]. Interestingly, the reduction of **3** did not lead to the corresponding hydrazine but rather to the *p*-amino

derivative of DPPH-H, namely, 2-p-aminophenyl-2-phenyl-1-picrylhydrazine (**4**), as shown in Figure 1. The oxidation of **4** affords the azo-diradical **5**, which was characterized by X-ray diffraction on single crystals and ESR spectroscopy (see below).

2.2. X-ray Structure and ESR Spectra of Compound 5

Compound **5** crystallizes in the monoclinic $C2/c$ space group, and the crystal structure contains azo-diradical and DCM molecules in a 2:1 ratio (Figure 2). The azo-diradical **5** is centrosymmetric, with half of the molecule in the asymmetric unit. Within the hydrazyl groups, the N2–N3 bond length is 1.338(2) Å, while the C–N bond lengths for the aromatic systems attached to them are: N2–C6 = 1.398(3), N2–C13 = 1.436(3) and N3–C7 = 1.363(3) Å. The central azobenzene moiety is planar, and the dihedral angle between the mean planes of the azobenzene fragment and the phenyl rings attached to the hydrazyl groups is 59.7°. The dihedral angle between the mean planes of the azobenzene and the aromatic rings of the picryl moieties is 77.2°. Typically, the nitro group from the *para* position of the picryl fragment is coplanar with the aromatic system, whereas the nitro groups from the *ortho* positions are twisted out of the plane. These two *ortho* nitro groups make dihedral angles of 33.5° (O1–N4–O2) and 57.1° (O5–N6–O6) with the aromatic ring of the picryl fragment.

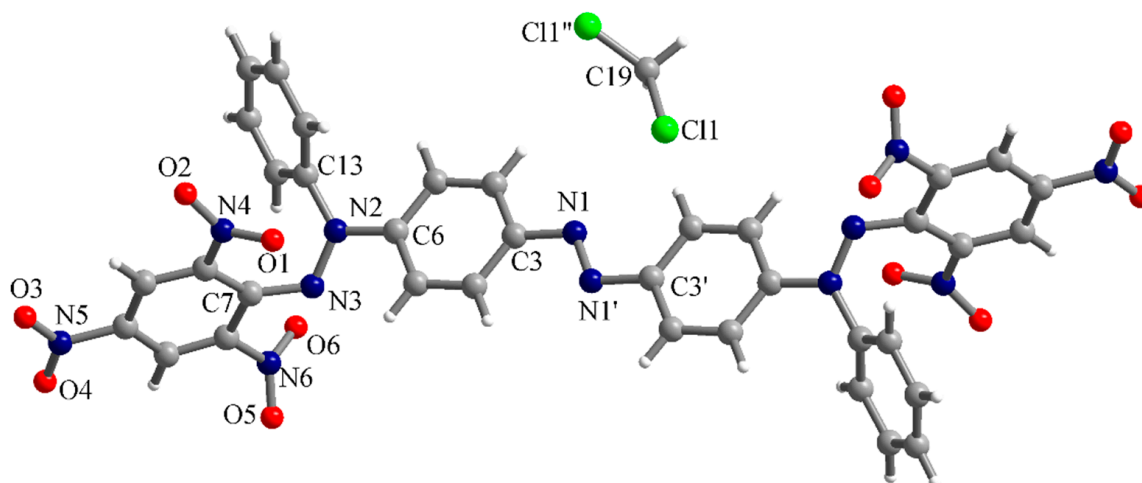


Figure 2. Perspective view of the crystal structure of **5** ··· 0.5 DCM (symmetry codes: ' = $-x, 1 - y, 1 - z$; '' = $-x, y, 0.5 - z$).

The examination of the packing diagrams shows the formation of channels running along the crystallographic c axis. The channels are demarcated by azobenzene moieties having two different orientations and host the DCM crystallization molecules (Figure 3a). The phenyl substituents of the hydrazyl groups establish $\text{CH} \cdots \pi$ interactions (3.04 Å) with the azobenzene fragments of neighboring molecules (Figure 3b).

As compound **5** is practically a diradical derived from DPPH, the ESR spectrum recorded in DCM showed the expected five lines with an intensity ratio of about 1/2/3/2/1, which is common when the hyperfine coupling constants a_{N1} and a_{N2} are quite similar, being about 9 Gauss (Figure 4a); as a solid, a single line was recorded by ESR spectroscopy, as usual for stable hydrazyl free radicals (Figure 4b), with a linewidth of 2.4 Gauss and a g value of 2.0037. It is worth mentioning that other betaine diradicals are also known [26]. The low-intensity signal of the ESR spectrum recorded in the solution could be due to the fact that compound **5** can behave as a diradicaloid, meaning that there is a possible shift from the open-shell structure to a closed-shell one (see more details in the next section).

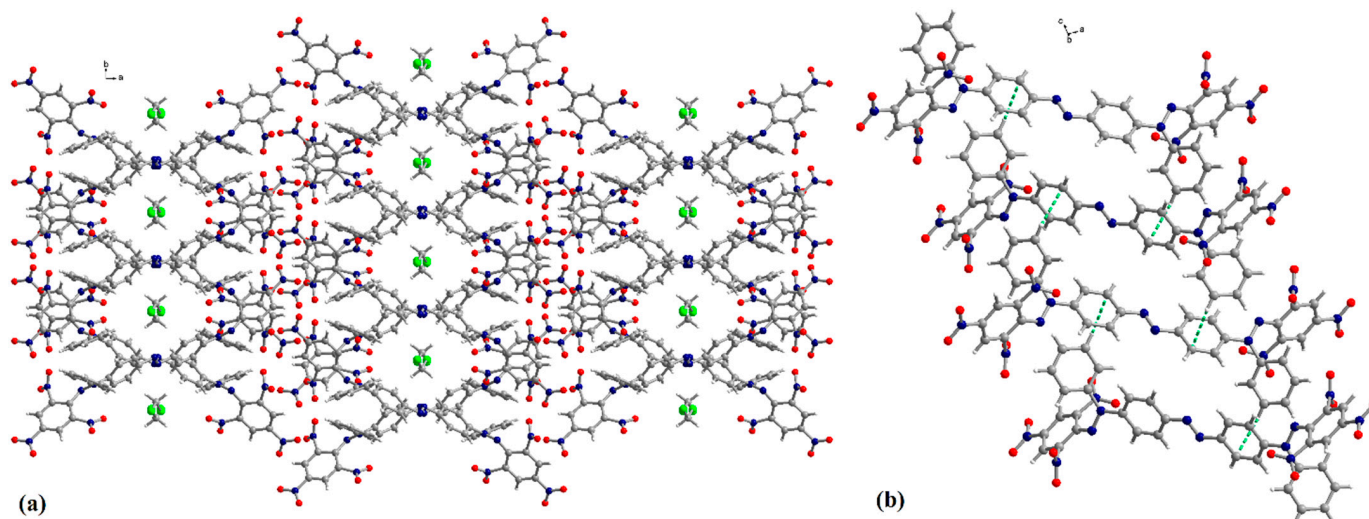


Figure 3. (a) View of the packing diagram along the crystallographic *c* axis and (b) details of the CH $\cdots$ π interactions.

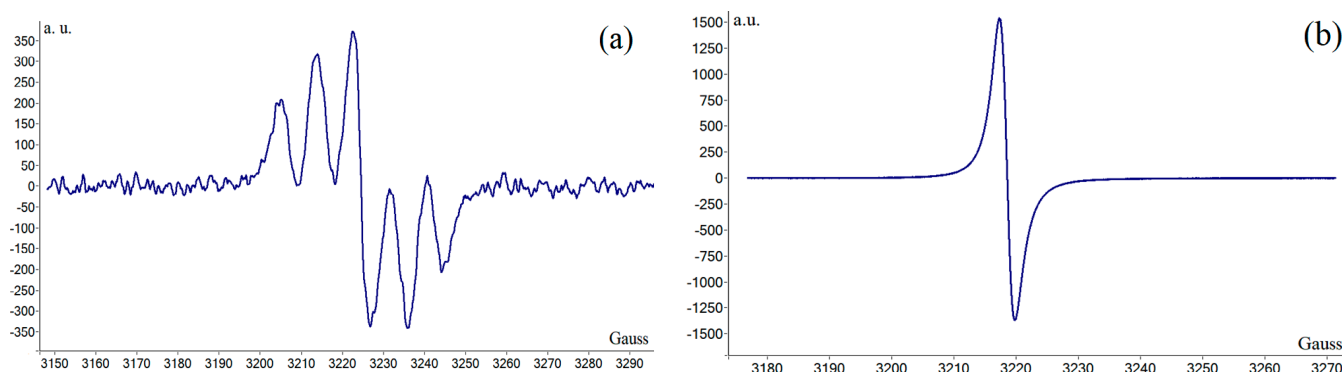


Figure 4. ESR spectrum of **5** recorded at room temperature in DCM (a) and as solid (b).

Because the total yield of the synthesis of **5** was very low, we assumed that it would be possible to obtain it starting from a simpler, similar sulfonamide derivative, like *N*-methoxy-4-methylbenzenesulfonamide (**6**) (Figure 5), instead of using the more complicated 5-(dimethylamino)-*N*-methoxy-naphthalene-1-sulfonamide (**1**) compound (as represented in Figure 1).

Thus, in the presence of a strong oxidant (lead dioxide), it should be possible to generate in a similar way (as previously demonstrated) the corresponding sulfaminy radical that would further couple with DPPH in a radical + radical reaction, with the formation of the same previously described for compound **3**. Unexpectedly, from the synthesis described in Figure 5, a new betaine was obtained, denoted as **8**. Structural characterization by NMR, MS, and IR confirmed the proposed structure (see the Materials and Methods Section for details). As all such similar betaines, **8** is also a very intensely colored compound, showing a very intense band in the UV-Vis spectrum at 577 nm (blue color). Moreover, upon reduction with ascorbic acid (vitamin C) or sodium ascorbate, the newly formed compound was not the *p*-amino derivative of DPPH-H (**4**) but **9** (Figure 5).

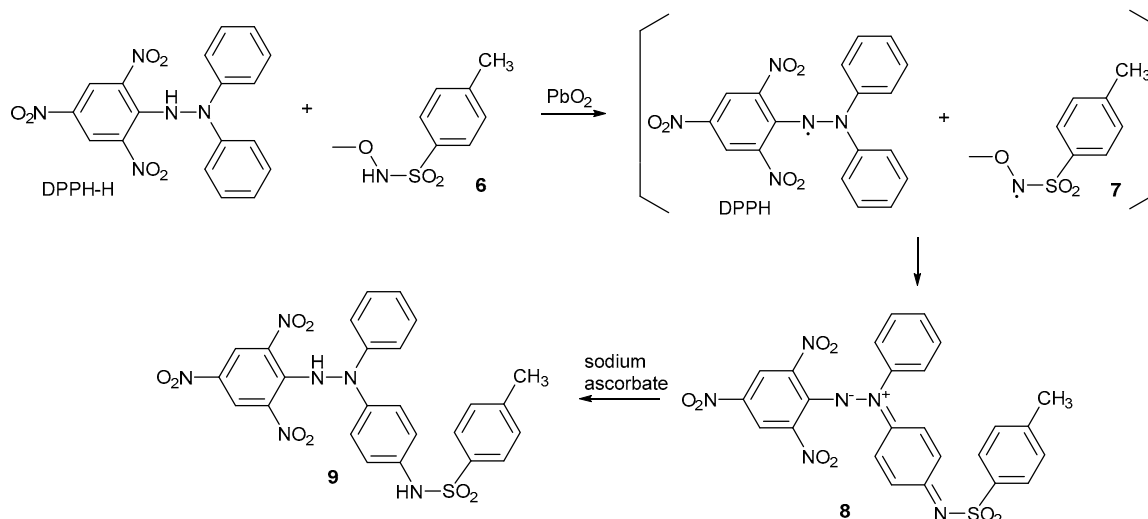


Figure 5. Synthesis of betaine **8** and its reduced counterpart **9**.

The structural characterization of **9** was also performed by NMR, IR, UV-Vis, and MS. All the data pointed to the proposed corresponding structure. While the starting betaine **8** was blue in color (577 nm), the reduced counterpart **9** was yellow (306 nm). For these compounds, the reduction and oxidation processes are reversible, meaning that compounds **8** and **9** can be easily interconverted by simple oxidation or reduction processes, and this behavior can be easily noticed by the naked eye, as the color changes from blue to yellow and *vice versa*.

To expand the scope of such syntheses, we tried two other amino derivatives obtained previously in our laboratory and used as luminescent precursors in azo-dye photoswitches [27], namely, compounds **10** and **11** (Figure 6). Their reaction with DPPH (or DPPH-H) under the same oxidative conditions led to the formation of two novel betaines, denoted as **14** and **15**, and, upon their reduction, to their counterparts **16** and **17** (Figure 6).

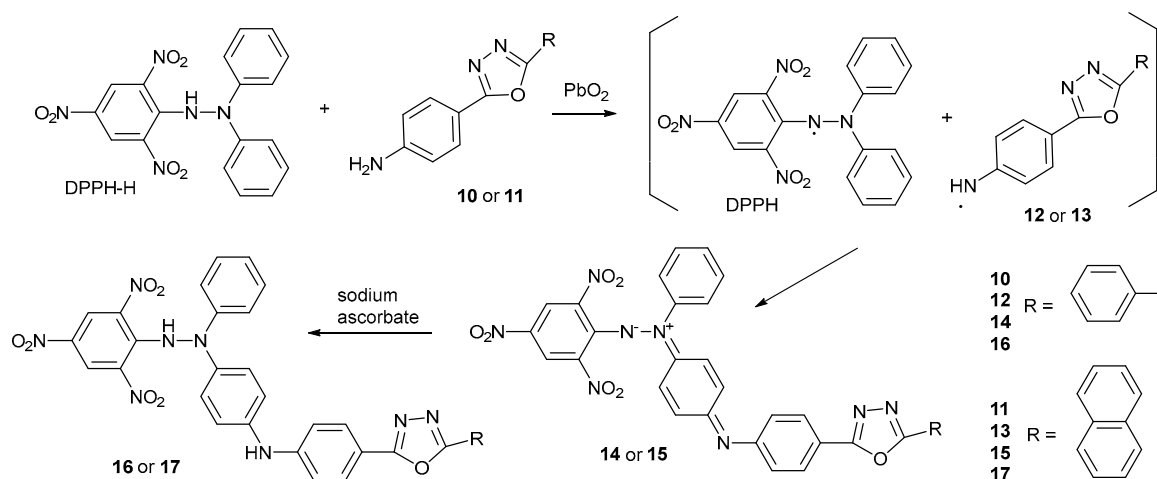


Figure 6. Synthesis of betaines **14** and **15** and their reduced counterparts **16** and **17**.

As usual, all new compounds **14–17** were characterized by IR, UV-Vis, and NMR (see the Materials and Methods Section for details). Thus, Table 1 compiles a summary of physical and chemical properties of the novel compounds obtained during this study.

Table 1. Summary of some properties and parameters for the newly synthesized compounds.

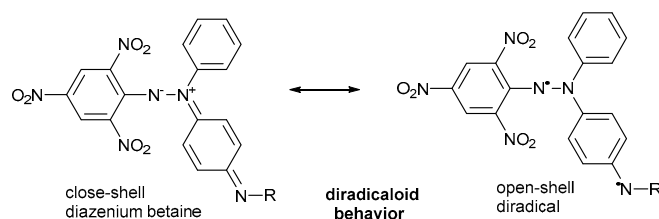
Compound	Details	M. W.	Yield (%)	R _f	λ _{max} (nm)	ε (10 ^{−4})
3	betaine	438	29	0.67 *	602	2.44
4	reduced form of 3	410	49	0.62 *	382	1.54
5	diradical	814	75	0.68 *	762	2.97
8	betaine	562	23	0.20 *	577	2.07
9	reduced form of 8	564	40	0.20 *	306	1.38
14	betaine	642	56	0.38 ^	603	2.83
15	betaine	678	59	0.35 ^	603	2.84
16	reduced form of 14	644	22	0.51 ^	344	4.70
17	reduced form of 15	680	12	0.62 ^	347	4.45

* DCM/silica gel; ^ ethyl acetate-petroleum ether 1:2 v/v/silica gel.

As a well-known general rule, as also noted in Table 1, betaines are highly intense blue-colored compounds (577–603 nm), while their reduced counterparts are yellow in color (306–382 nm). The most intense bathochromic shift was recorded for the diradical 5, which has a maximum wavelength absorption recorded at 762 nm (Table 1).

2.3. Diradicaloid Behavior of Betaines 3, 8, 14, and 15

The literature shows that such betaines can act as diradicaloids, and therefore they can practically exhibit the main characteristics of their two interconvertible forms, the closed- and open-shell ones [5,16], as shown in Figure 7.

**Figure 7.** Open-shell and closed-shell structures (mesomeric forms) of a diazenium betaine.

In the literature, diradicaloids that can be represented as Kekule structures have been investigated for their ambipolar or zwitterionic character, low band-gap energy, intense color, long wavelength absorption, and convertible spin state [28–30]. As aromaticity is an important concept for conjugated molecules, for closed-shell structures, the lowest-energy state is expected to be in the aromatic domain. Nitrogen-centered diradicaloids or nitrogen–oxygen-centered ones have been recently presented in the literature [16,31–33], and thus the hydrazyl moiety can be regarded as a good starting point, as such derivatives have multiple properties [34].

The diradicaloid behavior is a very complicated issue, as diradicals can be present in two forms, as a triplet or singlet diradical, depending on if the two unpaired electrons are coupled or not (additionally, such betaines can exhibit isomerism). As a consequence, the literature introduces, as a quantifiable unit, the diradical character index, which varies from 0% to 100% [35]. It is worth mentioning that the transition from one form to another can be simply triggered thermally.

One way to gather information about diradicaloids is to use ESR spectroscopy. Therefore, we tested our betaines, recording their ESR spectra both in solution (DCM) and in the solid state. While solutions of betaines 3, 8, 14, and 15 did not show an ESR signal, it was possible to record the corresponding ESR spectra in the solid state. Figure 8a shows the most intense spectrum, which was recorded for betaine 8, but for all the other betaines (3, 14, and 15), the ESR spectra were quite similar. Although these signals are weak, they demonstrate without doubt the presence of the unpaired electrons, supporting the diradicaloid behavior. As mentioned before, all these betaines are intense-colored compounds, and Figure 8b shows the UV–Vis spectrum of compound 8.

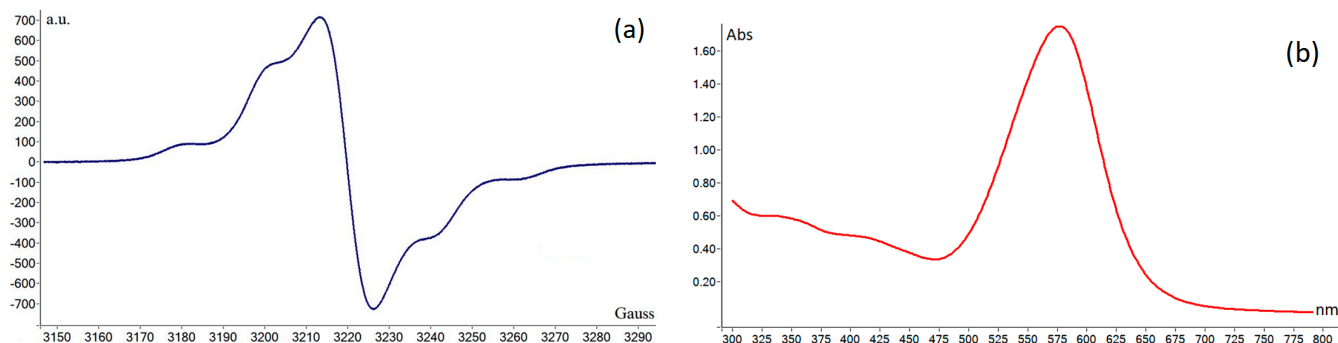


Figure 8. (a) ESR (as solid) and (b) UV-Vis spectrum (in DCM) of diazenium betaine 8.

The shape of the ESR spectrum in Figure 8 is very similar to those previously reported [5,16], consisting of a kind of quintet with a more intense central line. The linewidth of the central lines is between 6 and 12 Gauss, and the g value is consistent across all the spectra, corresponding to a hydrazyl radical (2.0037). Certainly, further theoretical and practical experiments will provide a deeper understanding of such peculiar diazenium betaines.

3. Materials and Methods

3.1. Chemical and Apparatus

All substances and materials (chemicals, solvents, TLC plates) were purchased from Sigma-Aldrich (St. Louis, MO, USA), Merck (Darmstadt, Germany), and Chimopar (Bucharest, Romania), and were used as received without further purification. IR spectra (ATR) were recorded on a Jasco FTIR 4700 spectrophotometer (Tokyo, Japan). NMR spectra were obtained using either a Bruker Fourier 300 MHz or 500 MHz instrument (Karlsruhe, Germany), employing appropriate solvents, like $\text{CHCl}_3\text{-d}_1$ or DMSO-d_6 . UV-Vis spectra were recorded in DCM as the solvent, using a dual beam spectrophotometer UVD-3500 (Los Angeles, CA, USA) or a Jasco (Tokyo, Japan) V-630 (10 mm quartz cell). For ϵ measurements, stock solutions of the compounds were prepared and further diluted to the required concentrations. The extinction coefficients (ϵ) were measured at five different concentrations, followed by linear fitting of the absorbance against concentration. The ESR spectrum was recorded in X band on a Jeol JES FA100 apparatus (Tokyo, Japan) at room temperature, with the following settings: frequency 8.99 GHz, center field 3300 G, sweep width 100 G, modulation width 1 G. MS spectra were recorded on a Thermo Scientific spectrometer (Waltham, MA, USA) for HR, while a Varian-310 apparatus was used for LR (Markham, ON, Canada). Compounds **1**, **6**, **10**, and **11** were obtained as described in the literature and verified by ^1H - and ^{13}C -NMR [25,27,36].

3.2. X-ray Crystallographic Analysis

X-ray diffraction data were collected at 293 K using a Rigaku XtaLAB Synergy-S diffractometer operating with a $\text{Mo-K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) micro-focus sealed X-ray tube. The structure was solved by direct methods and refined using full-matrix least squares techniques based on F^2 . The non-H atoms were refined with anisotropic displacement parameters, and hydrogen atoms were introduced at calculated positions (riding model). Calculations were performed using SHELX-2018 crystallographic software package (SHELXT for the structure solution and SHELXL for the structure refinement). A summary of the crystallographic data and the structure refinement for crystal **5**·0.5 DCM are given in Table 2, CCDC reference number: 2343759.

Table 2. Crystallographic data, details of data collection, and structure refinement parameters for compound **5**·0.5 DCM.

Compound	5 ·0.5 DCM
Chemical formula	C _{36.5} H ₂₃ ClN ₁₂ O ₁₂
<i>M</i> (g mol ^{−1})	857.12
Temperature, (K)	293(2)
Wavelength, (Å)	0.71073
Crystal system	Monoclinic
Space group	C2/c
<i>a</i> (Å)	40.203(2)
<i>b</i> (Å)	7.4012(4)
<i>c</i> (Å)	13.2318(6)
α (°)	90
β (°)	96.998(4)
γ (°)	90
<i>V</i> (Å ³)	3907.8(4)
<i>Z</i>	4
<i>D</i> _c (g cm ^{−3})	1.457
<i>F</i> (000)	1756
μ (mm ^{−1})	0.178
Goodness of fit on <i>F</i> ²	1.044
Final <i>R</i> 1, <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0589, 0.1850
<i>R</i> 1, <i>wR</i> ₂ (all data)	0.0718, 0.2005
Largest diff. peak and hole (eÅ ^{−3})	0.504, −0.239

3.3. General Procedure for Synthesis of Betaines **3**, **8**, **14**, and **15**

To 400 mg DPPH or DPPH-H (1 mmol), dissolved in 50 ml of DCM, we added the corresponding amino derivative (1 mmol) and a large excess of lead dioxide (10 g), and the mixture stirred for 3–5 days at room temperature. Reactions were monitored daily by TLC. After the formation of the desired compound stopped growing (very visible as an intensely colored blue spot), the mixture was filtered off using celite layers, and the solvent was removed. The crude product was column=chromatographed, and the corresponding betaine was obtained (very often a second purification step was necessary).

3.4. General Procedure for the Synthesis of the Reduced Counterpart Compounds **4**, **9**, **16**, and **17**

The corresponding betaine (100 mg) was dissolved in 50 mL of DCM. A solution of sodium ascorbate (5 g) in 50 mL of water was then added to the reaction mixture. Then, under powerful stirring, 15 mL of methanol was added; a change in color from dark blue to red-brown was noticed. The reaction was stirred for 2 h at room temperature until the starting material was fully converted. The organic layer was separated and washed with brine. The solvent was dried using anhydrous sodium sulfate and the solvent evaporated. The crude product was further purified by column chromatography. The resulting purified fraction was then dissolved in DCM and precipitated using a mixture of ethylic ether and petroleum ether, thus obtaining the pure reduced form of the corresponding betaine.

3.5. Synthesis of Diradical **5**

To 100 mg of compound **4** dissolved in 25 mL of DCM, 5 g of lead dioxide was added, and the solution was stirred at room temperature for 15 min, then filtered, and the solvent was removed. Purification was achieved using column chromatography. Slow evaporation of the solvent afforded black crystals. ESR (DCM, Gauss): $a_{N1} = a_{N2} = 9$. ESI-MS (+) *m/z* calcd. for C₃₆H₂₃N₁₂O₁₂ [*M* + *H*]⁺: 815.15; found: 815.3.

3.6. Compounds Characterization

Betaine 3, 2-(4-(methoxyimino)cyclohexa-2,5-dien-1-ylidene)-2-phenyl-1-(2,4,6-trinitrophenyl)-hydrazin-2-ium-1-ide. Dark-blue solid, yield: 29%. *R*_f = 0.67 (silica gel, DCM). *m.p.* 176–180 °C.

¹H-NMR (500 MHz, CDCl₃, δ ppm, J Hz): 8.50–8.48 (m, 4H, H_{Ar}), 7.71 (dd, 1H, H_{Ar}, 2.2 Hz, 10.3 Hz), 7.65 (dd, 1H, H_{Ar}, 2.5 Hz, 10.1 Hz), 7.59 (dd, 1H, H_{Ar}, 1.7 Hz, 10.3 Hz), 7.49 (t, 2H, H_{Ar}, 7.1 Hz), 7.43 (t, 4H, H_{Ar}, 8.0 Hz), 7.35 (t, 4H, H_{Ar}, 7.5 Hz), 7.31–7.26 (m, 2H, H_{Ar}), 6.99 (dd, 1H, H_{Ar}, 1.7 Hz, 10.1 Hz), 6.80–6.75 (m, 2H, H_{Ar}), 4.25 (s, 3H, OCH₃), 4.24 (s, 3H, OCH₃) ppm. ¹³C-NMR (125 MHz, CDCl₃, δ ppm): 151.0, 150.9, 148.6, 148.5, 146.2, 146.1, 140.7, 140.6, 139.1, 139.0, 135.0, 133.7, 133.6, 132.6, 131.9, 130.3, 130.29, 127.0, 126.9, 125.9, 124.3, 124.1, 124.0, 123.8, 123.6, 122.6, 121.5, 120.2, 64.68, 64.67 ppm. UV–Vis 602 nm (DCM). IR (cm^{−1}): 3074, 2940, 1597, 1512, 1449, 1315, 1166, 1050, 937, 830, 740, 627, 578, 484. HR-MS APCI (+) *m/z* calcd. for C₁₉H₁₄N₆O₇ [M + H]⁺: 439.0997; found 439.1008.

Compound 4, 4-(1-phenyl-2-(2,4,6-trinitrophenyl)hydrazineyl)aniline. Orange solid, yield: 49%. *R_f* = 0.62 (silica gel, DCM). *m.p.* 128–131 °C. ¹H-NMR (500 MHz, CDCl₃, δ ppm, J Hz): 10.20 (s, 1H, NH), 9.22 (bs, 1H, H_{Ar}), 8.53 (bs, 1H, H_{Ar}), 7.86 (d, 2H, H_{Ar}, 8.9 Hz), 7.40 (t, 2H, H_{Ar}, 7.6 Hz), 7.28 (t, 1H, H_{Ar}, 7.4 Hz), 7.20 (d, 2H, H_{Ar}, 7.6 Hz), 7.18 (d, 2H, H_{Ar}, 8.9 Hz) ppm. ¹³C-NMR (125 MHz, CDCl₃, δ ppm): 149.5, 147.8, 145.2, 141.8, 140.1, 136.8, 133.9, 130.1, 127.3, 126.4, 124.5, 124.0, 122.6, 118.7 ppm. UV–Vis 282 nm (DCM). IR (cm^{−1}): 3276, 2923, 2853, 1744, 1588, 1536, 1488, 1430, 1333, 1259, 1152, 1086, 931, 845, 723, 695, 457.

Betaine 8, 2-phenyl-2-(-4-(tosylimino)cyclohexa-2,5-dien-1-ylidene)-1-(2,4,6-trinitrophenyl)-hydrazin-2-ium-1-ide. Dark blue solid, yield: 23%. *R_f* = 0.20 (silica gel, DCM). *m.p.* 124–127 °C. ¹H-NMR (500 MHz, CDCl₃, δ ppm, J Hz): 8.66 (s, 2H, H_{Ar}), 7.88 (d, 2H, H_{Ar}, 9.9 Hz), 7.56 (m, 1H, H_{Ar}), 7.48 (m, 2H, H_{Ar}), 7.42–7.27 (m, 6H, H_{Ar}), 6.87 (m, 1H, H_{Ar}), 2.44 (s, 3H, CH₃) ppm. ¹³C-NMR (125 MHz, CDCl₃, δ ppm): 143.9, 143.5, 142.4, 141.9, 139.5, 138.1, 136.2, 133.3, 130.7, 129.7, 129.9, 128.6, 127.3, 127.0, 126.3, 123.9, 122.9, 120.9, 108.1, 108.0, 21.6. UV–Vis 577 nm (DCM). IR (cm^{−1}): 3071, 2920, 2851, 1594, 1518, 1315, 1260, 1142, 1078, 876, 818, 676, 596, 459, 407. HR-MS APCI (+) *m/z* calcd. for C₂₅H₁₈N₆O₈S [M + H]⁺: 563.0980; found 563.0958.

Compound 9, 4-methyl-N-(4-(1-phenyl-2-(2,4,6-trinitrophenyl)hydrazineyl)phenyl)benzenesulfonamide. Orange solid, yield: 40%. *R_f* = 0.20 (silica gel, DCM). *m.p.* 120–123 °C. ¹H-NMR (500 MHz, CDCl₃, δ ppm, J Hz): 10.04 (s, 1H, NH), 9.20 (bs, 1H, H_{Ar}), 8.50 (bs, 1H, H_{Ar}), 7.64 (d, 2H, H_{Ar}, 8.4 Hz), 7.33 (t, 2H, H_{Ar}, 8.4 Hz), 7.25 (d, 2H, H_{Ar}, 7.4 Hz), 7.21 (t, 1H, H_{Ar}, 7.4 Hz), 7.05 (d, 2H, H_{Ar}, 7.5 Hz), 7.01 (d, 2H, H_{Ar}, 9.2 Hz), 6.97 (d, 2H, H_{Ar}, 9.2 Hz), 2.40 (s, 3H, CH₃) ppm. ¹³C-NMR (125 MHz, CDCl₃, δ ppm): 145.7, 144.1, 143.4, 141.8, 140.0, 136.6, 136.1, 133.9, 133.6, 129.7, 129.2, 127.3, 126.3, 125.0, 122.9, 122.5, 120.9, 120.8, 21.6 ppm. IR (cm^{−1}): 3675, 3250, 2987, 2901, 1593, 1505, 1331, 1295, 1256, 1155, 1084, 910, 724, 657, 542, 454. UV–Vis 306 nm (DCM). HR-MS APCI (+) *m/z* calcd. for C₂₅H₂₀N₆O₈S [M + H]⁺: 565.1136; found 565.1105.

Betaine 14, 2-phenyl-2-(4-((4-(5-(*p*-tolyl)-1,3,4-oxadiazol-2-yl)phenyl)imino)cyclohexa-2,5-dien-1-ylidene)-1-(2,4,6-trinitrophenyl)hydrazin-2-ium-1-ide. Dark blue solid, yield: 56%. *R_f* = 0.38 (silica gel, ethyl acetate : petroleum ether = 1: 2 *v/v*). *m.p.* 142–146 °C. ¹H NMR (500 MHz, DMSO-*d*₆, δ ppm, J Hz) 8.71 (s, 1H), 8.69 (s, 1H), 8.18 (t, *J* = 8.9 Hz, 2H), 8.04 (t, *J* = 6.1 Hz, 2H), 7.86–7.74 (m, 1H), 7.59–7.55 (m, 3H), 7.45–7.35 (m, 5H), 7.25–6.97 (m, 4H), 2.42 (s, 3H) ppm. ¹³C NMR (125 MHz, DMSO-*d*₆, δ ppm) 170.3, 164.0, 163.6, 158.7, 153.3, 145.6, 144.0, 142.2, 141.1, 138.7, 138.4, 136.3, 132.7, 130.6, 130.0, 127.8, 127.3, 126.9, 126.6, 122.0, 120.6, 120.4, 21.1 ppm. UV–Vis 603 nm (DCM). IR (cm^{−1}): 3435; 3082; 2922; 2853; 1731; 1601; 1573; 1520; 1316; 1260; 1157; 1098; 820; 742; 609. HR-MS APCI (+) *m/z* calcd. for C₃₃H₂₂N₈O₇ [M + H]⁺: 643.1703; found: 643.1684.

Betaine 15, 4-((4-(5-(naphthalen-1-yl)-1,3,4-oxadiazol-2-yl)phenyl)imino)cyclohexa-2,5-dien-1-ylidene)-2-phenyl-1-(2,4,6-trinitrophenyl)hydrazin-2-ium-1-ide. Dark-blue solid, yield: 59%. *R_f* = 0.35 (silica gel, ethyl acetate : petroleum ether = 1: 2 *v/v*), *m.p.* 177–182 °C. ¹H NMR (500 MHz, DMSO-*d*₆, δ ppm, J Hz) 9.20 (t, *J* = 8.0 Hz, 1H), 8.72 (s, 1H), 8.71 (s, 1H), 8.43 (t, *J* = 7.3 Hz, 1H), 8.27–8.23 (m, 4H), 8.12 (d, *J* = 7.8 Hz, 1H), 7.80–7.68 (m, 4H), 7.65–7.53 (m, 4H), 7.39–7.35 (m, 2H), 7.27–7.24 (m, 2H), 7.17–7.15 (m, 1H) ppm. ¹³C NMR (125 MHz, DMSO-*d*₆, δ ppm) 163.9, 163.4, 158.7, 153.4, 145.4, 144.0, 141.1, 141.0, 138.7, 136.3, 136.2, 135.5, 133.5, 132.7, 130.6, 129.2, 128.9, 128.3, 128.0, 127.5, 127.3, 126.9, 126.8, 125.4, 124.0, 123.8, 122.8, 122.0, 120.3, 119.7 ppm. UV–Vis 603 nm (DCM). IR (cm^{−1}): 3399; 3073; 2921;

2851; 1595; 1567; 1528; 1313; 1266; 1154; 1095; 776; 700; 544. HR-MS APCI (+) m/z calcd. for $C_{36}H_{23}N_8O_7$ $[M + H]^+$: 679.1740; found: 679.1684.

Compound 16, 4-(1-phenyl-2-(2,4,6-trinitrophenyl)hydrazineyl)-N-(4-(5-(*p*-tolyl)-1,3,4-oxadiazol-2-yl)phenyl)aniline. Brown solid, yield: 22%. R_f = 0.51 (silica gel, ethyl acetate : petroleum ether = 1: 2 *v/v*) *m.p.* 130–132 °C. 1H NMR (500 MHz, DMSO- d_6 , δ ppm, J Hz) 8.55 (s, 1H, NH), 8.05 (s, 1H, NH), 7.97 (d, J = 8.0 Hz, 2H), 7.89 (d, J = 7.9 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.20–7.03 (m, 12H), 6.77 (m, 1H), 2.41 (s, 3H) ppm. ^{13}C NMR (125 MHz, DMSO- d_6 , δ ppm) 164.2, 162.9, 148.7, 144.2, 141.7, 138.5, 134.2, 133.6, 129.9, 129.1, 128.6, 128.2, 126.8, 126.3, 122.1, 120.9, 118.9, 118.6, 115.8, 113.7, 111.7, 21.1 ppm. UV–Vis 344 nm (DCM). IR (cm^{-1}): 3289; 3030; 1606; 1513; 1492; 1311; 1180; 821; 740; 696; 500. HR-MS APCI (+) m/z calcd. for $C_{33}H_{25}N_8O_7$ $[M + H]^+$: 645.1827; found: 645.1841.

Compound 17, 4-(5-(naphthalen-1-yl)-1,3,4-oxadiazol-2-yl)-N-(4-(1-phenyl-2-(2,4,6-trinitrophenyl)hydrazineyl)phenyl)aniline. Brown solid, yield: 12%. R_f = 0.62 (silica gel, ethyl acetate : petroleum ether = 1: 2 *v/v*). *m.p.* 99–102 °C. 1H NMR (500 MHz, DMSO- d_6 , δ ppm, J Hz) 10.99 (s, 1H, NH), 9.19 (m, 2H), 8.88 (s, 1H, NH), 8.34 (d, J = 7.3 Hz, 2H), 8.21 (d, J = 8.3 Hz, 2H), 8.09 (d, J = 8.1 Hz, 2H), 7.99 (d, J = 8.7 Hz, 2H), 7.79–7.71 (m, 4H), 7.67 (t, J = 7.4 Hz, 2H), 7.31 (t, J = 7.9 Hz, 2H), 7.25–7.21 (m, 2H), 7.09 (d, J = 8.1 Hz, 2H) ppm. ^{13}C NMR (125 MHz, DMSO- d_6 , δ ppm) 163.9, 163.0, 147.3, 146.0, 143.5, 141.2, 139.3, 138.9, 135.3, 133.5, 129.2, 129.1, 128.9, 128.6, 128.4, 128.2, 126.8, 125.4, 123.4, 122.9, 122.2, 119.9, 119.5, 118.3, 115.8, 115.0, 113.8, 112.9 ppm. UV–Vis 347 nm (DCM). IR (cm^{-1}): 3398; 3291; 3053; 2954; 1604; 1512; 1494; 1336; 1251; 1181; 1089; 775; 540. ESI-MS (+) m/z calcd. for $C_{36}H_{25}N_8O_7$ $[M + H]^+$: 681.18; found: 681.3.

4. Conclusions

The synthesis of four novel betaines (**3**, **8**, **14**, and **15**) was performed, and their structures were characterized using IR, UV–Vis, MS, and NMR. The reduction of these betaines yielded their hydrazine counterparts (**9**, **16**, and **17**), with the exception of betaine **3**, which was unexpectedly converted into the *p*-amino derivative of DPPH-H (**4**). The betaines are intensely blue-colored compounds, while the reduced derivatives are yellow in color. The *p*-amino derivative of DPPH-H (**4**) was further oxidized to produce a diradical (**5**), the molecular structure of which was confirmed by X-ray diffraction on a single crystal.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/chemistry6050052/s1>, Chart Data for Characterization of Betaine 14.

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