

A COMPUTATIONAL INVESTIGATION OF THE ^{14}N NQR PARAMETERS OF BORAZYNE **

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In this study, the ^{14}N NQR parameters of the possible isomers of borazyne were reported in the singlet and triplet states at the M062X/6-311G(d,p) level of theory. Electric field gradient tensors (q_{xx} , q_{yy} , q_{zz}), nuclear quadrupole coupling constants (χ_{zz} , χ_{yy} , χ_{xx}), asymmetry parameter (η), and nuclear quadrupole resonance frequencies (ν_+ , ν_- , ν_0) were estimated. Relative energy, frontier orbital energy, and HOMO-LUMO gap values of these isomers were calculated. From the energetic aspect, ortho and meta(2) isomers were the most stable isomers in the singlet and triplet states, respectively. The singlet state was a more stable spin isomer compared to the triplet state between all isomers, except the meta(2) isomer. Aromaticity analysis of the studied molecules on the basis of nucleus-independent chemical shift values showed that the aromaticity of the triplet state was stronger than that of the singlet state for ortho and para isomers. For the meta (2) isomer, the aromaticity of the singlet state was stronger than that of the triplet state. To calculate the atomic charge of nitrogen atoms, natural bonding orbital method analysis was used.

Keywords: borazyne, ^{14}N NQR parameters, nucleus-independent chemical shift, natural bonding orbital.

ЧИСЛЕННОЕ МОДЕЛИРОВАНИЕ ПАРАМЕТРОВ ^{14}N ЯДЕРНОГО КВАДРУПОЛЬНОГО РЕЗОНАНСА БОРАЗИНА

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В рамках теории M062X/6-311G (d,p) описаны ^{14}N ЯКР параметры возможных изомеров боразина в синглетном и триплетном состояниях. Оценены компоненты q_{xx} , q_{yy} , q_{zz} тензора градиента электрического поля, константа ядерной квадрупольной связи (χ_{zz} , χ_{yy} , χ_{xx}), параметр асимметрии η , частоты ядерного квадрупольного резонанса ν_+ , ν_- , ν_0 . Рассчитаны относительная энергия, энергия пограничной орбитали и разница между энергиями верхней и нижней молекулярных орбиталей этих изомеров. С энергетической точки зрения орто- и мета-(2) изомеры наиболее стабильны в синглетном и триплетном состояниях. Синглетное состояние — более стабильный спиновый изомер по сравнению с триплетным состоянием для всех изомеров кроме мета(2). Анализ ароматичности изученных молекул на основе ядерно-независимого химического сдвига показывает, что ароматичность триплетного состояния больше, чем синглетного, для орто- и параизомеров. Для мета-(2) изомера ароматичность синглетного состояния выше, чем триплетного. Для расчета атомного заряда атомов азота использован метод естественной орбитали.

Ключевые слова: боразин, параметры ядерного квадрупольного резонанса ^{14}N , ядерно-независимый химический сдвиг, естественная орбиталь.

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Introduction. Borazyne is a suggested intermediate product in the formation of borazanaphthalene and diborazine during the photolysis of borazine [1]. For many years, the experimental and theoretical investigations were reported for the explanation of the structure and properties of benzyne [2–6]. The replacement of CC by BN is known to lead to borazine; however, the isolation and characterization of it have been not reported. Several investigations have been published about the structure and properties of the borazine and related molecules [7–15], but a limited number of studies have been reported about borazyne [16, 17]. For example, the structure and aromaticity of B-substituted borazines and borazyne were found [18]. Because of the considerable difference between the electronegativity of boron and nitrogen, the ring delocalization of electrons in the borazyne ring is weakened.

Nuclear quadrupole resonance (NQR) spectroscopy is useful for characterization of physical properties [19]. The ^{14}N NQR parameters of many molecules were investigated for illustration of the structural details and the variations in the electronic environment of the nuclei [20–24]. The electric field gradient (EFG) tensor is very sensitive to the electrostatic surroundings at the sites of quadrupole nuclei with spin angular momenta higher than one-half ($I > 1/2$). For example, the ^{14}N nucleus has $I = 1$. Measurements of quadrupole coupling constants (χ) and asymmetry parameters (η) are possible with experimental NQR investigations. If experimental NQR studies are not accessible, high-level quantum chemical calculations can provide the reliable NQR parameters [25–31]. Because of the lack of experimental studies on the ^{14}N NQR parameters of borazines, we are interested in the computational investigation of these parameters. This study is useful for the estimation of the charge of quadrupole nuclei and electron distribution in these molecules. Providing the linear correlations between the calculated parameters is valuable for deriving the structure-property relationships.

The primary purpose of this work is to find the ^{14}N NQR parameters of the various isomers of borazyne in the singlet and triplet states, and to present the correlations between these parameters with aromaticity and the atomic charge.

Computational methodology. All calculations were performed with the Gaussian 09 suite program [32] using the hybrid meta-exchange-correlation functional of Truhlar and Zhao (M06-2X) [33]. The standard 6-311G(*d,p*) basis set was used in the calculations [34, 35]. Frequency calculations were employed to confirm the nature of the stationary points of the studied molecules.

The electrostatic interaction of the nuclear electric quadrupole moment and the electron charge surrounding the nucleus can increase nuclear quadrupole resonance (NQR) [36]. The Hamiltonian of this interaction for a nucleus with spin I is given in [37]:

$$H_Q = \frac{e^2 Q q_{zz}}{4I(2I-1)} \left[3I_z^2 - I^2 + \frac{\eta}{2} (I_+^2 + I_-^2) \right], \quad (1)$$

where e is the elementary charge, all I in the denominator include scalar values, while all I in the square brackets are operators [38]. Quantum chemical calculations result in the principal components of the EFG tensor, q_{ii} , in atomic units (1 a.u. = 9.717365×10^{21} V/m²), with $|q_{zz}| \geq |q_{yy}| \geq |q_{xx}|$; q_{xx} , q_{yy} , and q_{zz} are the components of EFG in the directions of x , y , and z , respectively.

Nucleus-independent chemical shift (NICS) values were calculated using the Gauge independent atomic orbital (GIAO) method [39]. These values were useful to clarify the aromaticity. The indicator is identified as the negative value of the absolute magnetic shielding calculated at the ring center [40] or another desired point of the system [41]. Negative values of NICS are attributed to aromatic rings.

The analysis has also been conducted by the natural bond orbital method [42] using the NBO program. NQR, NICS, and NBO calculations were performed using the optimized structures.

Results and discussion. *Energetic aspects.* Figure 1 presents the possible isomers of borazyne. The absolute energy (E) and relative energy (ΔE_1 and ΔE_2) values of the structural (*ortho*, *meta*, *para*) and spin isomers (singlet and triplet states) of borazyne are listed in Table 1. The calculated ΔE_1 values are related to the most stable structural isomer. On the other hand, the ΔE_2 values are related to the most stable spin isomer. It can be observed that *ortho* and *meta*(2) isomers are the most stable structural isomer in the singlet and triplet states, respectively. However, the singlet state is a more stable spin isomer compared to the triplet state between all isomers, except the *meta*(2) isomer.

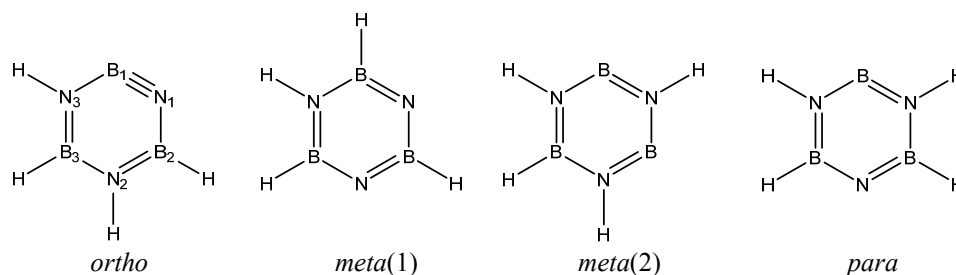


Fig. 1. The possible isomers of borazyne molecules.

TABLE 1. Absolute Energy (E , eV) and Relative Energy (ΔE_1 , ΔE_2 , eV) Values of the Different Isomers of Borazyne for Singlet and Triplet States at the M062X/6-311G(d,p) Level of Theory

| Isomer | E | | ΔE_1^{**} | | ΔE_2^* | |
|----------------|----------|----------|-------------------|---------|----------------|---------|
| | Triplet | Singlet | Triplet | Singlet | Triplet | Singlet |
| <i>ortho</i> | -6565.02 | -6567.57 | 0.82 | 0.00 | 2.56 | 0.00 |
| <i>meta(1)</i> | -6563.95 | -6565.86 | 1.88 | 1.71 | 1.90 | 0.00 |
| <i>meta(2)</i> | -6565.83 | -6564.96 | 0.00 | 2.61 | 0.00 | 0.87 |
| <i>para</i> | -6565.18 | -6566.05 | 0.65 | 1.52 | 0.87 | 0.00 |

* With respect to a more stable spin isomer.

** With respect to a more stable structural isomer.

Molecular orbital analysis. The frontier orbital energy and the HOMO-LUMO gap values of the possible isomers of borazyne in the singlet and triplet states for the studied isomers are calculated. The values in Table 2 show the largest HOMO-LUMO gap for the *ortho* isomer in the singlet state. Therefore, the principles of minimum energy (MEP) and maximum hardness (MHP) are compatible in this isomer, that is, while an isomer changes from the most stable to other less stable species (for these cases the energy increases, and the hardness decreases) [43–47].

TABLE 2. Frontier Orbital Energy and HOMO–LUMO Gap (eV) Values of the Different Isomers of Borazyne for the Singlet and Triplet States at the M062X/6-311G(d,p) Level of Theory

| Isomer | Triplet | | | Singlet | | |
|----------------|---------|------------------|------------------|---------|------------------|------------------|
| | gap | $E(\text{LUMO})$ | $E(\text{SOMO})$ | gap | $E(\text{LUMO})$ | $E(\text{HOMO})$ |
| <i>ortho</i> | 7.86 | 0.90 | -6.97 | 9.41 | 0.30 | -9.12 |
| <i>meta(1)</i> | 9.36 | 0.54 | -8.82 | 8.74 | 0.46 | -8.27 |
| <i>meta(2)</i> | 7.18 | 1.03 | -6.12 | 3.96 | -1.06 | -5.01 |
| <i>para</i> | 7.70 | 1.06 | -6.64 | 6.80 | -0.71 | -7.48 |

Aromaticity. The aromaticity in the singlet and triplet states of the various isomers of borazyne is illustrated by the calculation of nucleus-independent chemical shift (NICS) values (Table 3). These values are calculated at the center of the ring and 0.5, 1.0, 1.5, 2.0, and 2.5 Å above the center. Negative NICS values are observed for all isomers and states except the triplet state of the *meta(1)* isomer. As a result, all structures reveal aromaticity, but the *meta(1)* isomer is anti-aromatic. The most negative value of NICS corresponds

TABLE 3. NICS (ppm) Values of the Different Isomers of Borazyne for the Singlet and Triplet States at the M062X/6-311G(d,p) Level of Theory

| Isomer | Triplet | | | | | | Singlet | | | | | |
|----------------|---------|-------|-------|--------|--------|--------|---------|-------|-------|-------|--------|--------|
| | 2.5 | 2.0 | 1.5 | 1.0 | 0.5 | 0.0 | 2.5 | 2.0 | 1.5 | 1.0 | 0.5 | 0.0 |
| <i>ortho</i> | -2.71 | -4.59 | -8.13 | -14.21 | -21.88 | -25.78 | -0.86 | -1.35 | -2.10 | -3.26 | -4.80 | -5.58 |
| <i>meta(1)</i> | 0.95 | 1.90 | 3.89 | 7.15 | 10.00 | 10.51 | -1.77 | -2.83 | -4.63 | -7.97 | -16.01 | -24.55 |
| <i>meta(2)</i> | -1.00 | -1.60 | -2.56 | -3.72 | -4.18 | -3.83 | -0.68 | -1.26 | -2.34 | -3.72 | -4.35 | -4.01 |
| <i>para</i> | -1.54 | -2.64 | -4.73 | -8.38 | -13.29 | -15.94 | -0.95 | -1.53 | -2.46 | -3.90 | -5.65 | -6.42 |

to the center of the ring. Therefore, there is σ -aromaticity in all isomers and states except the triplet state of the *meta*(1) isomer. A comparison of NICS values in the singlet and triplet states shows stronger aromaticity of the triplet state as compared to the singlet state for *ortho* and *para* isomers. In the *meta*(2) isomer, the aromaticity of the singlet state is stronger than that of the triplet state.

¹⁴NQR parameters. *Electric field gradient tensor.* Table 4 represents the electric field gradient (EFG) tensors of ¹⁴N in the studied molecules. The EFG tensors in the nitrogen molecule include: $Q(xx) = Q(yy) = -Q(zz)/2$. To obtain the nuclear quadrupole coupling constants, χ_{ii} , the calculated q_{ii} values were used:

$$\chi_{ii} = e^2 Q q_{ii} / h, \quad i = x, y, z, \quad (2)$$

where Q is the nuclear quadrupole moment of the ¹⁴N nucleus, e is the elementary charge, and h is Planck's constant. The standard values of the quadrupole moment, Q , provided by Pyykkö [48], were utilized in Eq. (1), $Q(^{14}\text{N}) = 20.44 \text{ mb}$.

It can be seen that $Q(zz)$ values are larger for the nitrogen atom nonbonded to hydrogen as compared to nitrogen bonded to hydrogen.

TABLE 4. ¹⁴NQR Parameters

| X | ν_0 | ν_- | ν_+ | η | $\chi(xx)$ | $\chi(yy)$ | $\chi(zz)$ | $Q(xx)$ | $Q(yy)$ | $Q(zz)$ |
|-----------------|---------|---------|---------|--------|------------|------------|------------|---------|---------|---------|
| Singlet State | | | | | | | | | | |
| <i>ortho</i> | | | | | | | | | | |
| N1 | 0.029 | 2.169 | 2.198 | 0.020 | 1.427 | 1.485 | 2.912 | -0.297 | -0.309 | 0.606 |
| N2 | 0.382 | 1.069 | 1.451 | 0.455 | 0.458 | 1.222 | 1.680 | 0.095 | 0.254 | -0.350 |
| N3 | 0.786 | 1.360 | 2.146 | 0.673 | 0.383 | 1.955 | 2.338 | -0.080 | -0.407 | 0.487 |
| <i>Meta</i> (1) | | | | | | | | | | |
| N1 | 0.600 | 3.758 | 4.358 | 0.222 | 2.105 | 3.306 | 5.411 | 0.438 | 0.688 | -1.127 |
| N2 | 0.600 | 3.758 | 4.358 | 0.222 | 2.105 | 3.306 | 5.411 | 0.438 | 0.688 | -1.127 |
| N3 | 0.186 | 0.920 | 1.107 | 0.276 | 0.489 | 0.862 | 1.351 | 0.102 | 0.179 | -0.281 |
| <i>Meta</i> (2) | | | | | | | | | | |
| N1 | 0.745 | 0.858 | 1.603 | 0.908 | 0.075 | 1.565 | 1.640 | 0.016 | 0.326 | -0.342 |
| N2 | 0.745 | 0.858 | 1.603 | 0.908 | 0.075 | 1.565 | 1.640 | 0.016 | 0.326 | -0.342 |
| N3 | 0.103 | 1.628 | 1.731 | 0.092 | 1.017 | 1.222 | 2.239 | -0.212 | -0.255 | 0.466 |
| <i>para</i> | | | | | | | | | | |
| N1 | 0.663 | 1.327 | 1.989 | 0.600 | 0.443 | 1.768 | 2.211 | -0.092 | -0.368 | 0.460 |
| N2 | 1.222 | 1.761 | 2.983 | 0.773 | 0.360 | 2.804 | 3.163 | -0.075 | -0.584 | 0.659 |
| N3 | 0.663 | 1.327 | 1.989 | 0.600 | 0.443 | 1.768 | 2.211 | -0.092 | -0.368 | 0.460 |
| Triplet State | | | | | | | | | | |
| X | ν_0 | ν_- | ν_+ | η | $\chi(xx)$ | $\chi(yy)$ | $\chi(zz)$ | $Q(xx)$ | $Q(yy)$ | $Q(zz)$ |
| <i>ortho</i> | | | | | | | | | | |
| N1 | 0.571 | 3.007 | 3.577 | 0.260 | 1.624 | 2.765 | 4.390 | 0.338 | 0.576 | -0.914 |
| N2 | 0.530 | 1.043 | 1.573 | 0.608 | 0.342 | 1.402 | 1.745 | 0.071 | 0.292 | -0.363 |
| N3 | 0.565 | 1.019 | 1.584 | 0.652 | 0.302 | 1.433 | 1.735 | 0.063 | 0.298 | -0.361 |
| <i>meta</i> (1) | | | | | | | | | | |
| N1 | 0.823 | 2.007 | 2.830 | 0.510 | 0.790 | 2.435 | 3.225 | 0.164 | 0.507 | -0.671 |
| N2 | 0.823 | 2.007 | 2.830 | 0.510 | 0.790 | 2.435 | 3.225 | 0.164 | 0.507 | -0.671 |
| N3 | 0.235 | 1.050 | 1.284 | 0.302 | 0.543 | 1.013 | 1.556 | 0.113 | 0.211 | -0.324 |
| <i>meta</i> (2) | | | | | | | | | | |
| N1 | 0.600 | 0.935 | 1.535 | 0.729 | 0.223 | 1.423 | 1.647 | 0.047 | 0.296 | -0.343 |
| N2 | 0.493 | 0.998 | 1.491 | 0.594 | 0.337 | 1.323 | 1.659 | 0.070 | 0.275 | -0.346 |
| N3 | 0.493 | 0.998 | 1.491 | 0.594 | 0.337 | 1.323 | 1.659 | 0.070 | 0.275 | -0.346 |
| <i>para</i> | | | | | | | | | | |
| N1 | 0.648 | 0.962 | 1.610 | 0.756 | 0.209 | 1.505 | 1.715 | 0.044 | 0.313 | -0.357 |
| N2 | 0.369 | 3.043 | 3.412 | 0.172 | 1.782 | 2.521 | 4.303 | 0.371 | 0.525 | -0.896 |
| N3 | 0.648 | 0.962 | 1.610 | 0.756 | 0.209 | 1.505 | 1.715 | 0.044 | 0.313 | -0.357 |

Note. Electric field gradient tensors (q_{xx} , q_{yy} , q_{zz} in a.u), nuclear quadrupole coupling constant (χ_{zz} , χ_{yy} , χ_{xx} , in MHz), asymmetry parameter (η), and nuclear quadrupole resonance frequencies (ν_+ , ν_- , ν_0 in MHz) of borazyne for the singlet and triplet states at the M062X/6-311G(*d,p*) level of theory.

Nuclear quadrupole coupling constant. Usually, the NQR parameters are reported experimentally as the nuclear quadrupole coupling constant in units of frequency:

$$Q(CC) = \chi_{ii} = e^2 Q q_{zz} / h. \quad (3)$$

Nuclear quadrupole coupling constants of ^{14}N in the studied molecules are gathered in Table 4. The calculated $\chi(zz)$ for nitrogen atoms in N_2 free molecule is 5.850 MHz at the M062X/6-311g(d,p) level of theory. It can be seen that $\chi(zz)$ values are larger for the nitrogen atom nonbonded to hydrogen as compared to nitrogen bonded to hydrogen.

There is a good relationship between the average of $\chi(zz)$ and $\chi(xx)$ values of nitrogen atoms in each isomer with NICS (0.0) values in the singlet state:

$$\text{NICS}(0.0) = -9.8595 \langle \chi(zz) \rangle + 16.321; R^2 = 0.9603,$$

$$\text{NICS}(0.0) = -16.792 \langle \chi(xx) \rangle + 2.9846; R^2 = 0.9118,$$

where R^2 is the coefficient of determination which quantifies the fraction of the observed variation in y clarified by the linear relationship. The closer R^2 is to unity, the better the linear model elucidates the y variations in the $y = ax + b$ equation [49].

Asymmetry parameter. The asymmetry parameter (η) is defined as

$$\eta = |(q_{yy} - q_{xx}) / q_{zz}|, 0 \leq \eta \leq 1. \quad (4)$$

Table 4 represents the asymmetry parameters of ^{14}N in the examined molecules. These values show that the distribution of the electric charge around the nitrogen nucleus is considerably different from cylindrical symmetry in comparison with that in nitrogen molecules.

It can be seen that η values are larger for the nitrogen atom bonded to hydrogen as compared to nitrogen nonbonded to hydrogen in the *ortho* (in singlet and triplet states), *para* (triplet state), and *meta*(1) isomer (singlet state). But in the *para* isomer (singlet) and *meta*(1) (triplet state) isomer, η values are larger for the nitrogen atoms nonbonded to hydrogen as compared to the nitrogen bonded to hydrogen.

Nuclear quadrupole resonance frequencies. We have three energy levels for a nucleus of unit spin (such as ^{14}N), hence we get three nuclear quadrupole resonance frequencies [37]:

$$\nu_+ = (3/4)\chi_{zz}(1 + \eta/3), \quad (5)$$

$$\nu_- = (3/4)\chi_{zz}(1 - \eta/3), \quad (6)$$

$$\nu_0 = (3/4)\chi_{zz}\eta. \quad (7)$$

Table 4 represents the nuclear quadrupole resonance frequencies ^{14}N in the examined molecules. In these molecules, the nitrogen atoms are placed in the electric field of the other nuclei, hence the symmetry of the EFG surrounding them changes. This change results in the splitting of the energy levels of ^{14}N nuclei; owing to this, three NQR frequencies for ^{14}N are seen. The variances between the frequencies of nitrogen in these molecules can be associated with the direct participation of the electron pairs of N atom during the chemical bond formation or the diatropic current in the ring.

According to Table 4, it is indicated that the ν_+ and ν_- values for the nitrogen atom non-bonded to hydrogen differ as compared to nitrogen bonded to hydrogen both in the triplet and singlet states.

TABLE 5. Natural Charges of Nitrogen Atoms (in e) of Borazyne Isomers for the Singlet and Triplet States at the M062X/6-311G(d,p) Level of Theory

| X | Triplet | Singlet | X | Triplet | Singlet |
|-----------------|---------|---------|-----------------|---------|---------|
| <i>ortho</i> | | | <i>para</i> | | |
| N1 | -0.8061 | -1.0764 | N1 | -1.1315 | -1.1579 |
| N2 | -0.5456 | -1.1001 | N2 | -0.5771 | -1.1572 |
| N3 | -0.5759 | -1.1389 | N3 | -1.1315 | -1.1579 |
| <i>meta</i> (1) | | | <i>meta</i> (2) | | |
| N1 | -0.6144 | -0.6737 | N1 | -1.2132 | -1.1427 |
| N2 | -0.6144 | -0.6737 | N2 | -1.1449 | -1.1392 |
| N3 | -1.0934 | -1.0229 | N3 | -1.1449 | -1.1392 |

There is a good relationship between the average of v_+ and v_- values of nitrogen atoms in each isomers with NICS(0.0) values in the singlet state:

$$\text{NICS}(0.0) = -12.986 \langle v_+ \rangle + 19.635, R^2 = 0.9121,$$

$$\text{NICS}(0.0) = -12.823 \langle v_- \rangle + 12.078, R^2 = 0.9726.$$

The NBO charges. The partial atomic charges calculated by the NBO method for all of the structures are listed in Table 5. The results show that we have the less negative NBO partial atomic charge of N nuclei nonbonded to hydrogen in the singlet and triplet state, except the triplet state of the ortho isomer. There is a good relationship between the calculated NBO partial atomic charges of nitrogen atoms and the $\chi(zz)$ parameter in the triplet state except for the ortho isomer:

$$Q(\text{NBO}) = 3.5469 \chi(zz) + 5.7154, R^2 = 0.911.$$

Conclusions. In the present work, the estimation of the ^{14}N NQR parameters of different isomers of bozayne in the singlet and triplet states at the M062X/6311G(*d,p*) level of theory permits us to conclude the following. *Ortho* and *meta*(2) isomers are the most stable structural isomer in the singlet and triplet states, respectively. The singlet state is a more stable spin isomer compared to the triplet state between all isomers, except the *meta*(2) one. All studied isomers and states have σ -aromaticity except the triplet state of the *meta*(1) isomer. The aromaticity of the triplet state is larger than for the singlet state for *ortho* and *para* isomers. In the *meta*(2) isomer, the aromaticity of the singlet state is larger than for the triplet state. The average of v_+ and v_- values of nitrogen atoms in each isomer with NICS(0.0) values in the singlet state reveal good correlations. The calculated NBO partial atomic charges of nitrogen atoms and the $\chi(zz)$ parameter in the triplet state show a good linear relationship, except for the *ortho* isomer.

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