
A short note on the magnetic properties of a family of substituted *m*-bisallyl chlorobenzene diradicals viewed as partially ordered set

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Abstract: We investigate twelve distinct *m*-bisallyl diradicals which are chloro-substituted. These diradicals are produced when chlorine atoms successively substitute the replaceable hydrogens of the benzene framework of *m*-bisallyl diradical. The substitution-reaction network diagram, also known as the Hasse diagram, shows the diradicals arranged in various nodes according to the substitution pattern. The Gaussian 09 software is utilized to calculate the HOMO-LUMO gap (ΔE_{H-L}), related magnetic exchange coupling constant values (J), and corresponding abinitio total energies of the twelve chosen molecules in their ground-state. We determine the triplet state geometries and energies of each of the diradical using the unrestricted B3LYP approach with a 6-311++G(d,p) basis set. Keeping the methodology and the basis set unchanged, the J values are determined following the Broken Symmetry formalism developed by Noodleman's group. The computed triplet energies, the J values, and the ΔE_{H-L} values are observed to be partially ordered. With the use of the "poset average" and the "cluster-expansion" approach, all these physical parameters, such as triplet energies, the J values, and the ΔE_{H-L} values, are evaluated methodically. Both approaches yielded results those are consistent with each other and with the results of numerical computations.

Key words: Chlorobenzene; Gaussian; HOMO-LUMO.

1 Introduction

The substitution reaction is a very important tool for synthesizing new chemical compounds. It has been established that a family of chemical compounds can be produced by meticulously monitoring a guided set of substitution reactions. In the domain of "combinatorial chemistry", this guided set is precisely called a substitution reaction network, and a number of studies have been done on this subject [1]. Other than studying a guided set of reactions, these studies have the intention of achieving a systematic idea of the various properties of different molecules placed at different knots of the reaction network having a "precursor-product-type" association. Other than the substitution reaction networks, there are a number of significant ideas contributed by several groups

working in this field. One of the fore-runners, Prof. A. T. Balaban [2], mainly focused on degenerate rearrangement reaction networks. Historically, in 1870, Körner, in his work [3] on the characterization of the structure of benzene, used the idea of a substitution reaction network in an obscure way. However, Körner's concept was never formally expressed in the form of a reaction network. Therefore, the idea found no usefulness until Balaban re-introduced it, though comparatively for degenerate rearrangement networks [2]. For the last few decades, Klein et al. have focused on 'directed' reaction networks [4-14]. Following Klein's method, we have studied a substitution reaction network where the benzene of the diradical *m*-bisallyl benzene has been progressively substituted by chlorine atoms at different

positions without disturbing the previous substitution. It is clearly evident that this represents a general category of guided reactions forming networks which can easily be identified as a *partially ordered set or poset*.

At this point, we briefly discuss the topic of partially ordered sets. A set of elements denoted by \mathcal{P} is said to be partially ordered when there exists a relation “ \ni ”, between two elements $\mu, \nu, \in \mathcal{P}$ which follows the three requirements: (I) Reflexivity, i.e., $\mu \ni \nu$ (every element is related to itself); (II) Antisymmetric, i.e., if $\mu \ni \nu$ and $\nu \ni \mu$, then $\mu = \nu$ (two distinct elements cannot be related in both directions), and (III) the Transitivity, i.e., if $\mu \ni \rho$ and $\rho \ni \nu$, then $\mu \ni \nu$ [15]. For the present work, if a substitution reaction results in the structure ν being obtained from another structure μ , we can state that $\mu \ni \nu$ and consider “ \ni ” to be a partial ordering, which also allows for the trivial “null” reaction.

Beyond the work of Professor Klein’s group, several other research teams have investigated the applicability of partially ordered relationships to various chemical problems. Restrepo et al. employed this theoretical framework to derive a descriptor elucidating the environmental behavior of polluting alkanes in two distinct river systems—one located in a hilly region and the other in a lowland area [16]. Frank et al. proposed a comprehensive ranking methodology capable of exploring the full spectrum of possible descriptor hierarchies to yield total orderings. This procedure was applied to a set of 18 refrigerants—comprising previously used compounds, currently utilized substances, and proposed alternatives—characterized by their ozone depletion potentials, global warming potentials, and atmospheric lifetimes [17]. Interested readers may consult the excellent book edited by Fattore and Brüggemann for additional applications and further developments of this technique across various areas of chemical research [18].

In the present study, we have studied twelve different substituted *m-bisallyl* diradicals (Figure 1) generated from the successive replacement of *ortho- and para-*hydrogens of benzene framework of diradicals by chlorine atoms. In other words, the substituents at the two meta positions (corresponding to the two radical moieties) were fixed, while the ortho and para positions were successively substituted. As discussed earlier, the substituted-diradicals are placed in various nodes of the Hasse-diagram (Figure 2), in accordance with the substitution pattern. Some physical properties, say, triplet energies, the J values and the ΔE_{H-L} values are methodically analyzed by the two well-known methods, namely, ‘poset average’-method and the ‘cluster-expansion’-method.

The novelty of this work is that it establishes a sort of organization in the study of a family of substituted diradicals. It is often observed that researchers working on molecules of physical, chemical, or biological interest tend to select certain members of a molecular family, leaving several others unexplored. Sometimes, the chosen molecules may share similar structural features, yet exhibit significantly different values for the same physical or chemical properties. This makes those molecules mutually incomparable. For a family of molecules generated through systematic substitution of replaceable atoms or groups in a parent molecule, these discrepancies can be explained using the partially ordered relationships discussed in this note. The techniques used in this short note will enable one to generate and investigate the full family of molecules following a typical substitution pattern. The usefulness of these techniques has been discussed by Klein et al. However, their investigations primarily focused on certain physical and chemical properties of a family of molecules within the substitution reaction networks selected by their group. For the first time, we have investigated electronic spin-related properties, such as intramolecular magnetic coupling, using the

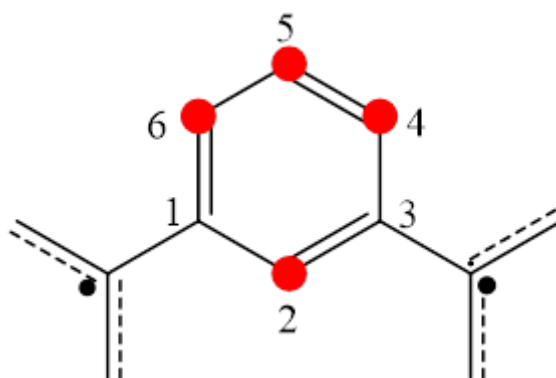


Figure 1: Structure of *m*-bisallyl benzene diradical. All through this work, we have followed the numbering scheme as shown. The substitution positions are marked with red dots.

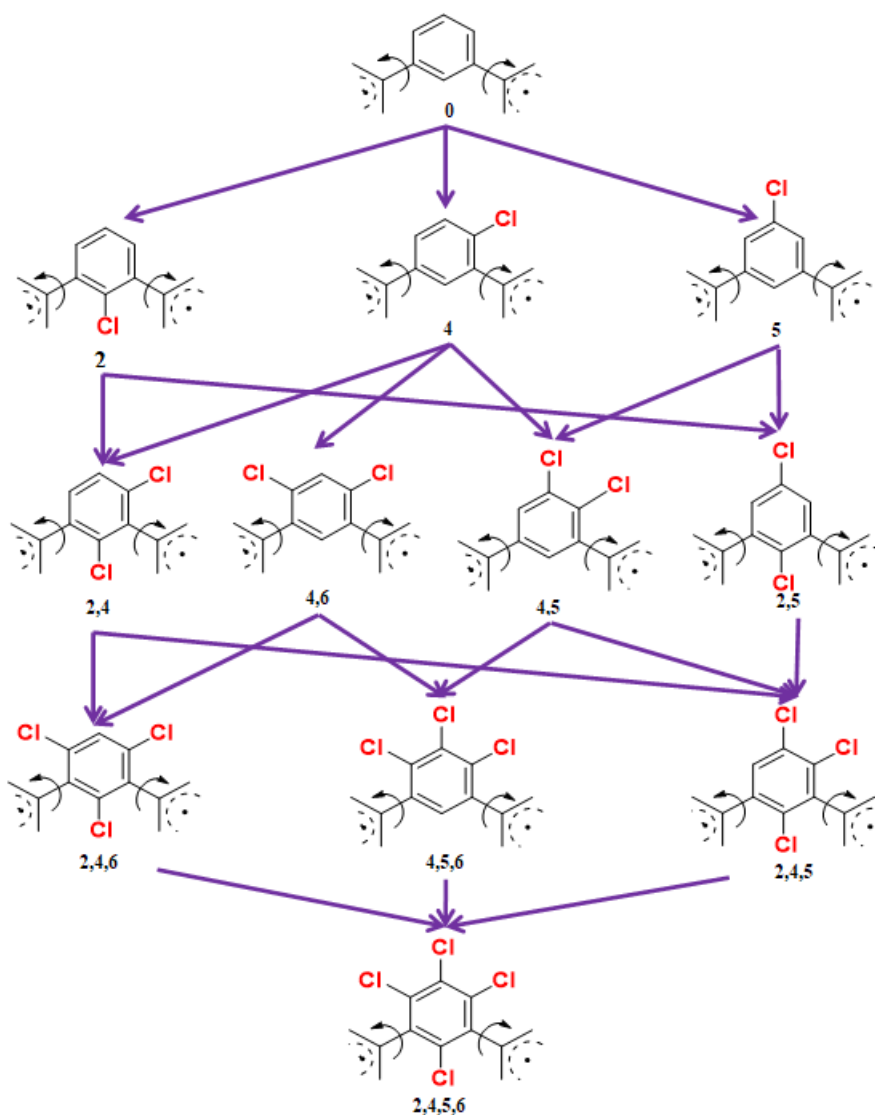


Figure 2: Substitution reaction network of substituted *m*-bisallyl chlorobenzene diradicals.

relevant concepts developed by Klein et al. The methods are discussed in the following sections.

2 Posetic Cluster Expansion

Having gone through the discussion on the partially ordered set in the previous section, one might anticipate that various physical and chemical properties of the members of the partially ordered set might follow a similar trend as decided by the partial ordering of the elements. Klein et al. have provided consistent evidence in support of this theory by addressing various substitution reaction networks [4]. Different approaches can be used to determine the molecular information missing from the poset. In first approach, better known as “poset average method”, the missing property can be interpolated by taking the average the property values of the immediate neighbors of the chosen member which lacks the related property value [4-14]. In another approach which seems to be more general in nature, the missing data can be interpolated by using the method of “cluster-expansion” which originates long before concepts of molecular structure were easily identifiable [19, 20]. In contemporary chemical literature, it is well established that the concept of characterizing molecular attributes can be attained through cluster expansion method in terms of substructures of a chosen structure. The method can be applied for various properties like total energy, HOMO-LUMO gap, heats of formation, etc. [21-23]. In 1964, Gian-Carlo Rota put forward a more generalized idea of the cluster-expansion by systematically

considering the POSETS mostly dealt in mathematics [24]. We explain this concept by taking a property $X(\mu)$, for a member μ of the POSET under discussion. It was established that one can express $X(\mu)$ in terms of another similar “cluster” property $x(\nu)$ for the preceding members of μ , expressed as ν in the relation

$$X(\mu) = \sum_{\nu \triangleright \mu}^{\mathcal{P}} x(\nu) \quad (1)$$

where $x(\nu)$ s are the fitting parameters. In conceptual terms, the number of the parameters $x(\nu)$ s, should match or even surpass the data that needs to be fit. In actuality, however, one looks for more simplifications, such as when the x -value decreases as ν grows to the point where, at big enough values of ν , one can ignore $x(\nu)$. Alternatively, the concept of “Cluster Expansion” in substructural partial ordering can be illustrated using a molecular property X . This property can be systematically decomposed into a primary order expansion by summing the contributions $x(\nu)$ from smaller substructures ν , such as atoms, bonds, functional groups, or even more complex interactions like pairs of neighboring bonds. We write the general cluster expansion in this article as

$$X(\mu) = \sum_{\nu}^{\geq \mu} f(\nu, \mu)x(\nu) \quad (2)$$

where $X(\mu)$ is the chosen molecular property X for structure μ , and $f(\nu, \mu)$ is the count of ways in which the spatial configurations of ν spans the substructures in a configuration $C \in \mu$. In the instance at hand, the expansions manifest as

$$\begin{aligned}
X(0) &= x(0) \\
X(2) &= x(0) + x(2); X(4) = x(0) + x(4); X(5) = x(0) + x(5) \\
X(2, 4) &= x(0) + x(2) + x(4) + x(2, 4); X(4, 6) = x(0) + 2x(4) + x(4, 6) \\
X(4, 5) &= x(0) + x(4) + x(5) + x(4, 5); X(2, 5) = x(0) + x(2) + x(5) + x(2, 5) \\
X(2, 4, 6) &= x(0) + x(2) + 2x(4) + 2x(2, 4) + x(4, 6) + x(2, 4, 6) \\
X(4, 5, 6) &= x(0) + 2x(4) + x(5) + x(4, 5) + x(4, 6) + x(4, 5, 6) \\
X(2, 4, 5) &= x(0) + x(2) + x(4) + x(5) + x(2, 5) + x(4, 5) + x(2, 4) + x(2, 4, 5) \\
X(2, 4, 5, 6) &= x(0) + x(2) + 2x(4) + x(5) + 2x(2, 4) + x(4, 6) + 2x(4, 5) + x(2, 5) + \\
&x(2, 4, 6) + x(4, 5, 6) + 2x(2, 4, 5) + x(2, 4, 5, 6)
\end{aligned} \tag{3}$$

where we label the $X(\mu)$ and $x(\nu)$ by the sites where the substitutable -H atom of the coupler ring has substituted for -Cl (considering equivalencies mediated by symmetry, such as $X(2, 4) = X(2, 6)$ and $x(2, 4) = x(2, 6)$). In a way, this is similar to the conventional sub-structural cluster expansion.

One can take the triplet energy and magnetic exchange coupling constant value (J) as the reckonable scalar properties of structure (X) and further illustrate the cluster expansion method. In this context, $x(0)$

refers to the energy of the unsubstituted diradical, $x(m)$ represents the energy when a substitution occurs at position m (as illustrated in Figure 1), $x(m, n)$ accounts for the additional interaction energy between sites m and n , and $x(m, n, l)$ captures the higher-order interaction among three sites, and so on. We hypothesize that energies of interactions decrease with the number of sites, maybe to the point where higher-order interactions are ignored.

It is possible to methodically flip the cluster expansion equation as

$$\begin{aligned}
x(0) &= X(0) \\
x(2) &= X(2) - X(0); x(4) = X(4) - X(0); x(5) = X(5) - X(0) \\
x(2, 4) &= X(2, 4) - X(2) - X(4) + X(0) \\
x(4, 6) &= X(4, 6) - 2X(4) + X(0) \\
x(4, 5) &= X(4, 5) - X(4) - X(5) + X(0) \\
x(2, 5) &= X(2, 5) - X(2) - X(5) + X(0) \\
&\dots
\end{aligned} \tag{4}$$

By applying these relationships, it is possible to estimate the more highly substituted X -values by referencing the x -values obtained from the less substituted parent X -values, neglecting the x -terms of greater-order therein. Alternatively, all X -values can be expressed in terms of x , and the interaction terms can then be fitted using a least-squares approach across all possible X -values. These equations serve as a tool for estimating the physical properties.

It is important to note that the proposed cluster expansion method differs

slightly from previously reported approaches [11,25-29], particularly in the way it processes substructures derived from molecular graphs. The emphasis here is on the global posetic structure, rather than solely on the local nature of the μ substructures represented in $x(\mu)$. Furthermore, a least-square fitting is used in a lot of these older works, but we also consider the posetic inversion here. Moreover, our strategy bears some resemblance to the "linear-free energy" approach suggested by Hammett [30] and Taft [31]. However,

their approach emphasizes the variation of substituents within a given substitution pattern, rather than examining a fixed substituent across fluctuating substitution patterns.

3 Implementation of Cluster-Expansion Method

A short discussion on the theory of magnetic interactions in organic diradicals is due here. In the last three decades, a significant amount of practical and theoretical work have been done in the field of molecular magnetism. Interested readers may follow the excellent book by Datta et al. [32] as well as other review articles [33-37] and the references therein for more details. The Heisenberg spin Hamiltonian [38] is frequently employed to describe the magnetic exchange interaction between two magnetic centres, labelled 1 and 2:

$$\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2 \quad (5)$$

where \hat{S}_1 and \hat{S}_2 represent the operators associated with spin angular momentum for the respective sites, and J is the extent of coupling between the sites termed as exchange coupling constant. A positive J value indicates that the high-spin configuration is energetically favored, characterizing the interaction as ferromagnetic. On the other hand, when the ground state is a low-spin state and antiferromagnetic interaction is represented by a negative value of J . For a diradical with one unpaired electron at each radical center, J can be written as

$$E_{(S=1)} - E_{(S=0)} = -2J. \quad (6)$$

The magnetic exchange coupling constant (J) associated with each diradicals can be estimated by adopting Noodleman's Broken Symmetry (BS) method [39-42]. This method involves utilizing both the spin-polarized triplet state derived from unrestricted formalism ($\langle S^2 \rangle = 2$ for a diradical) and a broken-symmetry (BS) solu-

tion. As Noodleman explained, when the magnetic orbitals — the singly occupied orbitals of two spin-bearing monomers — interact through overlap during the self-consistent field procedure, a state with mixed spin symmetry and reduced spatial symmetry emerges. This is known as the mixed-spin or broken-symmetry (BS) state. The BS state itself is not a true eigenstate of the spin operator and exhibits an $\langle S^2 \rangle$ expectation value of 1 for a diradical, representing an equal combination of singlet and triplet states. Pure spin states can subsequently be recovered from the BS state using a projection operator method proposed by Yamaguchi et al. [43-45] Thus, one can estimate the J values are using the well-known Yamaguchi formula

$$J_Y^{DFT} = \frac{(E_{BS}^{DFT} - E_{HS}^{DFT})}{(\langle S^2 \rangle_{HS} - \langle S^2 \rangle_{BS})} \quad (7)$$

where, E_{BS} and $\langle S^2 \rangle_{BS}$ denote the energy and the average spin-squared value for the broken-symmetry (BS) state, while E_{HS} and $\langle S^2 \rangle_{HS}$ represent those corresponding to the high-spin (HS) triplet state. It should be noted that the optimized triplet geometries of the diradicals were used to determine the BS energies, assuming that the BS states retain geometries similar to those of the triplet states.

In this study, we utilize the cluster expansion approach to determine the ground-state triplet energies of *m-bisallyl* chlorobenzene diradicals. The total energies are computed using the unrestricted B3LYP methodology combined with the 6-311+G* basis set, as it is used in the Gaussian 09 program package [46]. The energies of the triplet states of each diradicals are reported in Table 1, with all values benchmarked against the energies of unsubstituted diradicals, using $X(\mu) \equiv X_{cal}(\mu) - X_{cal}(0)$. Our cluster expansion model focuses on predicting X values for n-chloro-substituted isomers, excluding higher-order terms beyond $x(2) \equiv \alpha_1, x(4) \equiv \alpha_2, x(5) \equiv \alpha_3, x(2, 4) \equiv \beta_1, x(2, 5) \equiv \beta_2, x(4, 5) \equiv \beta_3$, and $x(4, 6) \equiv \beta_4$. Here, α and β repre-

sent simplified notations for the x parameters, with their typical values related to various properties listed in Table 2.

4 The ‘Poset Average Method’

In addition to the cluster expansion approach, different poset-attentive schemes can be utilized to effectively anticipate posetic qualities. In the “poset-average” method [6] any X value can be calculated by averaging the means of its previous and succeeding values. In other words, the mean value of the compounds ν' that are directly leading to μ in the network is taken first, subsequently the average of the compounds ν'' that are directly following μ is considered. These two mean values are then averaged. In other words, one estimates $X(\mu)$ for a structure inside the Hasse diagram as

$$X(\mu) \equiv \bar{X}(\mu) = \{\bar{X}(\nu') + \bar{X}(\nu'')\}/2. \quad (8)$$

Here, $\bar{X}(\nu')$ represents the average X values of isomers directly placed before μ in the Hasse diagram, while $\bar{X}(\nu'')$ denotes the mean of property values arising from the structures immediately succeeding μ . While this approach is conceptually simple, its practicality is limited by the need to know all attributes of the closest members of the substance being interpolated—information that is often unavailable, particularly for substances located at the top or bottom of the reaction-network poset. When data is lacking from the poset inner point, this method can be useful. No information about the inner part of the poset is lacking in this present example of the diradical coupler with chlorine substitution. By comparing the neighbor-predicted $\bar{E}_T(\xi)$ values to the real $E_T(\xi)$ values we can determine the significance of poset-average method simply by looking at the good agreement between the two. See Table 1.

Table 1: Calculated energies and magnetic exchange coupling constants (J) of the chosen diradical systems in UB3LYP/6-311++G(d,p) level of theory. Triplet energies and J values, obtained from cluster expansion method and poset-average method, are also reported.

Structure	E_{BS} (a.u.) $\langle S^2 \rangle$	E_T (a.u.) $\langle S^2 \rangle$	E_T (a.u.) Poset Average	E_T (a.u.) Inversion	$J(cm^{-1})$ Calc.	$J(cm^{-1})$ Poset Average	$J(cm^{-1})$ Inversion
D(0)	-464.5041415 (1.060281)	-464.5041903 (2.062493)		-464.5041903	10.687		10.687
D(2)	-924.1182771 (1.058415)	-924.1182653 (2.059017)	-924.1213729	-924.1182653	-2.588	4.773	-2.588
D(4)	-924.123105 (1.060025)	-924.1231353 (2.061204)	-924.1217273	-924.1231353	6.642	6.403	6.642
D (5)	-924.1268890 (1.060617)	-924.1269361 (2.062795)	-924.1221568	-924.1269361	10.315	6.670	10.315
D (2,4)	-1383.7371258 (1.059498)	-1383.7371221 (2.059606)	-1383.737455	-1383.73721	-0.812	-0.512	-6.633
D (4,6)	-1383.7404110 (1.058056)	-1383.7404128 (2.058233)	-1383.738293	-1383.74208	0.395	2.536	2.598
D (4,5)	-1383.7402268 (1.060021)	-1383.7402577 (2.060969)	-1383.738922	-1383.745881	6.775	3.542	6.270
D (2,5)	-1383.7399956 (1.058334)	-1383.7399889 (2.058359)	-1383.738083	-1383.741011	-1.470	0.494	-2.960
D (2,4,6)	-1843.3548669 (1.060173)	-1843.3548522 (2.060134)	-1843.352225	-1843.356155	-3.226	-2.332	-10.677
D (4,5,6)	-1843.3520499 (1.058325)	-1843.3520503 (2.058447)	-1843.353009	-1843.364826	0.0878	-0.435	2.226
D (2,4,5)	-1843.3535784 (1.059388)	-1843.3535653 (2.059363)	-1843.352403	-1843.359956	-2.875	-1.479	-7.005
D (2,4,5,6)	-2302.9657026 (1.060462)	-2302.9656823 (2.060362)		-2302.978901	-4.456		-11.049

Table 2: Parameters obtained using cluster expansion method obtained for triplet energy and magnetic exchange coupling constant values.

	$x(2) \equiv \alpha_1$	$x(4) \equiv \alpha_2$	$x(5) \equiv \alpha_3$	$x(2,4) \equiv \beta_1$	$x(2,5) \equiv \beta_2$	$x(4,5) \equiv \beta_3$	$x(4,6) \equiv \beta_4$
E_T (in a.u.)	-459.614075	-459.614075	-459.618945	0.000088	0.001022	0.005623	0.001668
J ($in\text{cm}^{-1}$)	-13.274966	-4.044473	-0.371934	5.820747	-2.202793	0.505026	1.489733

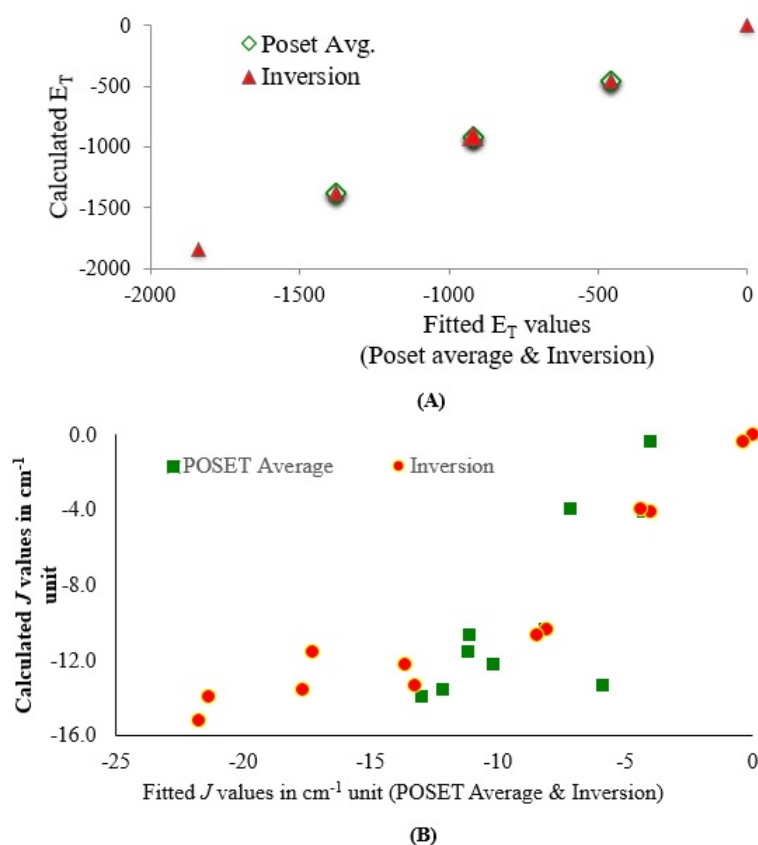


Figure 3: Plots of calculated (a) triplet energy and (b) J values (obtained using quantum chemical calculations of diradicals) versus estimated values using Poset Average Method and Cluster Expansion Method.

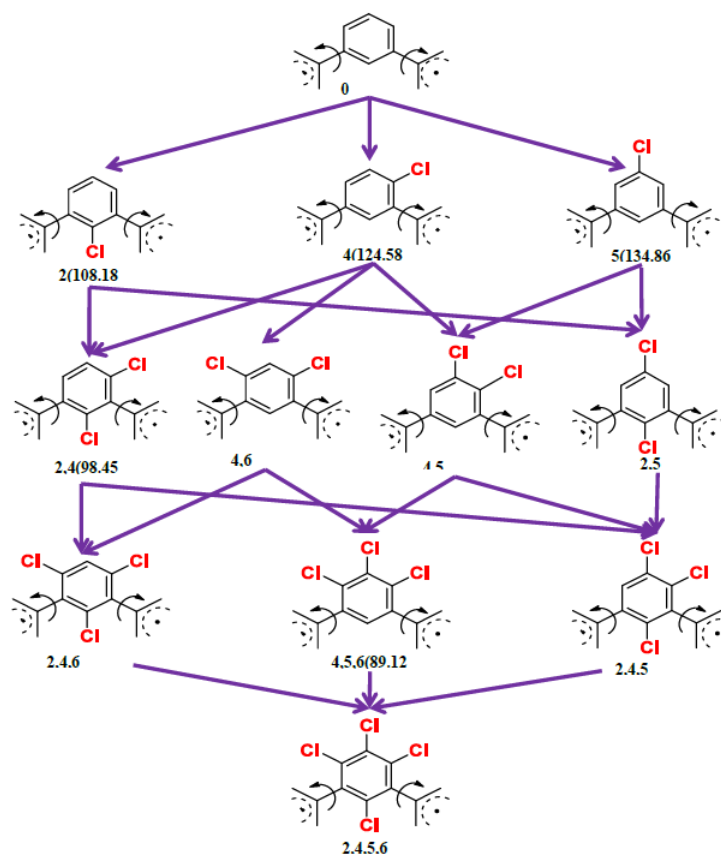


Figure 4: Hasse diagram based on the Substitution reaction network of substituted *m*-bisallyl chlorobenzene diradicals. The figures in the parenthesis shows the dihedral angles made by the plane of the radical moieties with the plane of the coupler as shown with the help of arrows.

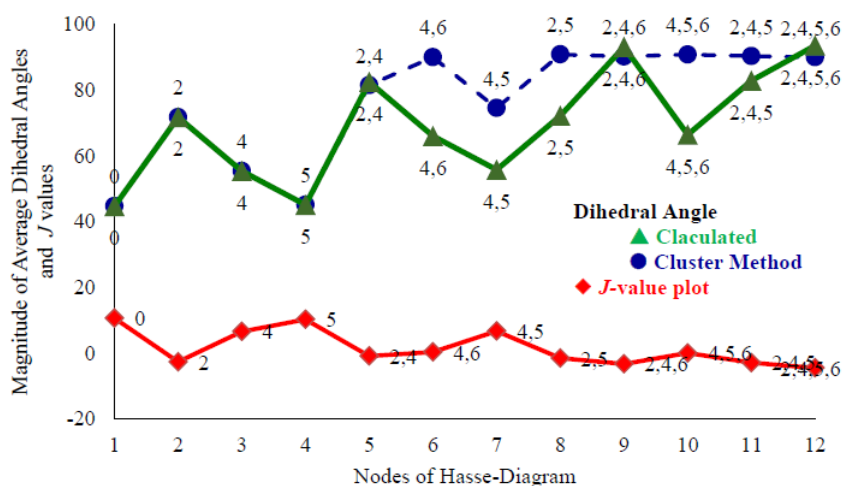


Figure 5: Comparison plot of J values with the average Dihedral angles obtained from Gaussian 09 calculations (▲, in green) and that obtained from the cluster expansion method (●, in blue) for different modes of Hasse diagram as shown in figure.

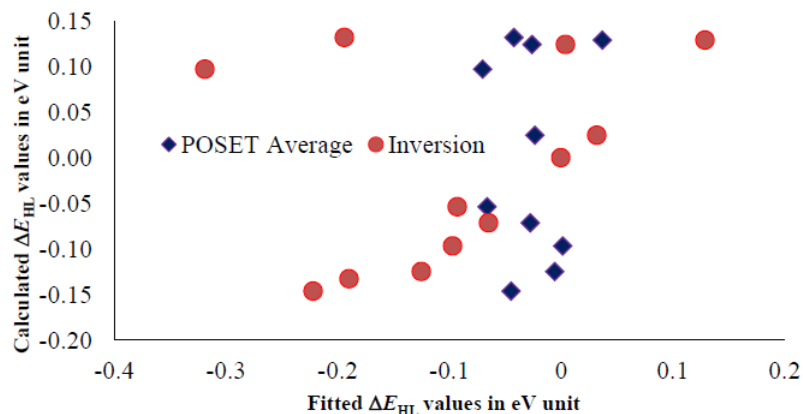


Figure 6: Plots of calculated ΔE_{HL} values (obtained using quantum chemical calculations of diradicals) versus estimated ΔE_{HL} values obtained using Poset Average Method and Cluster Expansion Method.

The fact that these two fits in Table 1 (and the ensuing parameters from Eqn. (8), displayed in Table 2), are so similar shows that the outcomes from either strategy are quite satisfactory. The E_T data also clearly shows that, for varying β values, the strength of pair-wise interactions generally diminishes as the distance between the corresponding pair of sites increases. The triplet energies, estimated using the POSET average method and inversion method, match very well with each other (correlation coefficient, $r \cong 1$). The effectiveness of these two methods can also be shown by comparing the results in a graphical way, as shown in Figure 3(A). However, the magnetic exchange coupling constant values (J) obtained either from the POSET average method (correlation coefficient, $r = 0.77$) or from the inversion method (correlation coefficient, $r = 0.93$) do not correspond very well. See Figure 3(B). In search of the cause of this problem, we have investigated the role of the dihedral angle made by the plane of radical moieties with the plane of the couplers. In Figure 4, we construct the Hasse diagram exhibiting the average dihedral angles made by the two radical moieties with the plane of the coupler. As expected, one can easily observe that the magnetic exchange coupling constant values of all the diradicals maintain a negative corre-

lation ($r = -0.88$) with the calculated dihedral angles [47,48]. However, the dihedral angles obtained from the cluster expansion method maintain a better correlation ($r = -0.93$) with the J values compared to the dihedral angles obtained from Gaussian calculations. This can be evident from the pictorial description given in Figure 5. This shows that the J value not only depends on the structure of the species concerned but also on the corresponding structures of its parents and daughters situated at the nodes of the Hasse diagram. However, this statement should be verified with more theoretical insight in the future for generalization.

A similar kind of analysis was done, taking ΔE_{HL} as the scalar property X . We perform single-point energy calculations for each of the 12 species in their closed shell singlet form using the restricted B3LYP methodology and the 6-311++g(d,p) basis set. The results were analyzed to obtain the HOMO-LUMO gap (ΔE_{HL}). However, we ended up having a not-so-good correlation between the calculated ΔE_{HL} and those obtained from either the POSET average method ($r = 0.12$) or the cluster average method ($r = 0.56$). See Figure 6. The cause of this poor correlation may be the choice of methodology and a multi-determinant approach may improve the correlation, which is left for future work.

A justification for relying heavily on computational data is necessary here. The current study encounters a significant challenge because of the dearth of reliable information for the molecules in question. This lack of data is caused by certain poset members that are either extremely unstable or have not yet been synthesized. As a result, the datasets for different aspects of these structures are still lacking.

5 Conclusion

Given the broad and fundamental nature of the concepts discussed and applied here, this discussion can extend beyond the specific system we have chosen.

Partial order theory is useful in chemistry for two main tasks: ranking substances and predicting their properties. In ranking, objects are arranged by relations like “more poisonous than” or “more reactive than”, producing a poset that often contains many pairs that can't be ordered. On extending the theory discussed here, one may end up in setting up any subjective biasfree ordering from a given poset [15]. The second application uses chemical relations such as “can be obtained from” to build posets of structurally related molecules (e.g., substituted benzenes) and then predict properties using poset-average, and cluster-expansion methods. The methods discussed in this work are so powerful that they can even be used to estimate the cooperative free energies of hemoglobins across different oxygenation states [15].

Essentially, the progressive reaction poset model can be thought of as being based on the idea of a periodic table. Mendeleev's table of elements is an excellent illustration of this type of periodic table. Specifically, chains in the poset are analogous to the connections seen within columns of Mendeleev's table, including the relationships between elements in an A-column and those in the corresponding B-column one row below. Although nuclear reactions between elements in the periodic table are largely theoretical, the chemical properties

of elements exhibit a distinct partial ordering [50–53]. Consequently, the principles and methods developed within the framework of our substitution reaction posets may have far-reaching applications.

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