molbank

MDPI

Communication

4,4′-Bis(1-(4-nitrophenyl)-2-(2,4,6-trinitrophenyl)hydrazineyl)-1,1′-biphenyl and Its Corresponding Stable Diradical

Miron T. Caproiu [1] and Petre Ionita [2,*]

[1] Institute of Organic and Supramolecular Chemistry, Spl. Independentei 202B, 060023 Bucharest, Romania; dorucaproiu@gmail.com
[2] Faculty of Chemistry, University of Bucharest, 90 Panduri, 050663 Bucharest, Romania
* Correspondence: petre.ionita@chimie.unibuc.ro

Abstract

Starting with DPPH-diradical, the corresponding dinitro-derivative was obtained in a biphasic system using solid sodium nitrite and 15-crown-5 ether as the nitrating reagents. The new compound was characterized using 1H- and 13C-NMR, IR, and UV-Vis. After undergoing oxidation, a new stable diradical was obtained, and this was characterized using ESR, IR, and UV-Vis. This process demonstrates that the well-known chemistry based on DPPH can be extended to DPPH-diradical.

Keywords: DPPH; dimer; radical; diradical; diradicaloid

1. Introduction

Free radicals are a class of intriguing compounds that possess unusual properties, with paramagnetism being the most representative [1]. Their reactivity strongly depends on their structure, meaning that they can easily be tailored for specific requirements [2].

Currently, there is increased interest in their usage in state-of-the-art applications, like organic batteries, sensors, catalysis and redox reactions, and semiconductors, among others [3–6].

The DPPH (2,2-diphenyl-1-(2,4,6-trinitrophenyl)hydrazyl) stable radical is a well-known compound, first obtained in 1922, that presents common properties to any other closed-shell molecule, like the ability to be handled under usual conditions of air, light, humidity, and temperature without losing its 100% radical character, both as a solid and in solution [7]. Because DPPH does not dimerize and is an intensely colored compound, its main applications are as an ESR (electron spin resonance) standard and in the evaluation of total antioxidant activity [8]. However, DPPH dimer can be obtained via an alternative synthesis method, and the oxidation of this leads to the creation of DPPH-diradical [9].

Diradicals are even more unusual compounds, as they show unique electronic and magnetic properties and have high potential in a plethora of applications [10–12], like organic materials for solar cells, energy storage, and singlet fission.

In this communication, we outline the synthesis of a new derivative of the DPPH-dimer and DPPH-diradical, namely their nitro-congeners, denoted as compounds **1** and **2** (Figure 1).

check for updates

Academic Editors: Nicholas Leadbeater and Fawaz Aldabbagh

Received: 14 July 2025
Revised: 11 August 2025
Accepted: 22 August 2025
Published: 26 August 2025

Citation: Caproiu, M.T.; Ionita, P. 4,4′-Bis(1-(4-nitrophenyl)-2-(2,4,6-trinitrophenyl)hydrazineyl)-1,1′-biphenyl and Its Corresponding Stable Diradical. *Molbank* **2025**, *2025*, M2045. https://doi.org/10.3390/M2045

Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

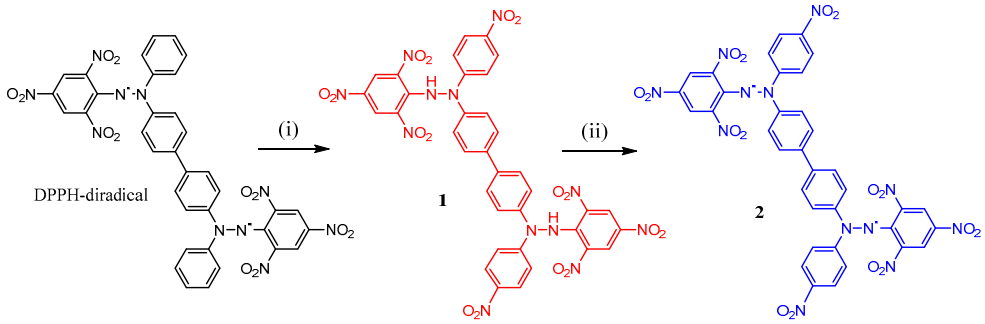


Figure 1. Synthesis of compounds (**1**) and (**2**): (i) $NaNO_2$/15-C-5; (ii) PbO_2.

2. Results and Discussion

2.1. Synthesis

By reacting DPPH-diradical with solid sodium nitrite in the presence of 15-crown-ether (15-C-5), a transfer agent, compound **1** (4,4′-bis(1-(4-nitrophenyl)-2-(2,4,6-trinitrophenyl)hydrazineyl)-1,1′-biphenyl) is obtained. This reaction occurs via a radical mechanism [13]. Firstly, sodium nitrite is transferred from the solid state into the DCM solution as a supramolecular complex, allowing it to react with the organic radical moiety. The radical extracts one electron from the nitrite anion, yielding nitrogen dioxide, which is subsequently captured by another radical moiety to form the nitro-derivative, as is known to happen in the case of DPPH [14]. After work-up has taken place, compound **1** is obtained as a pure yellow-orange solid via column chromatography. Diradical **2** is obtained via the oxidation of compound **1**, as the hydrazine moiety is converted into the hydrazyl radical. It is important to notice that a color change occurs, as diradical **2** is violet-colored (Figure 1).

2.2. Characterization of Compounds **1** *and* **2**

In the ^{1}H-NMR spectrum of compound **1**, all the corresponding peaks related to its structure can be seen (Figure S1 from Supplementary Information (SI)). Thus, the *H*-nucleus from the -N*H*- moiety is observed at 10.23 ppm as a broad singlet, while the *H*-nuclei from the picryl moiety appears at 9.25 and 8.59 ppm with very broad singlets. The biphenyl part is represented by doublet signals at 7.60 and 7.29 ppm, and the nitrophenyl part is represented by doublet signals at 8.21 and 7.19 ppm. In the ^{13}C-NMR spectrum, signals are present between 116.7 and 150.8 ppm (SI, Figure S2), consistent with the molecular structure.

Both compounds **1** and **2** are intensely colored either as solids or in solution. Thus, dihydrazine **1** is orange as a solid and yellow in solution, while diradical **2** is dark red-violet, whether as a solid or in solution (Figure 2). Compound **1** has a single absorption band at λ_{max} 335 nm while diradical **2** shows two absorption bands at 364 nm and 502 nm (Figure 2). Usually, the band around 340 nm is due to the presence of nitro-groups that allow n-π* electron transitions; hydrazyl radicals always show a supplementary band around 520 nm, as the presence of the unpaired electron leads to an extended conjugation.

Regarding the IR spectra, both compounds **1** and **2** look similar, with some small differences due to small shifts in the bands corresponding to different parts of the molecules. The structural evidence of the nitro groups is well represented by the two intense peaks that are present at around 1350 and 1550 cm^{-1}; aromatics are shown at about 3000–3100 cm^{-1}, while the amine group appears at 3400 cm^{-1} (SI, Figure S3).

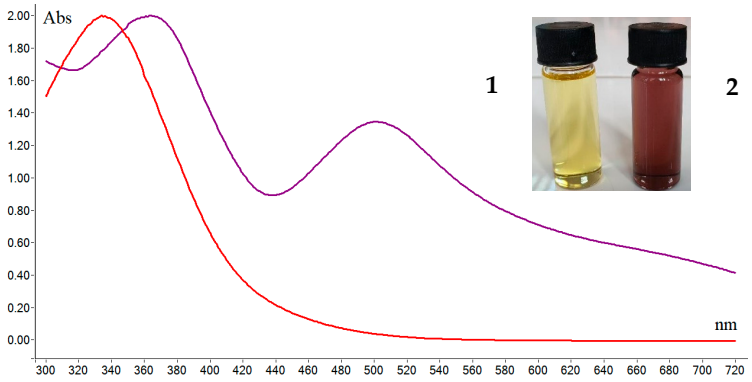


Figure 2. UV-Vis spectra of compounds **1** (red) and **2** (purple) in DCM (inset–an actual picture).

As compound **2** is a stable diradical (the test showed that after months, the diradical structure is preserved as a solid and in solution), the specific ESR spectroscopy showed (as expected) the non-equivalence of the hyperfine coupling constants a_{N1} and a_{N2}, and the values obtained by the simulation of the spectrum were 9.9 G and 7.0 G, respectively. A large linewidth value of 3.3 G was also noticed (Figure 3); it is worth mentioning that in the case of DPPH-diradical initially, the two hyperfine coupling constants were equivalent (8.2 G).

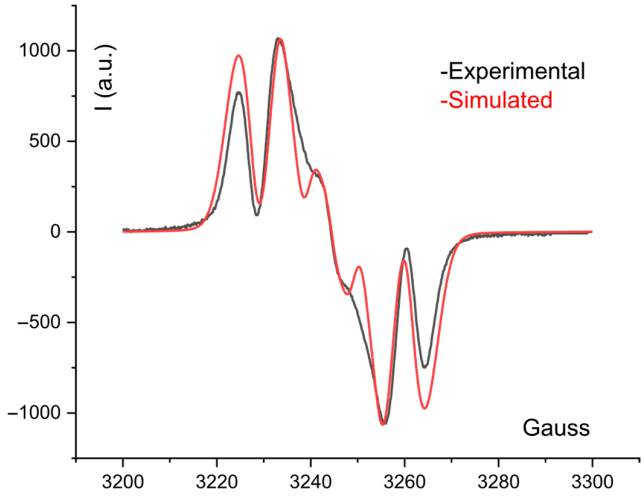


Figure 3. ESR spectrum of compound **2**.

3. Materials and Methods

All the chemicals and materials used in this study were purchased from Merck or Chimipar (Bucharest, Romania) and used as received. The process used to obtain DPPH-diradical is outlined in [9]. The NMR spectra were recorded in deuterated chloroform using Bruker 500 MHz apparatus (Ettlingen, Germany); the UV-Vis spectra were recorded in DCM using Labomed UVD-3500 double-beam apparatus (Los Angeles, CA, USA); the IR spectra were recorded using a Jasco spectrometer (Easton, MD, USA); the ESR spectrum was recorded in DCM using Jeol Jes FA100 apparatus (Tokyo, Japan). The simulation of the ESR spectrum was performed using WinSim free software [15].

3.1. Compound **1**, *4,4′-Bis(1-(4-nitrophenyl)-2-(2,4,6-trinitrophenyl)hydrazineyl)-1,1′-biphenyl*

A total of 100 mg (0.125 mmol) of DPPH-diradical was dissolved in 50 mL of DCM, to which 500 mg (7 mmol) of sodium nitrite and 450 mg (2 mmol) of 15-crown-5 ether were added. The mixture was stirred for one hour, after which it was left to settle until the next day. After filtration, the organic solution was extracted twice with 100 mL of diluted

hydrochloric acid (1 M), and the separated DCM solution was dried over anhydrous sodium sulfate. After the filtration and removal of the solvent, the residue was chromatographed on silica gel with DCM as the eluent. Yield: 70%. Red-orange solid. $C_{36}H_{22}N_{12}O_{16}$ M. W. 878. R_f = 0.50 (silica gel/DCM). Elemental analysis: required (%): C: 49.21; H: 2.52: N: 19.13; found (%): C: 49.29; H: 2.53: N: 19.08. ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm, J Hz): 10.23 (s, 2H, NH); 9.25 (s, 2H, picryl); 8.59 (s, 2H, picryl); 8.21 (d, 4H, nitrophenyl, 9.2); 7.60 (d, 4H, phenyl, 8.8); 7.29 (d, 4H, phenyl, 8.8); 7.18 (d, 4H, nitrophenyl, 9.2). ^{13}C-NMR (125 MHz, $CDCl_3$, δ ppm): 150.80; 143.76; 141.24; 139.50; 137.67; 129.09; 125.32; 124.47; 116.70. IR (cm^{-1}): 3432; 3278; 3087; 2927;2855; 1619; 1591; 1539; 1493; 1338; 1296; 1173; 1109; 931; 848; 724; 688; 537.

3.2. Compound **2**, *4,4′-Bis(1-(4-nitrophenyl)-2-(2,4,6-trinitrophenyl)hydrazyl)-1,1′-biphenyl Diradical*

A total of 40 mg (0.05 mmol) of compound 1 was dissolved in 50 mL of DCM, to which 500 mg (2 mmol) of lead dioxide was added. The mixture was stirred for 15 min, after which filtration occurred and the solvent was removed. Yield: 95%. Red-violet-black solid. $C_{36}H_{20}N_{12}O_{16}$ M. W. 876. R_f = 0.67 (silica gel/DCM). Elemental analysis: required (%): C: 49.32; H: 2.30: N: 19.17; found (%): C: 49.45; H: 2.43: N: 19.03. IR (cm^{-1}): 3435; 3278; 3082; 2922; 2853; 1595; 1521; 1436; 1333; 1171; 1108; 1076; 1002; 915; 851; 820; 734; 539. ESR (DCM): a_{N1} = 9.9 G; a_{N2} = 7.0 G.

4. Conclusions

In this study, we demonstrated that DPPH-diradical can easily be nitrated via an unconventional procedure, using sodium nitrite and a crown ether as the transfer agents. The structure of the new nitrated derivative **1** was elucidated using UV-Vis, IR, and NMR spectroscopy. Oxidation of **1** affords in almost quantitative yields the stable diradical **2**, which was also characterized by UV-Vis, IR, and ESR.

Supplementary Materials: The following supporting information can be downloaded online: Figure S1: ^{1}H-NMR spectrum of **1** in $CDCl_3$; Figure S2: ^{13}C-NMR spectrum of **1** in $CDCl_3$; Figure S3: IR spectra of compound **1** (red) and **2** (purple).

Author Contributions: Conceptualization, P.I.; methodology, M.T.C. and P.I.; writing—original draft preparation, M.T.C. and P.I.; writing—review and editing, M.T.C. and P.I.; funding acquisition, P.I. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by UEFISCDI, project number PN-IV-P1-PCE2023-0267.

Data Availability Statement: The original contributions presented in this study are included in the article/Supplementary Materials. Further inquiries can be directed to the corresponding author.

Acknowledgments: P.I. thanks Gabriela Ionita for recording the ESR spectrum and Daniela Culita for recording the IR spectra.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Chechik, V.; Carter, E.; Murphy, D.M. *Electron Paramagnetic Resonance*; Oxford Chemistry Primers; Oxford University Press: Oxford, UK, 2016.
2. Ionita, P. The Chemistry of DPPH Free Radical and Congeners. *Int. J. Mol. Sci.* **2021**, *22*, 1545. [CrossRef] [PubMed]
3. Barbosa, J.C.; Fidalgo-Marijuan, A.; Dias, J.C.; Gonçalves, R.; Salado, M.; Costa, C.M.; Lanceros-Méndez, S. Molecular design of functional polymers for organic radical batteries. *Energy Storage Mater.* **2023**, *60*, 102841. [CrossRef]
4. Friebe, C.; Zens, C.; Kupfer, S.; Schubert, U.S. Additive-Free Organic Radical Batteries Prepared through Electrochemical Polymerization of TEMPO-Decorated Terthiophene. *J. Phys. Chem. C* **2023**, *127*, 1333–1344. [CrossRef]

5. Howey, D.A.; Roberts, S.A.; Viswanathan, V.; Mistry, A.; Beuse, M.; Khoo, E.; DeCaluwe, S.C.; Sulzer, V. Free Radicals: Making a Case for Battery Modeling. *Electrochem. Soc. Interface* **2020**, *29*, 30. [CrossRef]
6. Nguyen, T.P.; Easley, A.D.; Kang, N.; Khan, S.; Lim, S.-M.; Rezenom, Y.H.; Wang, S.; Tran, D.K.; Fan, J.; Letteri, R.A.; et al. Polypeptide organic radical batteries. *Nature* **2021**, *593*, 61–66. [CrossRef] [PubMed]
7. Goldschmidt, S.; Renn, K. Zweiwertiger Stickstoff: Über das α,α-Diphenyl-β-trinitrophenylhydrazyl. *Ber. Dtsch. Chem. Ges.* **1922**, *55*, 628–643. [CrossRef]
8. Chen, O.; Zhuang, J.; Guzzetta, F.; Lynch, J.; Angerhofer, A.; Cao, Y.C. Synthesis of water-soluble 2,2′-diphenyl-1-picrylhydrazyl nanoparticles: A new standard for electron paramagnetic resonance spectroscopy. *J. Am. Chem. Soc.* **2009**, *131*, 12542–12543. [CrossRef] [PubMed]
9. Dobre, A.F.; Lete, C.; Kuncser, V.E.; Iacob, N.; Madalan, A.M.; Ionita, G.; Harada, M.; Kitagawa, Y.; Ionita, P. The Dimer of the DPPH Stable Radical. *ACS Omega* **2025**, *10*, 36662–36671. [CrossRef] [PubMed]
10. Shimizu, A. *m*-Quinodimethane-Based Fused-Ring Diradicals with Singlet and Triplet Ground States. *Chemistry* **2025**, *7*, 40. [CrossRef]
11. Yamada, S.; Shigemoto, I.; Kawakami, T.; Isobe, H.; Shoji, M.; Miyagawa, K.; Yamaguchi, K. Quantum Mechanical Approaches to Strongly Correlated Electron Systems: Structure, Bonding, and Properties of Diradicals, Triradicals, and Polyradicals. *Chemistry* **2025**, *7*, 38. [CrossRef]
12. Betkhoshvili, S.; Poater, J.; Moreira, I.d.P.R.; Bofill, J.M. Fully Conjugated Heteroatomic Non- and Quasi-Alternant Polyradicals. *Chemistry* **2025**, *7*, 45. [CrossRef]
13. Ionita, P.; Caproiu, M.T.; Luca, C.; Constantinescu, T.; Caldararu, H.; Balaban, A.T. Selective (15N) nitration of 2,2-diphenyl-1-(2,4- or 2,6-dinitrophenyl)-hydrazines or -hydrazyls. *J. Label. Comp. Radiopharm.* **1998**, *41*, 791–799. [CrossRef]
14. Weil, J.A.; Sane, K.V.; Kinkade, J.M. The reaction between 2,2-diphenyl-1-picrylhydrazyl and nitrogen dioxide. *J. Phys. Chem.* **1961**, *65*, 710–712. [CrossRef]
15. Available online: https://www.niehs.nih.gov/research/resources/software/tox-pharm/tools (accessed on 1 June 2025).

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.