# High-Spin Blatter's Triradicals

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## Abstract

Robust organic triradicals with high-spin quartet ground-state provide promising applications in molecular magnets, spintronics, etc. In this context, a triradical based on Blatter's radical has been synthesized recently possessing two doublet-quartet energy gaps with 70% occupation of quartet ground state at room temperature. The traditional broken-symmetry (BS)-DFT computed energy gaps are reported to be somewhat overestimated in comparison to the experimentally observed values. In this work, we have employed different *ab initio* methods on this prototypical system to obtain more accurate doublet-quartet energy gaps for this triradical. The spin constraint broken symmetry (CBS)-DFT method has been used to reduce the overestimation of energy gaps from BS-DFT. To address the issues of spin-contamination and multi-reference nature of low-spin states affecting the DFT methods, we have computed the energy gaps using appropriately state-averaged CASSCF and NEVPT2 computations. Using a series of active spaces, our calculations are shown to provide quite accurate values in concordance with the experimentally observed results. Further, we have proposed and modeled another three triradicals based on Blatter's radical which are of interest for experimental synthesis and characterization. Our computations show that all these triradicals also have quartet ground state with similar energy difference between the excited doublet states.

## 1 Introduction

Organic open-shell molecules have garnered substantial attention in recent years as potential functional materials with vast applications in molecular spintronics,[1–3] organic batteries,[4,5] spin filters,[6,7] memory devices,[8–10] and organic magnets,[11,12] etc. Multi-spin molecular systems i.e., di-, tri- or poly-radicals are captivating radical moieties whose ground-state can be manipulated by controlling their intramolecular exchange interactions.[13–15] However, thermal stability and synthetic difficulty of high-spin radicals have always remained a challenge to obtain these exotic molecules for their processability and device fabrication. A number of persistent radicals including nitronyl nitroxide, imino nitroxide, oxoverdazyl, dithiadiazolyl, nitroxide, phenoxide etc., have been known over the years.[16–18] Recently, amino(carboxy) radicals are proposed to be thermally stable at room temperature for weeks, by Mahoney et al.[19,20] Another exceptionally stable radical is the 1,2,4-benzotriazinyl (Blatter's) radical synthesized by Blatter et al. in 1968,[21] which has gained attention since the last few years due to easy synthetic strategies proposed by Koutentis[22,23] followed by Constantinides[24,25] and Kaszyński et al.[26–28] There are several reports on the applications and magnetic properties of Blatter's radicals so far.[29–31] The stable thin films of Blatter's radical are created by Ciciullo et al. further opening the doors to be utilized in devices.[32] Its stability has been validated by interfacing with gold substrates by Low et al.[33] Very recently, Gallego et al. achieved the simultaneous enhancement in the conductance and the Seeback-coefficient by bridging the Blatter's radical between gold electrodes.[34]

Tetraphenylhexaazaanthracene (TPHA) is the earliest compound containing Blatter radical with the zwitterionic ground-state.[35] Recently, Rajca et al. synthesized stable diradicals by coupling the Blatter radical with the nitronyl nitroxide radical and di-Blatter diradical

(Figure 1).[36–38] Alongside, several hybrid diradicals have been modeled and strong ferromagnetic interactions have been predicted by our group by employing *ab initio* CASSCF/NEVPT2 methods.[39] Lately, an appreciable enlargement in exchange interactions has been realized by taking advantage of oxygen-functionalized planar analogues of Blatter's radical.[40] Zheng et al. have also synthesized di-Blatter's diradicals with singlet ground-state.[41–43] We have investigated different isomers of di-Blatter's diradicals by coupling the radical moieties through fused benzene ring and observed antiferromagnetic exchange for stable isomers due to the existence of micromagnetic spin-centers.[44] By increasing the number of benzene rings between the two radical moieties, we also realized ferromagnetic interactions with a larger coupler. By using *push-pull* substitutions on TPHA, we have recently demonstrated that diradical character can be enhanced and ferromagnetic ground-state can be obtained.[45] There has been plentiful of research works, both experimental and theoretical, devoted to the various synthetic strategies and guidelines on the design of high-spin diradical moieties incorporating stable spin-sources.[46–48]

In contrast, only a handful of reports are there on the thermally stable triradicals.[49–53] Triradicals with three unpaired electrons give rise to quartet as ground-state when all the three localized spins are ferromagnetically coupled to each other. If two of the unpaired electrons are antiferromagnetically coupled, it results in doublet as ground-state. Recently, Mishra et al. have reported on-surface synthesis of a non-benzenoid triradical with quartet ground-state.[54] Tretyakov and co-workers have reported a verdazyl-nitronyl nitroxide triradical with quartet ground state.[55] The triradical trications based on thianthrene featuring a doublet ground state have been synthesized by Tang et al.[56] A propeller shaped triradical has been recently reported by by Kodama et al. with doublet ground state.[57] So far, only two works on triradicals featuring Blatter's radical have been reported. First one is a star shaped symmetrical triradical possessing Blatter's radical synthesized by Zissimou et al. with computationally determined doublet-quartet ($\Delta E_{D,Q}$) energy gap of 0.109 kcal/mol (38.1 $cm^{-1}$) using BS-DFT (UB3LYP/6-31G (2d,p)) method.[58] The quartet ground-state is recently confirmed by CW and pulse EPR spectroscopy.[59] Second work is a triradical obtained by coupling Blatter's radical with the two nitronyl nitroxide radical by Rajca et al. It is reported to possess two doublet-quartet energy gaps, $\Delta E_{D1,Q} \approx 0.2$–$0.3$ kcal/mol (69.9–104.9 $\mathrm{cm}^{-1}$) and $\Delta E_{D2,Q} \approx 1.2$–$1.8$ kcal/mol (419.7–629.6 $\mathrm{cm}^{-1}$).[60,61]

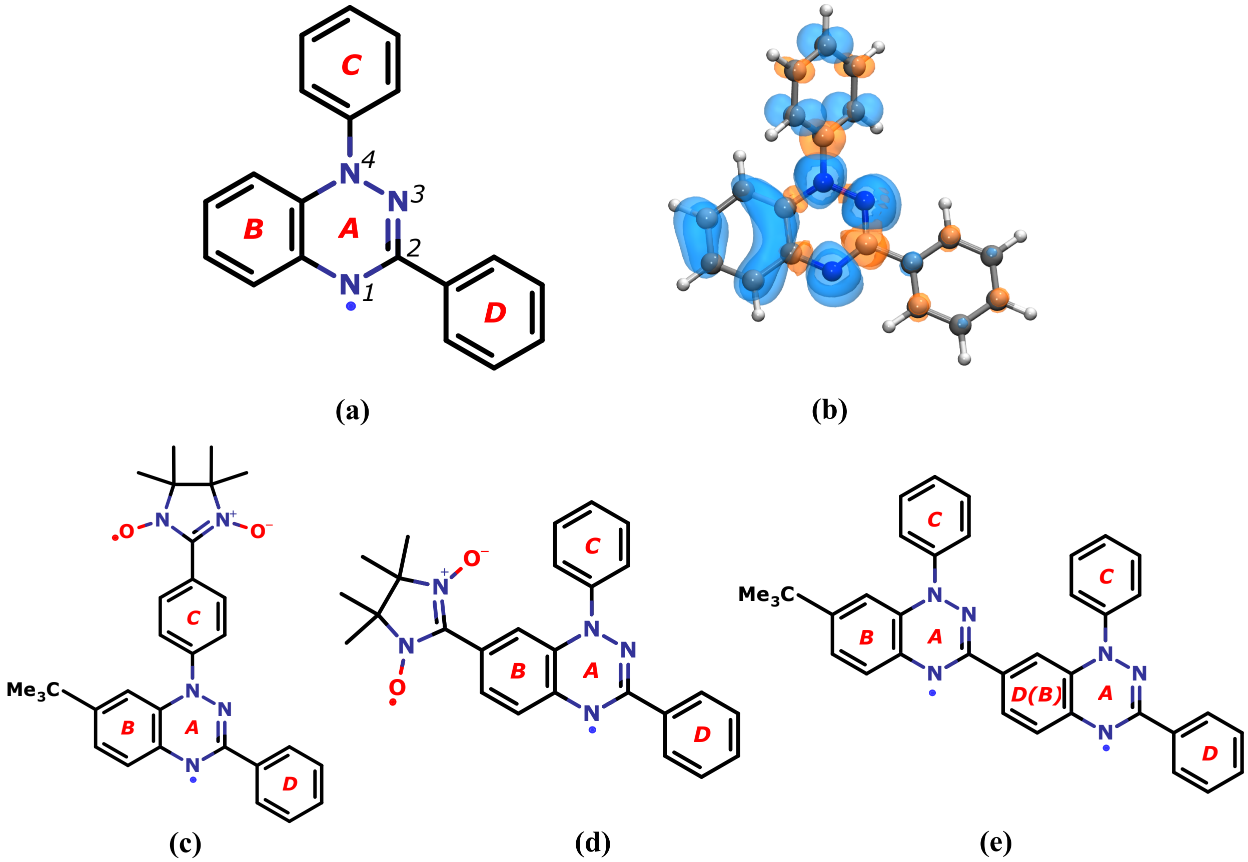


**Figure 1:** Structure of (a) Blatter's monoradical (b) Löwdin spin-density distribution of the Blatter's monoradical (c) diradical obtained by coupling NN radical with ring C (Bl-NN(C)) of Bl (d) NN radical with ring B (Bl-NN(B)) of Bl and (e) with itself i.e., di-Blatter (Bl-Bl) diradical by fusing the ring D of one Bl with B ring of another Bl radical.

The fundamental structure of Blatter's radical consists of four aromatic rings A, B, C, and D, as shown in Figure 1a where the unpaired electron is mainly localized on rings A and B. Ring C also has measurable spin density. However, ring D is isolated with only little signatures of spin-density (Figure 1b). Herein, we have investigated the electronic structure and doublet-quartet energy gaps of the recently synthesized Blatter's based triradical by Rajca and co-workers[60] as shown in Figure 2, employing different computational tools based on DFT and multiconfiguration methods. Since the BS-DFT energy gaps reported by Rajca et al., are overestimated compared to their experimental results, we have employed the CBS-DFT method which is known to provide better results as compared to BS-DFT. In addition to the DFT methods, we also utilized SA-CASSCF/NEVPT2 multi-reference methods to compute the doublet-quartet energy gaps using different active spaces. By making a blueprint of our computational scheme used for the Rajca's triradical system and by utilizing the basic structural framework of the highly stable Blatter's radical, we have designed three additional Blatter's based triradicals. The two triradicals, denoted as Bl-Bl-NN(B), Bl-Bl-NN(C) in Figure 4, are obtained by coupling di-Blatter diradical (Figure 1c) with the nitronyl nitroxide radical through ring B and ring C of Blatter's radical. The third one is exclusively based on Blatter's radical, i.e., tri-Blatter triradical, denoted as Bl-Bl-Bl (Figure 4). The design principle for these triradicals is combination of already existing diradicals as shown in Figure 1, thereby making the proposed systems realistic with a possibility to be synthesized and studied in near future.

## 2 Computational Details

The HDVV Hamiltonian for a system with three spin-centers (S=1/2) in an asymmetrical topology is given by Eq. 1

$$\hat{H}_{HDVV} = -\sum_{<i,j>} J_{ij}.\hat{S}_i.\hat{S}_j = -J_{12}.\hat{S}_1.\hat{S}_2 - J_{23}.\hat{S}_2.\hat{S}_3 - J_{13}.\hat{S}_1.\hat{S}_3 \tag{1}$$

where $\hat{S}_i$ and $\hat{S}_j$ are the spin angular momentum operators and $J_{ij}$ is the magnetic exchange coupling constant between the magnetic sites $i$ and $j$. The symbol $<i,j>$ indicates that the sum refers to the interactions between nearest neighbours only. When three spins are coupled, this results in one quartet ($S = \frac{3}{2}$) state and two doublet states ($S = \frac{1}{2}$) giving rise to two different quartet-doublet energy gaps. For the case of two spin-centers where only one coupling constant appears in the above Hamiltonian, it can be shown to be related to the energy gap between the resulting singlet and triplet states. This allows coupling constants to be extracted from electronic structure calculations of singlet and triplet states. For the case of symmetric couplings where $J_{12} = J_{23} = J_{13} = J$, the two doublets will be degenerate allowing one to extract $J$ from quartet-doublet energy gap as,

$$J = \frac{2}{3}[E_D - E_Q] \tag{2}$$

where E$_D$ and E$_Q$ are the energies of doublet and quartet states respectively. The positive and negative values of $J$ indicate the quartet and doublet as the ground-state respectively. When one of the coupling is assumed to be negligible due to larger distance between spin-centers, the two quartet-doublet energy gaps can be used to extract two coupling constants unambiguously. For the case for three spin-half centers, as discussed by Reta et al.,[62,63] it is not possible to extract three different coupling constants from two quartet-doublet energy gaps. Although the energy of high-spin (E$_Q$) state can be determined accurately from computations, the determination of energies of low-spin (E$_D$) state is a challenging problem within the single-reference methods (UHF or UKS), due to their multideterminantal nature. An alternative approach to calculating the exchange coupling constant within DFT is proposed by Yamaguchi et al.[64] as

$$J = \frac{E_{BS} - E_{HS}}{< S^2 >_{HS} - < S^2 >_{BS}} \tag{3}$$

where E$_{BS}$ is the energy of a broken-symmetry approximation to the low-spin state. However, the calculated $J$ with the above formula does not eliminate the spin contamination errors. Therefore, with the assumption that the spin-contamination in the high spin state is negligible i.e., $< S^2 >_{HS} \cong < S^2 >_{HS}^{exact}$, the spin-projected energy of LS state, (E$_{AP}^{LS}$), without spin contamination error is obtained as follows[65,66]

$$E_{AP}^{LS} = \alpha E_{BS} - \beta E_{HS} \tag{4}$$

$$\alpha = \frac{< S^2 >_{HS} - < S^2 >_{LS}^{exact}}{< S^2 >_{HS} - < S^2 >_{BS}}$$

$$\beta = \alpha - 1$$

Substituting the values of $\alpha$ and $\beta$ in Eq. 4, the energy gap between the doublet and quartet i.e., $\Delta E_{DQ}$ is given by

$$\Delta E_{DQ} = E_{AP}^{LS} - E_{HS} = \alpha(E_{BS} - E_{HS}) \tag{5}$$

For a triradical, $< S^2 >_{LS}^{exact}$=0.75, thus, substituting the value of $\alpha$ and $< S^2 >_{LS}^{exact}$ in Eq. 5, the $\Delta E_{DQ}$ becomes,

$$\Delta E_{DQ} = \frac{< S^2 >_{HS} -0.75}{< S^2 >_{HS} - < S^2 >_{BS}}(E_{BS} - E_{HS}) \tag{6}$$

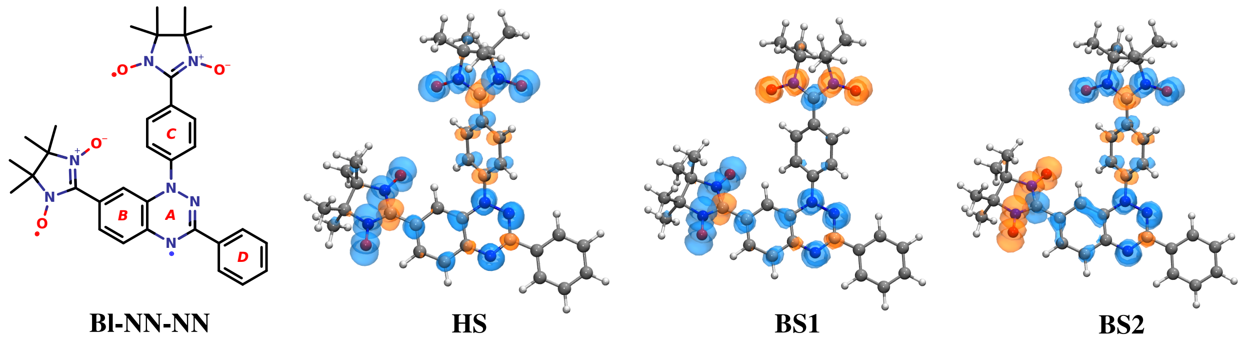
which can be employed to compute spin-contamination corrected quartet-doublet energy gaps using broken-symmetry DFT computations. Within the DFT framework, an alternative tool in the electronic structure toolbox to evaluate the doublet-quartet energy gap is the spin-constraint DFT (CBS-DFT) which provides the advantage of calculating the total energy by constraining the spin-magnetic moment on the specified spatial zones.[67,68] The doublet-quartet energy gap is then calculated employing Eq. 6 using CBS-DFT calculated energies.

For all triradicals in this study, the geometries are optimized in high-spin state employing the UB3LYP/def2-TZVP method.[69–71] The high-spin state optimized geometries are used for further calculations. The calculations are accelerated by using the resolution-of-identity (RI) approximation in conjunction with the auxiliary basis set def2/J and chain of spheres (COSX) numerical integration technique.[72] For DFT methods, energy gaps are computed by using the approximate spin-projection (AP) method[65,66] as in Eq. 6. For CBS-DFT calculations, UB3LYP/6-31G(d) method is used. In addition to the DFT methods, to avoid the problem of spin-contamination and to access dynamical and non-dynamical electron correlations, wavefunction-based methods have been used. The state-averaged complete active space self-consistent field, i.e., SA-CASSCF[73,74] and n-electron valence second-order perturbation theory (NEVPT2)[75] calculations with def2/TZVP basis set are performed on the DFT high-spin state optimized geometrical structures for CAS(3,3), CAS(5,5), CAS(7,7) and CAS(9,9) active spaces. For each active space, state-averaging uses one quartet and two doublet states with equal weights. For larger active spaces, the orbitals obtained from CAS(3,3) active space have been used as an initial guess. The triradical character, i.e., the degree to which the system pocesses three unpaired electrons localized on different moeities within the molecule, is quantified on the basis of natural orbital occupation numbers of CASSCF calculations. Such a radical must have three active natural orbitals with occupation number of nearly one, and this feature must persist when active space is enlarged. In order to ensure that state-averaging does not mask this feature, we have computed natural orbitals for each of the averaged states separately. All calculations are performed using ORCA[76,77] and CBS-DFT calculations are performed in NWChem.[78]

## 3 Results and Discussion

The Blatter's based triradical which is recently synthesized by Rajca et al. is shown in Figure 2. This is a combination of two previously synthesized diradicals by them, as shown in Figures 1c and 1d. As discussed before, it is reported to have high-spin quartet ground state with 70% population at room temperature and possess two doublet excited states with doublet-quartet energy gaps of 0.2 kcal/mol (69.9 cm$^{-1}$) and 1.2 kcal/mol (419.7 cm$^{-1}$) estimated using EPR spectroscopy. Slightly larger energy gaps of 0.3 kcal/mol (104.9 cm$^{-1}$) and 1.83 kcal/mol (629.6 cm$^{-1}$) are obtained with SQUID magnetometry measurements.

In this work, we have employed this triradical as a representative system to benchmark and standardize the computational methodology. At first, doublet-quartet energy gaps of this triradical are computed employing DFT based BS-DFT and CBS-DFT methods. As discussed before,[62,63] in the case of three localized spins in three centers, low energy spectra



**Bl-NN-NN** **HS** **BS1** **BS2**

**Figure 2:** Blatter's based triradical (Bl-NN-NN) and the Löwdin spin density distribution of the triradical in the HS ground state and two excited BS1 and BS2 states at an isovalue of 0.003 $\mu_B$/Å.

comprises of only one quartet and two doublet spin states. The computed energies of the quartet and the two BS states with their $<S^2>$ values are shown in Table 1. A large $<S^2>$ value of 1.87 is obtained for the two BS states deviates from the ideal $<S^2>$ of 0.75 for a doublet state. This indicates significant amount of spin-contamination in the BS doublet states from higher states of larger spin values. The doublet-quartet energy gaps exempted from spin contamination errors employing Eq. 6 are collected in Table 1. The $\Delta E_{D1,Q}$ and $\Delta E_{D2,Q}$ of 316.0 and 824.0 cm$^{-1}$ calculated from the BS-DFT overestimate the experimentally observed values of 69.9–104.9 and 419.7–629.6 cm$^{-1}$ respectively. On the other hand, the energy gaps values are remarkably improved with CBS-DFT resulting in 176.2 and 658.6 cm$^{-1}$ for $\Delta E_{D1,Q}$ and $\Delta E_{D2,Q}$ respectively.

**Table 1:** Computed energies of HS and BS states and doublet-quartet energy gaps for Bl-NN-NN triradical obtained from BS-DFT (UB3LYP/def2-TZVP) and CBS-DFT (UB3LYP/6-31G(d)). The spin-squared values ($<S^2>$) in HS and BS states are provided in italics. The energy gaps in the last two columns have been obtained by applying Eq. 6.

| **Method** | **Energies (Eh)** | | | $\Delta E_{D1,Q}$ (cm$^{-1}$) | $\Delta E_{D2,Q}$ (cm$^{-1}$) |
|---|---|---|---|---|---|
| | **E(HS)** $<S^2>_{HS}$ | **E(BS1)** $<S^2>_{BS1}$ | **E(BS2)** $<S^2>_{BS2}$ | | |
| **BS-DFT** | -1962.661141 | -1962.660216 | -1962.658729 | 316.0 | 824.0 |
| | *3.88* | *1.87* | *1.87* | | |
| **CBS-DFT** | -1963.097395 | -1963.096988 | -1963.095476 | 176.2 | 658.6 |
| | *3.88* | *1.88* | *1.88* | | |

For multi-reference calculations, it is well-known that proper choice of active space and the number of roots included in state-averaging are crucial for the prediction of appropriate results. This is also been experienced in our previous work[79] and has also been reported by Llanos et al.[80] in the study of inorganic systems. For the description of triradicals, the minimal active space required for qualitative description involves three unpaired electrons distributed in the three active orbitals i.e., CAS(3,3). This active space leads to 7 orbital configurations giving rise to 1 quartet and 8 doublet configuration state functions (CSFs). Inclusion of all the roots in the state-averaging scheme results in quite large values of $\Delta E_{DQ}$ of 317.3 and 2907.5 cm$^{-1}$ at SA-CASSCF level (Table S1) and corresponding NEVPT2 predicts incorrect ground-spin state. This result highlights the importance of selection of only low-lying roots. For a triradical system with three unpaired electrons localized in different regions, the most important orbital configuration is [111] where each electron occupies orbitals localized around those regions. This configuration gives rise to 1 quartet and two doublet states which contribute to the low-energy spectrum. Therefore, it is necessary to include these states in state-averaging to obtain active orbitals which can describe these three states properly. With this state-averaging scheme, we have carried out SA-CASSCF calculation with CAS(3,3) active space followed by enlargement of active space to CAS(5,5), CAS(7,7) and CAS(9,9). To check the low-energy spectrum, we have computed the CAS-CI energies (without further optimizing orbitals) of two quartets and three doublets for each of these active spaces. The results shown in Figure S1 and Table S2 demonstrate that the second quartet and the third doublet are much higher in energy. Therefore, it can be concluded that the low-energy spectrum contains only 1 quartet and 2 doublet states, as expected for a triradical with localized electrons. After confirming this, NEVPT2 computations have been carried out on each state. Both SA-CASSCF and NEVPT2 results are shown in Table S3.

All calculations confirm that the Rajca's triradical (Bl-NN-NN) has quartet ground state. The CAS(3,3) calculations yield the first doublet-quartet energy gap of 101.5 cm$^{-1}$ and the second doublet-quartet energy gap of 641.3 cm$^{-1}$ (see Figure 3 and Table S3). This value is in nice agreement with the experimentally predicted value. However, the energy gap is underestimated to 37.2 and 117.4 cm$^{-1}$ when dynamical correlations are taken into account through NEVPT2. Therefore, to acquire quantitative accuracy, incorporating the correlation of $\pi$-orbitals of the coupler is essential. Consequently, CAS(3,3) active space was expanded to CAS(5,5), CAS(7,7) and CAS(9,9) taking into account the orbitals of the coupler possessing sizable tails on the radical centers. The computed doublet-quartet energy gaps with the consideration of different active spaces are shown in Figure 3 and Table S3.

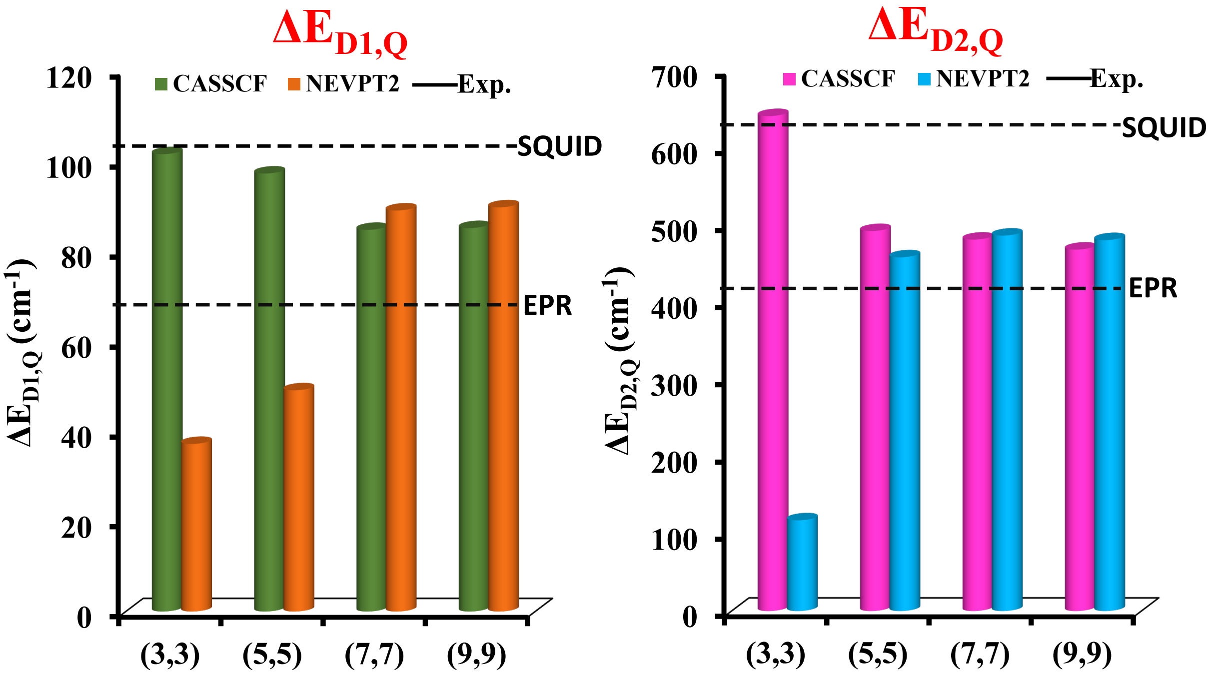
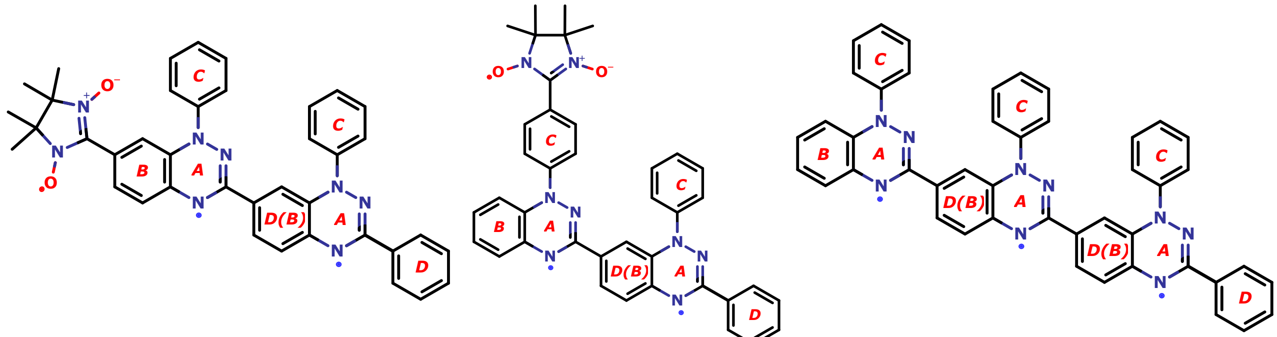


**Figure 3:** Computed doublet-quartet energy gaps (cm$^{-1}$) for Bl-NN-NN with different active spaces. The green and orange bars signify $\Delta E_{D1,Q}$ computed from CASSCF and NEVPT2 respectively. The pink and blue bars represent $\Delta E_{D2,Q}$ calculated from CASSCF and NEVPT2 respectively. The dotted lines mark the values obtained experimentally from EPR spectroscopy and SQUID magnetometry by Rajca et al.[60]

From the figure, it can be observed that for smaller active spaces, the NEVPT2 provides smaller energy gap values in disagreement with experimental results. However, as the active space is enlarged to CAS(7,7) and CAS(9,9), both the CASSCF and NEVPT2 results become roughly equivalent. The CAS(9,9) active space provides comparable doublet-quartet energy gaps as obtained from CAS(7,7) and in concordance with experimentally observed energy gaps highlighting that this active space is adequate enough to provide sufficient electronic correlations to bring agreement with experimental results. For this reason, we have used CAS(9,9) active space for further calculations on other triradicals.

To understand the triradical character better, natural orbital occupation numbers of three nearly singly occupied active orbitals ($n_{SOMO}$) resulting from SA-CASSCF is considered for each active space. As can be seen in Table S4, all calculations show occupation number of 1.00, 1.00, 0.99 for the three SOMOs, which confirms the triradical nature of the molecule. To confirm triradical nature of each state, natural orbitals of each state have been computed for all active spaces. The results shown in Table S5 further confirm the presence of three unpaired electrons in three singly occupied active orbitals, with remaining active orbitals either nearly fully occupied or unoccupied.

After establishing computational procedures to obtain reliable doublet-quartet gaps from DFT and wavefunction-based multi-reference methods on the prototypical system of Rajca's triradical, we proceed further to model three possible triradicals based on Blatter's radical system as shown in Figure 4. These triradicals have been designed based on the already experimentally reported Blatter's based diradicals. The triradical Bl-Bl-NN(B) is designed by the union of two diradicals Bl-NN(B) and Bl-Bl (the two diradicals are shown in Figure 1d and 1e). The Bl-Bl-NN(C) is formed by a combination of Bl-NN(C) and Bl-Bl (Figure 1c and 1e). The last triradical, Bl-Bl-Bl, is an exclusive system obtained by coupling the Bl-Bl



**Bl-Bl-NN (B)** **Bl-Bl-NN (C)** **Bl-Bl-Bl**

**Figure 4:** Modeled triradicals obtained by coupling Blatter's diradical with NN and Bl radical i.e., Bl-Bl-NN(B), Bl-Bl-NN(C) and Bl-Bl-Bl.

diradical with itself via ring B(D) (Figure 1e).

As in the previous case, we have confirmed the triradical character of these molecules by looking at the natural occupation numbers of their SOMOs as obtained from the CAS(9,9) calculations. The occupation numbers 1.00, 1.00 and 0.99 are obtained (Table S7), confirming the ideal triradical nature of these molecules. Further analysis of occupancy of natural orbitals for each states obtained from CAS(9,9) also confirms the existence of three unpaired electrons in the three natural orbitals in these states (Table S8).

After gaining insights into the triradical character of these molecules from CASSCF method, we have computed the relevant energy gaps of these molecules by employing the DFT methods (BS-DFT and CBS-DFT), SA-CASSCF(9,9) and NEVPT2 methods. The computed $\Delta E_{D1,Q}$ and $\Delta E_{D2,Q}$ are collected in Table 2 and the energies of the different states from different methods are provided in Table S10-S14 of supplementary information. A comparison of these two $\Delta E_{D,Q}$ computed from all these methods for the triradicals is demonstrated in Figure 5. These calculations confirm that all the putative triradicals possess quartet ground state with large doublet-quartet energy gaps. Amongst them, the Bl-Bl-NN(B) exhibits largest $\Delta E_{D1,Q}$ and $\Delta E_{D2,Q}$ of 168.0 and 518.7 cm$^{-1}$ as computed with SA-CASSCF(9,9)-NEVPT2 calculations. It must be noted that these energy gaps are even larger than the triradical reported by Rajca et al. Considering the excellent agreement of this method with experimental results for the Rajca's triradical, we believe that the modeled triradicals and their estimated gaps are reliable. Thus, we anticipate such larger energy gaps between the quartet-doublet states provides a possibility to obtain a triradical with nearly full thermal occupation for the high-spin ground state, if synthesized. It is noteworthy that the Bl-Bl-Bl triradical also possess comparatively larger $\Delta E_{D,Q}$ values of 92.0 and 436.3 cm$^{-1}$ making it to be yet another promising candidate for practical applications in organic molecular magnets.

**Table 2:** Computed doublet-quartet energy gaps for the modeled triradicals obtained from BS-DFT, CBS-DFT, SA-CASSCF (9,9) and NEVPT2.

| | Method | Bl-NN-NN | Bl-Bl-NN(B) | Bl-Bl-NN(C) | Bl-Bl-Bl |
|---|---|---|---|---|---|
| $\Delta E_{D1,Q}$ | **BS-DFT** | 316.0 | 398.3 | 358.2 | 371.7 |
| | **CBS-DFT** | 176.3 | 277.7 | 321.9 | 332.5 |
| | **CASSCF** | 84.4 | 161.7 | 51.1 | 116.9 |
| | **NEVPT2** | 89.0 | 168.0 | 65.9 | 92.0 |
| $\Delta E_{D2,Q}$ | **BS-DFT** | 824.0 | 908.8 | 411.2 | 383.5 |
| | **CBS-DFT** | 658.6 | 815.2 | 389.6 | 349.8 |
| | **CASSCF** | 467.9 | 484.9 | 288.2 | 560.6 |
| | **NEVPT2** | 480.2 | 518.7 | 293.6 | 436.3 |

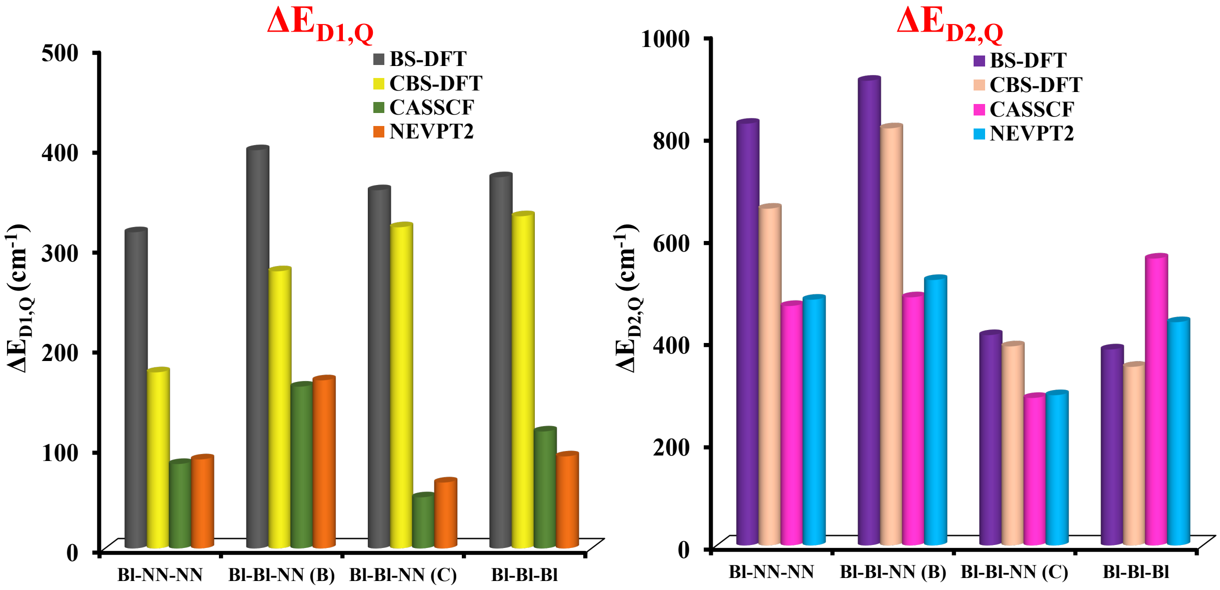


**Figure 5:** Computed doublet-quartet energy gaps for all the triradicals obtained with BS-DFT, CBS-DFT, SA-CASSCF(9,9) and NEVPT2. The first plot signifies $\Delta E_{D1,Q}$ and the second plot represents $\Delta E_{D2,Q}$.

# 4 Conclusion

In summary, we have employed state-of-the-art DFT and wavefunction-based multi-reference methods to investigate doublet-quartet energy gaps of the recently synthesized Blatter's based triradical namely, Bl-NN-NN. The standard DFT based broken symmetry method with hybrid B3LYP functional yields exaggerated values in disaccordance with the experimentally reported values from EPR and SQUID techniques. The CBS-DFT improved them providing proximate results to experiments. Since both these methods are limited by large spin-contamination of the low-spin state, wavefunction-based SA-CASSCF/NEVPT2 methods including both static and dynamical correlations comes out as a method of choice for computing accurate energy gaps in the reported triradical. However, special care needs to be taken to choose roots to be included in state-averaging procedure such that they arise from different spin-couplings of localized electrons. Further, upon validation of the computational scheme, we have investigated the energy gaps for three modeled Blatter's based triradicals viz. Bl-Bl-NN(B), Bl-Bl-NN(C) and Bl-Bl-Bl. All of them have been shown to have quartet as ground state with significant $\Delta E_{D1,Q}$ and $\Delta E_{D2,Q}$ values. The molecules Bl-Bl-NN(B) and Bl-Bl-Bl exhibit even larger energy gaps than the experimentally synthesized triradical. Thus, they present themselves as possible alternative organic molecules with magnetically robust quartet ground-state. We believe that this work paves way to synthesizing further triradicals with large doublet-quartet energy gaps and promising applications in organic magnetic and electronic materials.

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**Supporting Information Available:** DFT computed energies, CASSCF/NEVPT2 computed energies, occupation numbers of SOMOs and natural orbitals, wavefunction analysis of all the triradicals. This material is available free of charge via the Internet at http://pubs.acs.org.

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