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# Molecular Switches of the LD-CISSS Type Based on Ni(II) Azomethine Bis-Chelate Complexes. Quantum Chemical Modeling

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**Abstract**—(DFT/B3LYP/6-311++G(d,p)) calculations were performed to study Ni(II) azomethine bis-chelates with photoactive moieties (imidazole and benzimidazole derivatives of azo compounds, azomethines, and stilbenes) exhibiting the behavior of molecular magnetic switches by the light-driven coordination-induced spin state switching (LD-CISSS) mechanism. The structural and energy characteristics of the complexes favorable to or restricting the applicability of these complexes as molecular switches were determined.

**Keywords:** quantum chemical modeling, molecular magnetic switches, coordination compounds, stereoisomerization

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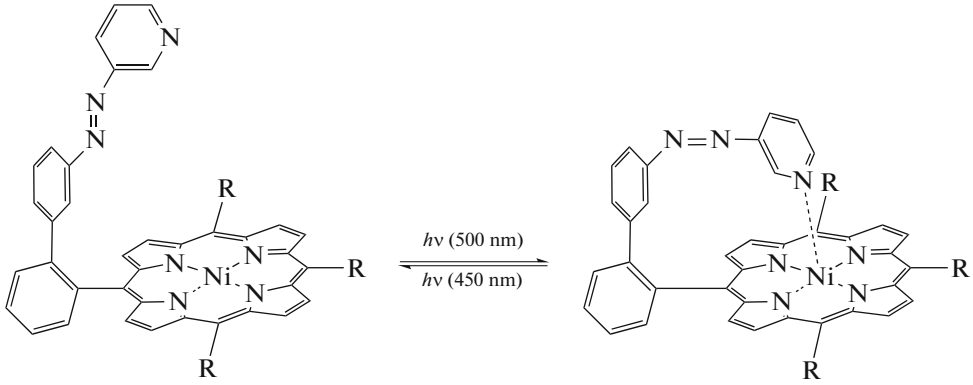
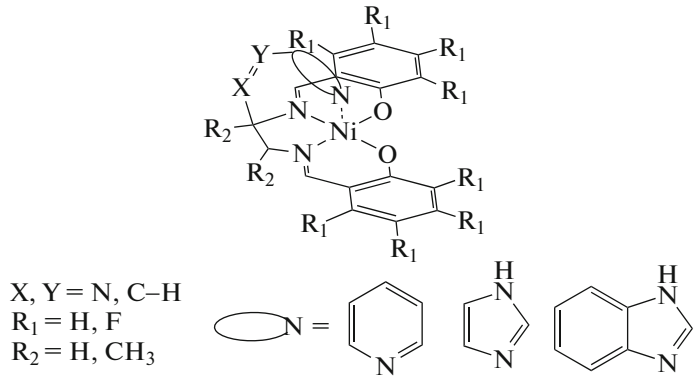
## INTRODUCTION

Transition metal complexes with organic ligands exhibiting photocontrolled magnetic properties [1–3] and capable of functioning as molecular switches in spintronic devices [4, 5] are also used as sensors [6] and contrast agents in MRI [7]. One of the effects responsible for the switching of the magnetic properties under irradiation is the light-induced excited spin state trapping (LIESST) [8], which is observed, most often, for iron compounds. This mechanism operates at low (helium) temperatures, which complicates its use in electronic devices. Another approach to switching the molecular states of transition metal complexes is the ligand-driven light-induced spin change (LD-LISC) [9], which is observed at room temperature. However, the remote position of the photoactive moiety from the coordination site results in relatively minor changes in the magnetic characteristics. Both LIESST and LD-LISC mechanisms are based on the spin-crossover effect. A new promising approach to the control over magnetic characteristics of transition metal complexes is the recently proposed mechanism of light-driven coordination-induced spin state switching (LD-CISSS) [10–14]. In relation to the nickel porphyrin complex, it was shown that visible light irradiation causes isomerization of the photochromic arylazo moiety of the ligand that provides steric conditions for the coordination of the pyridine donor site to the metal atom, which induces transition of the complex molecules from the diamagnetic ground state to the paramagnetic state, while further irradiation returns the system into the initial low-spin state (Scheme 1). The reversible transformations occur in solution at room temperature, and their implementation does not depend on cooperative effects such as magnetic ordering and packing of molecules in the crystals.




**Scheme 1.**

In order to search for new photoswitchable coordination systems exhibiting the LD-CISSS effect, we performed quantum chemical modeling of a series of nickel complexes **I–XXV** based on tetradentate *N*,*N*'-bis(salicylidene)ethylenediamine (Salen) functionalized with photoactive groups, which included N-heterocyclic (pyridine (Py), imidazole (Im), benzimidazole (BIm)) derivatives of azo compounds, azomethines, and stilbenes (Scheme 2). The synthetic accessibility of complexes of this type was indicated by data on the preparation of analogous transition metal complexes with Salen ligands containing a coordinated ethylpyridine group [15]. The considered structural motif of the photoisomerizing moiety of the ligand is analogous to that used previously in the design of LD-CISSS type molecular switches [16, 17].




**Scheme 2.**

## CALCULATION PROCEDURE

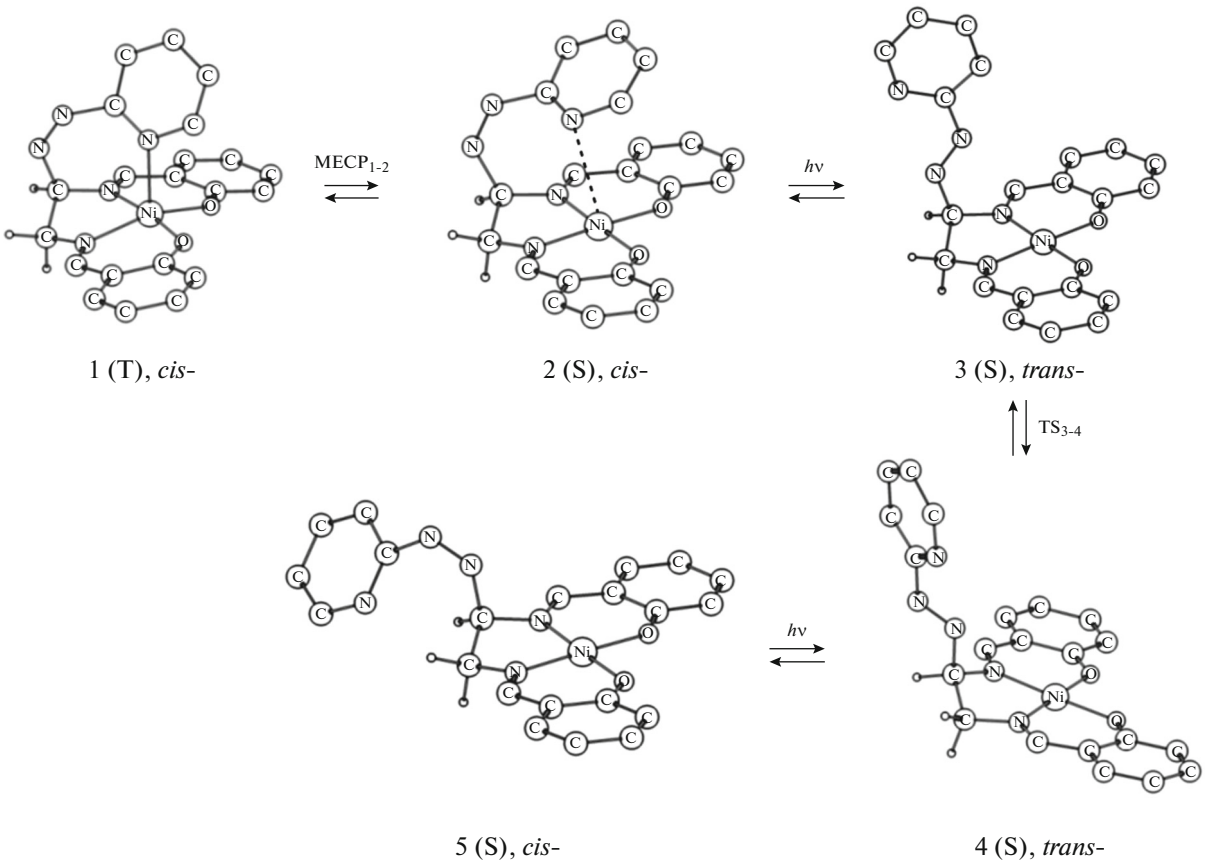
Quantum chemical calculations were performed using the Gaussian09 program [18] by the density functional theory method (DFT) [19] with the hybrid B3LYP functional [20, 21] in combination with the 6-311++G(d,p) basis set. The stationary points in the potential energy surface (PES) were identified and analyzed by full geometry optimization followed by calculation of the vibrational spectra. The spin-forbidden rearrangements in the complexes were studied by finding the minimum-energy crossing points (MECP) of the singlet and triplet PES using an algorithm proposed by Harvey [22]. The graphical images of molecular structures were drawn by the ChemCraft software [23].

## RESULTS AND DISCUSSION

Scheme 3 depicts the mechanism of possible intramolecular rearrangements of nickel coordination compounds **I–XXV**. The molecular structures of the configurational and conformational isomers of complex **I**, corresponding to minima in the triplet (T) 1 and singlet (S) 2–5 PES show the sequence of transitions between high-spin paramagnetic isomer 1 with a five-coordinate Ni(II) ion and low-spin diamagnetic isomer 3 with the *trans*-configuration of azo group, which are the outermost structures for the switch. The intermediate low-spin isomer 2 contains the arylazo group in the *cis*-configuration. Isomers 4 and 5 can arise as the side products of thermally induced transformations of the singlet *trans*-form 3.

According to Scheme 3, behavior of the compounds as molecular magnetic switches requires the reversible light-induced *cis–trans* isomerization of the azo moiety accompanied by transition between the high-spin and low-spin states of the complex $1 \rightleftharpoons 3$. Calculations show that as this takes place, isomers 4 and 5 are formed as side products of thermally induced transformations of the singlet *trans*-form 3. In compound 5, the coordinatively active pyridine donor site is located outside the metal ion region, which precludes the possibility of formation of an additional $N \rightarrow Ni$ coordination bond and makes the light-induced *trans-cis*-photoisomerization and the $5 \rightarrow 1$ pathway irreversible. Indeed, in complex **I**, the barrier for the $3 \rightarrow 4$ isomerization accompanied by the rotation of the azo moiety around the C–N bond is only 1 kcal/mol (Scheme 3, Table 1), and these isomers are energetically equivalent. Hence, in order to possess the properties of a molecular magnetic switch, the model complexes should have isomers 3 more energetically favorable than 4.

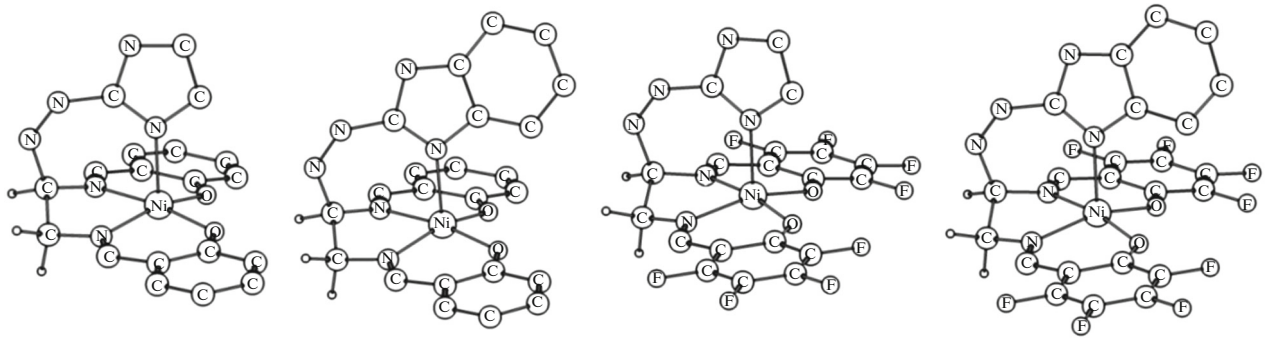
Another condition for the functioning of compounds as photomagnetic switches is the energy preference of triplet isomer 1 over singlet isomer 2. Only in this case, spin-forbidden $2 \rightarrow 1$ isomerization, which brings the system after the photoinitiated rearrangement $3 \rightleftarrows 2$ back to the initial high-spin state, is possible. In complex **I** (Py), this condition is not met (Table 1); meanwhile, for compounds with imidazole **II** (Im) and benzimidazole **VI** (BIm) N-coordinatively active moieties, isomers 1 are energetically more favorable than isomers 2 (Scheme 4, Table 1).




1 (T), *cis*- 2 (S), *cis*- 3 (S), *trans*-

5 (S), *cis*- 4 (S), *trans*-

**Scheme 3.**



**II** (isomer 1) (Im, $R_1$ = H) Triplet T

**VI** (isomer 1) (BIm, $R_1$ = H) Triplet T

**III** (isomer 1) (Im, $R_1$ = F) Triplet T

**VII** (isomer 1) (BIm, $R_1$ = F) Triplet T

**Scheme 4.**

In order to find model complexes with more stable triplet states 1, we considered coordination systems with perfluorinated carbon atoms of the Salen six-membered rings. According to DFT calculation data (Table 1), this structural modification promotes additional stabilization of high-spin states in compounds **III**, **V**, **VII**, and **IX** ($R_1$ = F) by more than 2 kcal/mol. The molecular structures of isomers 1 of nickel complexes **II** (Im, $R_1$ = H), **VI** (BIm, $R_1$ = H), **III** (Im, $R_1$ = F), and **VII** (BIm, $R_1$ = F) are summarized in Scheme 4.

The probability of spin-forbidden 2 → 1 isomerization is determined by not only the energy preference of triplet isomer 1 over singlet isomer 2, but also the height of the isomerization barrier, i.e., the energy difference between isomer 2 and MECP (1–2) point. According to DFT calculations (Table 1), this value markedly decreases for nickel complexes with fluori-

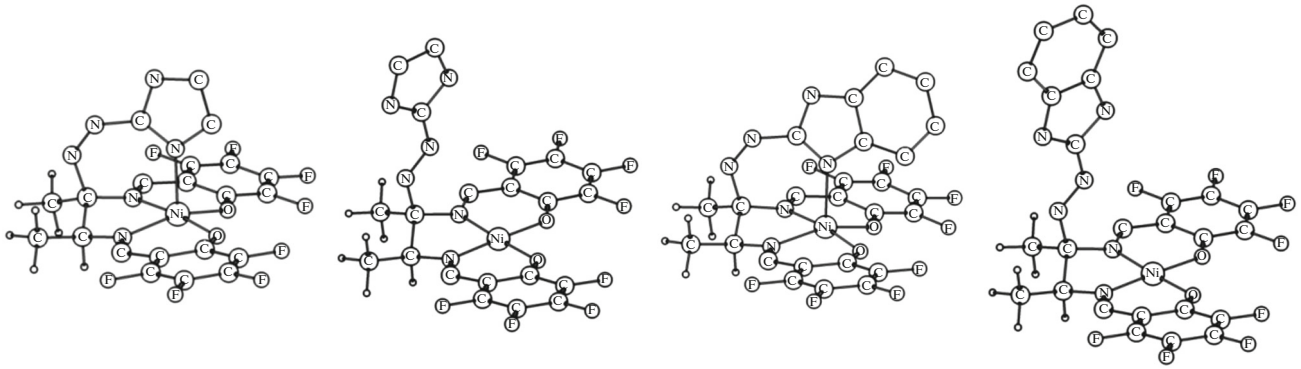
**Table 1.** Calculated relative energies ($\Delta E$, kcal/mol) of the singlet (S) and triplet (T) states of isomers 1–5, transition states (TS (3–4)), barriers for 3 $\rightleftharpoons$ 4 isomerization (δ), MECP (1–2) energies, and $r$(N → Ni) lengths of the coordination bond for nickel complexes (models **I**–**IX**)

| Models **I**–**IX** | $R_1$ | $R_2$ | $\Delta E$ (kcal/mol) for isomers 1–5 of nickel complexes (models **I**–**IX**) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | 1 (T) $\Delta E$ $r$ (Å) | MECP $\Delta E$(1–2) $r$ (Å) | 2 (S) $\Delta E$ $r$ (Å) | 3 (S) $\Delta E$ | TS (3–4) $\Delta E$ δ(3 → 4; 3 ← 4) | 4 (S) $\Delta E$ | 5 (S) $\Delta E$ |
| **I** (Py) | H | H | 0.0<br>2.093 | | −1.1<br>2.962 | −15.6 | −14.7<br>(0.9; 1.2) | −15.9 | −6.6 |
| **II** (Im) | H | H | 0.0<br>2.047 | 7.7<br>2.350 | 4.2<br>2.734 | −12.8 | −11.3<br>(1.5; 0.4) | −11.7 | −5.6 |
| **III** (Im) | F | H | 0.0<br>2.038 | 8.9<br>2.358 | 6.3<br>2.681 | −9.3 | −8.4<br>(0.9; 0.3) | −8.7 | −3.0 |
| **IV** (Im) | H | $CH_3$ | 0.0<br>2.045 | 7.2<br>2.341 | 3.3<br>2.859 | −14.7 | | ←* | 4.0 |
| **V** (Im) | F | $CH_3$ | 0.0<br>2.036 | 8.5<br>2.352 | 5.6<br>2.737 | −11.4 | | ←* | 6.8 |
| **VI** (BIm) | H | H | 0.0<br>2.056 | 7.6<br>2.352 | 3.7<br>2.764 | −12.5 | −11.0<br>(1.5; 0.5) | −11.5 | −5.2 |
| **VII** (BIm) | F | H | 0.0<br>2.045 | 8.9<br>2.366 | 6.3<br>2.678 | −8.5 | −7.5<br>(1.0; 0.4) | −7.9 | −2.0 |
| **VIII** (BIm) | H | $CH_3$ | 0.0<br>2.050 | 7.3<br>2.340 | 3.2<br>2.866 | −14.4 | | ←* | 3.7 |
| **IX** (BIm) | F | $CH_3$ | 0.0<br>2.042 | 8.8<br>2.357 | 5.7<br>2.709 | −10.6 | | ←* | 7.3 |

* Geometry optimization of the molecule transforms initial isomer 4 to isomer 3.

nated Salen ligands, which also promotes the spin-forbidden 2 → 1 reaction.

In order to generate steric restrictions that would suppress the undesirable pathway 3 → 4 → 5, bringing the molecular system beyond the limit of the reaction channel 1 → 2 → 3 → 2 → 1, we considered the coordination compounds containing methyl groups in the ethylene bridge. According to the results (Table 1, Scheme 5), the structures of isomers 4 in nickel complexes **IV**, **V** (Im, $R_2 = CH_3$), and **VIII**, **IX** (BIm, $R_2 = CH_3$) do not correspond to PES stationary points, i.e., they are not formed; this is favorable for the desirable reaction channel of the molecular magnetic switch: 1 → 2 → 3 → 2 → 1.



**V** (isomer 1) (Im, $R_1 = F$, $R_2 = CH_3$) Triplet T

**V** (isomer 3) (Im, $R_1 = F$, $R_2 = CH_3$) Singlet S

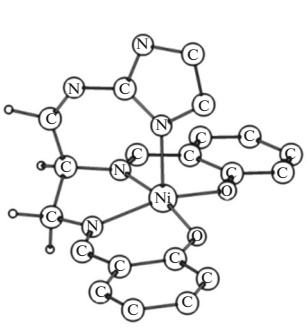
**IX** (isomer 1) (BIm, $R_1 = F$, $R_2 = CH_3$) Triplet T

**IX** (isomer 3) (BIm, $R_1 = F$, $R_2 = CH_3$) Singlet S

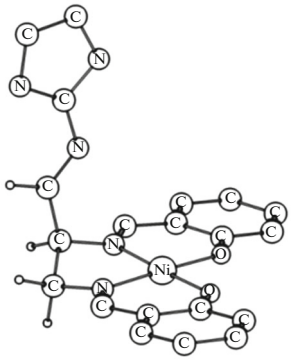
**Scheme 5.**

Thus, DFT modeling of the molecular structures of the stereoisomeric nickel complexes with Salen ligands modified with azoimidazole and benzimidazole derivatives revealed the systems capable of functioning as molecular switches between their diamagnetic and paramagnetic four- and five-coordinate structures via reversible photoinitiated formation and cleavage of the N → Ni coordination bond by the LD-CISSS mechanism.

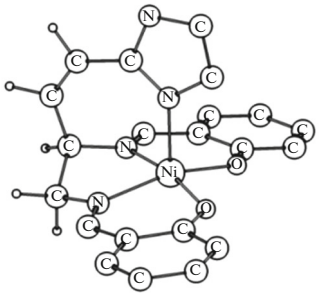
A similar DFT study was carried out for nickel complexes with photoactive moieties based on azomethines (models **X**–**XVII** (AM)) and stilbenes (models **XVIII**–**XXV** (SB)). The results are summarized in Scheme 6 and Table 2.



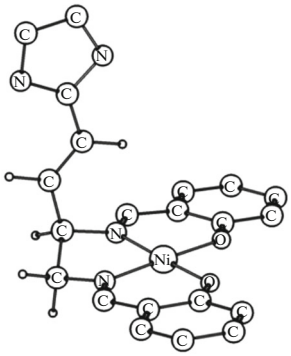
**X** (AM, isomer 1)
(Im, $R_1$ = H, $R_2$ = H)
Triplet T
*cis*-structure



**X** (AM, isomer 3)
(Im, $R_1$ = H, $R_2$ = H)
Singlet S
*trans*-structure



**XVIII** (SB, isomer 1)
(Im, $R_1$ = H, $R_2$ = H)
Triplet T
*cis*-structure



**XVIII** (SB, isomer 3)
(Im, $R_1$ = H, $R_2$ = H)
Singlet S
*trans*-structure

**Scheme 6.**

As follows from the data presented in Table 2, the energy preference of high-spin isomers 1 over low-spin isomers 2 necessary for the molecular magnetic switch behavior is attained in complexes with photoactive moieties based on azomethines **X**–**XVII** and stilbenes **XVIII**–**XXV**. In these coordination compounds, like in the azo group derivatives considered above, perfluorination of the Salen carbon atoms promotes an increase (by more than 2 kcal/mol) in the energy preference of the high-spin isomer 1 over the low-spin isomer 2 (see Table 2). The fluorination effect of Salen ligands is favorable for the spin-forbidden 2 → 1 isomerization as a component of the reversible reaction cycle 1 → 2 → 3 → 2 → 1.

As indicated above, a necessary condition for the molecular magnetic switches of the considered nickel complexes is the energy preference of isomer 3 over isomer 4 and the presence of a substantial barrier between them that suppresses the undesirable rotation of the photoactive group as a result of 3 → 4 isomerization. According to the calculation results presented in Tables 1 and 2, these properties are inherent in the complexes with imidazole and benzimidazole azo compounds and stilbene derivatives, which makes it possible to consider them as promising models of LD-CISSS type molecular switches.

Thus, the DFT modeling of nickel Salen complexes **I**–**XXV** with photoactive (azo, azomethine, and stilbene) moieties indicates that they could be used to fabricate photocontrolled molecular magnetic switches functioning by the LD-CISSS mechanism via reversible formation–cleavage of the additional N → Ni coordination bond.

## FUNDING

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## CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

**Table 2.** Calculated relative energies ($\Delta E$, kcal/mol) of the singlet (S) and triplet (T) states of isomers 1–5, transition states (TS (3–4)), barriers for 3 $\rightleftharpoons$ 4 isomerization ($\delta$), and $r$(N $\rightarrow$ Ni) lengths of the coordination bond for nickel complexes (models **X**–**XXV**)

| Models **X**–**XXV** | $R_1$ | $R_2$ | $\Delta E$ (kcal/mol) for isomer 1–5 of nickel complexes (models **X**–**XXV**) | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | 1 (T)<br>$\Delta E$<br>$r$ (Å) | 2 (S)<br>$\Delta E$<br>$r$ (Å) | 3 (S)<br>$\Delta E$ | TS (3–4)<br>$\Delta E$<br>$\delta(3 \rightarrow 4;$<br>$3 \leftarrow 4)$ | 4 (S)<br>$\Delta E$ | 5 (S)<br>$\Delta E$ |
| **X** (AM, Im) | H | H | 0.0<br>2.051 | 5.4<br>2.785 | –5.3 | –4.6<br>(0.7; 1.5) | –6.1 | –5.2 |
| **XI** (AM, Im) | F | H | 0.0<br>2.040 | 7.7<br>2.695 | –1.2 | –0.6<br>(0.6; 1.1) | –1.7 | –1.0 |
| **XII** (AM, Im) | H | $CH_3$ | 0.0<br>2.047 | 4.5<br>2.902 | –6.6 | –6.0<br>(0.6; 1.9) | –7.9 | 0.3 |
| **XIII** (AM, Im) | F | $CH_3$ | 0.0<br>2.037 | 7.0<br>2.742 | –2.8 | –2.1<br>(0.7; 1.4) | –3.5 | 3.4 |
| **XIV** (AM, BIm) | H | H | 0.0<br>2.063 | 4.6<br>2.817 | –5.6 | –4.8<br>(0.8; 1.7) | –6.5 | –5.3 |
| **XV** (AM, BIm) | F | H | 0.0<br>2.048 | 7.3<br>2.722 | –1.0 | –0.3<br>(0.7; 1.2) | –1.5 | –0.7 |
| **XVI** (AM, BIm) | H | $CH_3$ | 0.0<br>2.059 | 4.1<br>2.995 | –6.8 | –6.3<br>(0.5; 1.9) | –8.2 | –0.4 |
| **XVII** (M, BIm) | F | $CH_3$ | 0.0<br>2.046 | 6.8<br>2.744 | –2.4 | –1.8<br>(0.6; 1.5) | –3.3 | 4.6 |
| **XVIII** (SB, Im) | H | H | 0.0<br>2.052 | 5.5<br>2.761 | –3.8 | –0.3<br>(3.5; 2.4) | –2.7 | –4.2 |
| **XIX** (SB, Im) | F | H | 0.0<br>2.041 | 7.7<br>2.677 | 1.4 | 4.3<br>(2.9; 2.4) | 1.9 | 0.1 |
| **XX** (SB, Im) | H | $CH_3$ | 0.0<br>2.052 | 4.6<br>2.804 | –5.4 | –1.4<br>(4.0; 2.0) | –3.4 | 0.1 |
| **XXI** (SB, Im) | F | $CH_3$ | 0.0<br>2.041 | 6.8<br>2.718 | –0.3 | 3.0<br>(3.3; 1.9) | 1.1 | 4.5 |
| **XXII** (SB, BIm) | H | H | 0.0<br>2.065 | 4.9<br>2.765 | –4.4 | –0.7<br>(3.7; 2.5) | –3.2 | –4.6 |
| **XXIII** (SB, BIm) | F | H | 0.0<br>2.051 | 7.5<br>2.683 | 1.3 | 4.4<br>(3.1; 2.6) | 1.8 | 0.1 |
| **XXIV** (SB, BIm) | H | $CH_3$ | 0.0<br>2.067 | 4.2<br>(2.807) | –5.9 | –2.0<br>(3.9; 2.0) | –4.0 | –0.1 |
| **XXV** (SB, BIm) | F | $CH_3$ | 0.0<br>2.051 | 6.6<br>2.702 | –0.4 | 3.0<br>(3.4; 2.0) | 1.0 | 4.8 |

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