Quantifying Aromaticity in 4c-2e bonded species.

Chapter 3
Chapter 3(a)

Probing the aromaticity of 4c-2e bond in the paradigmatic cases of TCNE$_2$ ($^{2-}$) and Ni$_2$S$_4$ intermediates.

ABSTRACT: The dimer of TCNE($^{(-1)}$) is a paradigmatic case of 4c-2e bond. Since its first discovery the aromatic nature of 4c-2e bonds has been speculated to be aromatic. We for the first time carry out detailed investigation of this case of 4c-2e bond using NICS and MICD techniques to establish the presence of aromaticity and delocalized bond. We further proceed to establish a new case of 4c-2e bond in a dimer of Nickel Supersulfido complex and probe the 4c-2e bond involving the S$_4$ moiety using MICD and NICS techniques.
3(a).1 Introduction

4c-2e bonded intermediate is a rare chemical bonding motif. Very few instances of this unique bonding situation have come to the fore. The dimer of TCNE\textsuperscript{(1)} is considered to be the paradigmatic case for 4c 2e bonding where the two monomeric units of TCNE\textsuperscript{(1)} are held by exceptionally long C-C bonds. The presence of unusual long bonds in the dimeric species was predicted by Novoa and co-workers through the spectroscopic techniques (IR and UV/VIS), structural and magnetic characterization (1). Their theoretical studies using DFT and MCSCF confirmed the presence of this unusual bonding. This particular dimer has attracted significant amount of attention and have led to a host of theoretical studies.(2) The works by Head-Gordon and co-workers have revealed that dynamical correlation plays a pivotal role in the description of 4c-2e bond of TCNE\textsubscript{2(2-)}.(3) Their study also found the wavefunction of TCNE\textsubscript{2(2-)} to be a mixture of 76\% closed shell character along with a 24\% biradical nature and hence deciphering the bond order of the 4c-2e bond to be 0.74. Lu\textsuperscript{-} and co-workers showed that the C-C long range bond involved in TCNE\textsubscript{2(2-)} remains invariant when different counter cations are involved.(4) This provides the crucial information, regarding the nature of the bond, that the formation of 4c-2e bond is the inherent feature of dimer dianion, as long as the Coulombic repulsion between the monomeric units are removed. Since then other cases of four center two electron bond have been shown to exist, like dimer of TTF\textsuperscript{+} and organo-borane compounds, and all and most of them exhibit long range bonds.[5] One of the unique attributes that has been speculated for a four center two electron bond has been the aromatic stabilization of moiety involved in the formation of the 4c-2e bond. Though the role of aromaticity
has been implicated in conferring stability to the TCNE dimer and analogous species, no detailed theoretical work exist and this aspect is not established as of yet.

We in this chapter discuss two cases of four centre two electron bond where aromaticity has been investigated and established on the basis of traditionally used NICS (6) and the state of the art MICD computation (7). In the first case A) we study and establish the aromaticity of the most well-known case of 4c-2e bond i.e. TCNE$_2^{2-}$ and thus it form a primer for associating aromatic stabilization to the formation of 4c-2e bonds despite the presence of long bond bonds. In the second case B) which we discuss below we establish 4c-2e bond between two super-sulfido units stabilised by Ni$_2$+ complex and also show there the presence of aromaticity among the four S atoms. This work forms a prelude to the existence of 4c-2e bonded intermediate in oxidation reaction, which we have unearthed for the two electron oxidation of hydrazine, and there too we have shown yet once more the presence of aromaticity in 4c-2e bonded structure. This section has been discussed in details in the next chapter.

3(a).2 Results and Discussion

A) Aromatic of four center two electron bond in dimer of TCNE $^{(1-)}$

The bonding between the monomeric unit of TCNE$_2^{2-}$ has been found to be four center two electron bonds. We herein investigate the aromaticity of the 4c-2e bond present in TCNE$_2^{2-}$. NICS computations were carried out at different points surrounding the four membered ring involved in the 4c-2e bond formation using B3LYP functional within Density Functional Theory along with 6-31++G(d,p) basis set. From the center of mass which essential is the geometrical center of the four membered ring we scan the NICS$_{iso}$ value along the three axes as shown in Figure 1.
Our computations reveal that heavily deshielded regions exist specifically for the regions around the location of the four center bond and also at the center of the four-membered ring involved in the formation of 4c-2e nbond. These heavily significantly deshielded regions are consistent with the presence of aromaticity (see Figure 1).

Figure 1: Plots of NICS scan along various axes. The inset figure shows the reference frame for the axes.

To further establish the fact that indeed if magnetically induced currents exist around the 4c-2e bond we carried out the state-of-the-art MICD computations which not only gives a very good estimation of aromaticity by actually integrating the induced current density but also gives the current density plots and hence is also a proof for existence of delocalized bond over the four centers. The MICD computations were performed with the B3LYP functional and 6-31+g* basis set. The current density integration was done across a plane dissecting the C-C long bonds involved in 4c-2e
bond. The integration value came up to be 12 nA/T, which is considered to be aromatic based on previous computations which standardized nonaromatic species to have integration value less than 4 nA/T and aromatic benzene to have the integration value of approximately 23 nA/T. The plot of the magnetically induced current density shows streamline currents flowing across all the four centers involved in the bond formation and hence provides further evidence for the existence of delocalized bond over the four centers (see Figure 2).

Figure 2: MICD plot for dimer TCNE\textsuperscript{(1)} is plotted 1 a₀ above (+Z) the molecular plane of four membered ring. The dimensions of the plot are 6 × 6 a₀. The magnetic field dipole vector is directed toward the reader. The vector arrow color intensity is proportional to the norm of the current density vector. The dimensions of the plot are 6 × 6 a₀.
B. Aromaticity of Four Sulfur two electron bond:

Driess and co-workers have recently isolated the first instance of “side-on” supersulfidonickel (II) complex, which exhibit a TCNE dimer like bonding motif.[8] The \( \text{S}_2^2^- \) supersulfido moiety being an elusive entity have solely been detected on the basis of spectroscopic studies.[8] Through complexation reaction only a few “end on” supersulfido complexes have been isolated and no instance of “side on” supersulfido complex are known to exist, prior to the work by Driess and co-workers. When \([\text{[LNi}_2(\text{toluene})] \) (L-, CH\{CMe(2,6-iPr_2C_6H_3)N}\}_2^-) was treated with elemental sulphur, one electron oxidation occurred and the supersulfidonickel homologue 1 was generated. The supersulfidonickel complex 1 with the “side-on” \( \text{S}_2^- \) ligand when crystalized at -60°C, brown crystals were precipitated which upon investigation with X crystallographic techniques revealed dimer formation.[8] The supersulfidonickel complex being doublet radicals had dimerized to form singlet species. The geometry was revealed by X ray crystallographic techniques reveal dimerization via very long S-S bonds between the monomeric supersulfido nickel units. The S-S bonds lengths were found to be around 2.77 Å, and is significantly elongated with respect S-S single bond lengths i.e. 2.03 Å as present in analogous moieties. However the bond lengths were also too short to be considered as S-S van der Waals bonds which are typically around 3.6 Å. The association and bonding interaction warrants thorough investigation by quantum chemical computations. The source of stabilisation gained by the formation of long range S-S bonds upon dimerization also requires significant attention.
Computational Details.

All gas-phase intermediates and transition-state structures are optimised using the B3LYP hybrid density functional and employing 6-31++g** basis functions on \( \text{CHN}\) S P atoms and LANL2 pseudo potential on Ni atom and LANL2DZ basis for valence shell of Ni in GAUSSIAN09 package. The system was modelled using a truncated ligand wherein the side chain have been terminated by H atoms, to save the computational cost. The intermediates are characterized by the presence of all real frequencies and transition states by single imaginary frequency and all real frequencies for the rest of the modes.

Results and Discussion.

The dimer was found to be stabilized by 12.6 kcal/mol\(^{-1}\) by free energy. Hence the dimer was found to be stable at the low temperature of -60 \(^\circ\)C and hence could be isolated via crystallization. When the dissociation of the dimer into monomeric unit was done using NEVPT2 \([9]\) technique (to account for the multireference nature of the system at dissociation), we observed a distinct minima at 2.8 Å S-S bond length. This is consistent with similar studies carried on other instances of 4c-2e bond.\([1]\) To investigate the nature of this magnitude of stabilization we resorted to inspection of the molecular orbitals of the dimer. The dimer was found to be formed upon bonding between the \( \pi^* \) orbitals of the monomeric units (see Figure 3).
Figure 3: a) Optimized geometry of the dimer depicting the long range S-S bonds present in the S4 unit. b) The SOMO of the monomeric unit. c) The NEVPT2 plot for the dimerization process i.e. along S-S bond distance using a (4,4) active space.
Figure 4: The relevant molecular orbitals for bonding between the four S atoms of the dimer. All the MOs clearly show the presence of 4c-2e bond.
The inspection of the frontier molecular orbitals clearly showed the formation of 4c-2e electron bond as we have discussed in the previous chapter (see Figure 4). As the aromaticity of 4c-2e species have been implicated by earlier studies and found by our own computations we were inclined towards investigation of the $S_4$ unit stabilized by Ni2+ cations. The investigation was initiated using NICS technique which has been the most popular method of choice for studying aromaticity. NICS computations were performed at various points around the $S_4$ moiety and S-S bonds and plotted.

Figure 5: Plots of NICS scan along various axes. The inset figure shows the reference frame for the axes.

The plot of NICS $zz$ value across the various axis (as shown in Figure 5) clearly depicts the presence of heavily deshielded zones, and it particularly maximum (shows the least values) around the vicinity of the S-S bonds.
The dimerization of the Ni complex and hence the formation \( S_4 \) unit having elongated S-S bonds has been indicated by NICS studies to be stabilised by the presence of aromaticity. To corroborate the role of aromaticity and further investigate the delocalised nature of the bond, we carried out state of the art MICD computations using B3LYP functional to get a visual representation of the magnetically induced currents, which are typical of aromatic systems along with the strength of the induced ring currents. The computation was performed by selecting a plane for integration of the magnetically induced ring current. The plane was selected to be placed across the S-S long bonds so as to properly gauge the amount of current flowing between the two monomeric units and hence shed light upon the strength of interaction (see Figure 6).

The MICD computation gives induced current integration value of 22.5 nA/T across the S-S long distance bonds connecting the monomeric unit and 21.2 across the S-S short bonds of the monomeric unit. To give a perspective to the aforementioned integration value, we computed similar MICD computation on benzene, which is a hallmark molecule for aromaticity, and the value turned out to be around 23 nA/T. The presence of this high value of magnetically induced ring current clearly indicates towards the presence of high aromatic stabilisation. Benzene being symmetrical gives the same value across each of the six bonds, whereas our present case gives a different value across the two different integration planes, owing to the absence of such symmetry. Nevertheless both the value correspond with presence of clockwise ring currents and is significantly aromatic.
Upon inspection of the induced current density plot we found streamline clockwise currents flowing across all the S atoms of S₄ moiety, similar to the one that we found in the case of oxidation of hydrazine (see Figure 7 and Figure 1). This indicates to the presence of delocalised bonds among the four S atoms and is in excellent agreement with the data obtained from the NICS computations.
Figure 7 a) MICD plot for Ni dimer in plotted in the molecular plane of $S_4$. The dimensions of the plot are $6 \times 6 \, \text{a}_0$. The magnetic field dipole vector is directed toward the reader. The vector arrow color intensity is proportional to the norm of the current density vector b)
MICD plot for Ni dimer in plotted 1 a0 above (+Z) the molecular plane of S4. The dimensions of the plot are 6 × 6 a0. The magnetic field dipole vector is directed toward the reader. The vector arrow color intensity is proportional to the norm of the current density vector

Conclusion

Here in this we have inspected the presence of inspected the presence of 4c-2e bond in a dimer of “side on” supersulfido nickel complex. The formation of dimerization has been found to brought on by two long S-S bond distances, which are very characteristic of 4c-2e bonds. The aromatic stabilisation and presence delocalised bond has been thoroughly investigated using NICS and MICD techniques. We have for the first time established the link between aromatic stabilisation for 4c-2e bond by NICS and MICD computation.

Reference


Chapter 3(b)

The curious case of oxidation of hydrazine: electron loss through an aromatic 4c-2e intermediate

ABSTRACT: Oxidation by triplet dioxygen has a vast variation as far as mechanistic intricacies are concerned. The chapter deals with a previously unknown paradigm of $O_2$ activation/oxidation reaction which propagates through a 4 center 2 electron (4c-2e) bound intermediate. Static DFT and ab initio quantum chemical techniques have been used to unravel the mechanistic details of the oxidation reaction of hydrazine and its methylated analogues, which proceeds via formation of an unconventional 4c-2e bonded species along the route to oxidation products. The events of formation of the 4c-2e species in aqueous phase for hydrazine and its congeners have been captured using ab-intio molecular dynamics simulation. The aromaticity for these 4c-2e bonded intermediates have been thoroughly investigated using NICS and MICD techniques.
3(b).1 Introduction
Degradation of aqueous solution of hydrazine is known to occur, for ages, due to the aerial oxidation by atmospheric oxygen. This phenomenon has warranted laboratory chemists to store hydrazine in refrigerators under cold condition in air tight sealed bottles. The oxidation of hydrazine by molecular dioxygen \( \text{O}_2 \) has been used for quite some time now as a principal ingredient for reduction of olefins and alkynes. This recipe for reduction is based on the simple fact that aerial oxidation of hydrazine by \( \text{O}_2 \) is known to produce diazene, \( (\text{N}_2\text{H}_4 + \text{O}_2 \rightarrow \text{N}_2\text{H}_2 + \text{H}_2\text{O}_2) \) in both cis and trans form, with the cis isomer serving as a perfect selective reductant.[1] Traditionally, addition of transition metal based salts of copper and iron and organocatalysts have been employed to enhance the rates of the reaction so as to facilitate the production of cis diimide, so as to fasten the overall reduction procedure.[2] However, continuous flow apparatus experiments conducted by Kappe and co-workers have achieved appreciable rate of reduction without any use of transition metal catalyst or any organocatalyst.[3] The aerial oxidation of hydrazine by \( \text{O}_2 \) has picked up by researchers since 1907 and have been extensively studied for its thermodynamics and kinetics including catalytic oxidations that we discussed earlier.[4] The intricacies of aerial oxidation of hydrazine not only is of primal interest to basic chemistry, it holds special implications in dioxygen activation reactions which has gained lot of recent interest.[5] Despite the fact that aerial oxidation of hydrazine at a glance presents itself with an unnatural simplicity the detailed mechanistic pathway is yet to be deciphered. The fact that hydrazine has singlet ground state and oxygen a triplet ground state, poses the major haunch to the simplicity of dioxygen activation by hydrazine. The reaction starts with singlet hydrazine and triplet oxygen hence having an overall
triplet reactant, producing all singlet products like H₂O₂, H₂O, N₂ and N₂H₂, thus suggesting the reaction to be spin forbidden. Spin forbidden reactions have traditionally been mostly reported for systems involving transition metals which by the virtue of their high atomic number facilitates spin forbidden reactions by having a significant magnitude of spin orbit coupling.[6] These reactions are of fundamental importance to chemistry and has been extensively studied both experimentally and theoretically.[6]

The dimethyl congeners of hydrazine though undergoes similar aerial oxidation as hydrazine, with the oxidation being kinetically and thermodynamically more facile, the product distribution is notably different from the hydrazine oxidation case. 1,2-dimethyl hydrazine (SDMH), which has been attributed as a carcinogen, owes it toxicity dimethyl azide formed upon aerial oxidation.[7] Similarly unsymmetrical 1,1 dimethyl hydrazine or UDMH undergoes oxidization by aerial oxygen to N-nitrosodimethylamine (NDMA), and is of major concern as NDMA itself is potent carcinogen and a major water pollutant.[8] Despite all these, and experimental efforts a detailed knowledge of the mechanistic route for the aerial oxidation of hydrazine and dimethyl congeners remain unknown. In this chapter we try to unravel the mechanistic footprints of the aforementioned oxidation reactions using state of the art quantum chemical and ab-initio molecular dynamics. In the process of unraveling the mechanistic details of the aerial oxidation of hydrazine and its dimethyl congeners we have found out that the reaction proceeds through a four centered two electron bonded intermediate (4c-2e bonded). Earlier instances of 4c-2e bonded species have been found to be present in species like Tetracyanoethylene anion dimer [(TCNE)₂⁻].
Tetrathiafulvalene cation dimer \([(TTF)^{2+}]\), Boranes and Carboranes and several others.[9-12] The dimer of TCNE\(^{(-)}\) anion radical along with other cases which forms via 4c-2e bonding has been isolated experimentally.[11,12] The bonding of these species have also been extensively studied theoretically and the existence of 4c-2e bond have proven on sound quantum chemical grounds. The observation of exact event of formation an intermediate holds its own specialty and no theoretical study capturing the event of formation of such a 4c-2e species has ever been reported. In this chapter, we also capture for the first time, using \textit{ab-initio} molecular dynamics, the exact event for formation of such a 4c-2e bonded intermediate. We also have conducted the detailed dynamical study of the 4c-2e bonded species in solvent phase which not only gives an insight to the structural parameters of the intermediates, but also extensively highlights towards its stability and reactivity in solvent phase. To summarize the chapter deals with a detailed theoretical perspective on the mechanistic pathways of oxidation of hydrazine and its dimethyl congeners by \(O_2\) on using static and dynamic quantum chemical.

3(b).2 Computational Methods:

3(b).2.1 Static Quantum Computational Details: Geometries of all intermediates and transition states were obtained by full geometry optimization using \(\omega B97x-D\) functional and 6-311++G(d,p) basis set for hydrazine. 6-31++G(d,p) basis set was used for the methylated congeners. All geometry optimizations were done in solvent phase approximated by CPCM solvation model. After the geometry optimization the intermediates were confirmed by the absence of any imaginary modes, while transition states had just one imaginary mode. The imaginary mode was carefully
inspected to determine the nature of the transition state and the reaction coordinate involved. The geometries were also found to be consistent in both gas phase and solvent phase geometry optimization. Very little changes in the energetics of the reaction was found when we did solvent optimization to the energetics obtained by doing single point solvent phase computations on gas phase optimized geometries. The reliability of DFT was also tested by optimizing every transition state and intermediates with CCSD along with 6-311++G(d,p) basis set for hydrazine and 6-31++G(d,p) basis sets for the methylated congeners. For further accuracy of the CCSD data, single point computations were done with aug-cc-pvtz basis set. The methodology for obtaining thermochemical parameters from molecular Hessian use ideal gas laws. To account for the non-ideality involved in the thermochemical parameters of molecules in solvent phase, the gas phase entropy was scaled by 0.5 factor. This approximation in fairly common and has been employed in a number of studies. G09 quantum chemistry suite was used for computing static quantum chemical computations.

3(b).2.2 CPMD Computational Details: Packmol package was used to solvate INT1 and INT2 by water molecules. The INT1 and INT2 along with 8 explicit water molecules were taken and optimized with ω-B97XD(CPCM)/6-31++G** and the corresponding optimized geometry was solvated with 44 water molecules in a box of 12.020×12.020×12.020 Å³. Periodic boundary conditions using the aforementioned box were used to account for the bulk behavior of water and CPMD simulations employing the Kohn-Sham density functional theory (PBE functional) with the plane wave basis set with a cut off of 25 Ry was carried out. Simulations were carried out within the Canonical ensemble simulations at 300 K maintained using Nosé-Hoover
chain thermostat. A fictitious mass of 700 au was used for the electronic orbital degrees of freedom and a time step of 0.072 fs was used for the integration of equations of motion. At first the coordinates of INT1 and INT2 were fixed and the solvating water molecules were equilibrated for 720 femto seconds. After that the constraints were removed from INT1 and INT2 to run the actual simulations.

3(b).3 Results and Discussion

The investigation was initiated by location of the Minimum Energy Crossing Point (MECP) point for the aerial oxidation hydrazine by O2 by using the code developed by Harvey et al.[13] interfaced with Gaussian09. The MECP was found to be located 27.0 kcal/mol (at ωB97XD(CPCM)/6-31++G**) above the reactants by enthalpy (see geometry of MECP in Figure 1). The MECP point with 8 explicit water molecules to account for the first solvation sphere in aqueous solution was also located using similar techniques. Upon inclusion of 8 explicit water molecules the enthalpic cost for reaching the MECP point was estimated to be 24.1 kcal/mol (at ωB97XD(CPCM)/6-31++G**). Due to the quasi-degeneracy of S0 and T1 states at the MECP, the chances for the wavefunction to be multireference is very high and requires investigation with CASSCF based theories. The MECP point was hence investigated using CASSCF, NEVPT2 and MRCI level of theory. The CASSCF, NEVPT2 and MRCI computations on the DFT optimized MECP geometry revealed the S0 - T1 energy gap to be less than 1 kcal mol-1 and hence an approximate MECP at those level of theories too.
Figure 1. DFT (ωB97XD(CPCM)/6-311++g**) optimized intermediates and transitions states predicted during the course of oxidation of hydrazine.

The fact that MECP involves a spin transition, spin orbit coupling plays a pivotal role in the spin forbidden reaction. The spin orbit coupling has X, Y and Z components. The O-O bond was oriented to be parallel to the Z axis. The z component of spin orbit coupling was estimated to be 126 cm⁻¹. The X and Y have negligibly small magnitudes. The origin of this high magnitude has been discussed in details by Prabhakar et al.[14]

This high value of Z component of spin orbit coupling stems from a rotation from π_y to π_x orbital about the z axis (see Scheme 1).
Scheme 1. Schematic representation of the origin of spin orbit coupling represented graphically, enabling the transition from triplet to singlet state

The scalar relativistic effects were accounted using the Douglas Kroll Hamiltonian up to 2\textsuperscript{nd} order term for the one electron terms along with the Breit Pauli Hamiltonian for the two electron term to compute the spin-orbit coupling.

Technically spin-orbit coupling contribution between singlet and triplet wavefunction is computed in two steps: firstly, the SO Hamiltonian is added to the molecular electronic Hamiltonian as a general first-order perturbation to construct the total Hamiltonian of the form $H = H_{el} + H_{SO}$. The spin-orbit matrix elements $H_{SO}$ are calculated between the singlet and triplet configurations (i.e., $^1\Psi$ and $^3\Psi$) with the spin-orbit full Breit-Pauli (BP) operator of the form

$$H_{SO} = \frac{1}{2m^2c^2} \left[ \sum_i \sum_{\alpha} \frac{Z_{i\alpha}e^2}{r_{i\alpha}^3} l_{i\alpha} \cdot S_i - \sum_i \sum_{\alpha} \frac{e^2}{r_{ij}^3} l_{ij} \cdot (S_i + 2S_j) \right]$$

which contains both one and two electron terms. Here $I$ and $S$ are orbital and spin angular momentum operators and $i$ and $a$ denote electron and nucleus, respectively.
Followed by that the $H = H_{el} + H_{SO}$ matrix is being diagonalized on the basis of SA-CASSCF/NEVPT2(4,4) wave functions to yield the desired spin-orbit splitting directly using Orca program package.

The MECPs for dimethyl congeners were also located using similar techniques. The MECP for these cases was found to be 17.4 kcal/mol and 19.5 kcal/mol higher, by enthalpy, than the corresponding reactants for SDMH and UDMH respectively (see Figure 2).

![Figure 2: 1,2 MECP geometry between a) 1,2 dimethyl hydrazine (SDMH) and O₂ and b) 1,1 dimethyl hydrazine (UDMH) and O₂. Important bond lengths are shown in Å.](image)

The trend for the enthalpic barrier for MECP for the dimethyl congeners bears clear indication that the positive inductive effect of the associated methyl groups facilitates the electron transfer process from N end to O end (see Scheme 1). The spin transition is followed by the bonding of one of the oxygen ends of the O₂ moiety to one of the N ends of the hydrazine or its methylated analogues, with the other oxygen interacting via a H-bond to hydrogens of hydrazine, thus forming INT1 (see Figure 1).
reaction mechanism emerging from INT1 has been investigated using ωB97XD(CPCM)/6-311++G** level of theory. The intermediates and transition states for aerial oxidation hydrazine are depicted in Scheme 2 and have been further verified at Coupled Cluster level of theory.

Scheme 2. Predicted mechanistic steps for oxidation of hydrazine at ωB97XD(CPCM)/6-311++G**. The relative Gibbs free energy barriers (along with enthalpic changes in parenthesis) have also been provided. (For Gibbs free energy profiles see Fig S35-37 in SI and see Tables S4, S5 and S6 for CCSD(T) free energies).
Computations revealed that formation of INT1 to be endoergic by 33.2 kcal/mol with respect to the reactants, hydrazine and oxygen, (28.7 kcal/mol at CCSD(T) (CPCM=water)/aug-cc-pvqz//CCSD(6-311++G**), please see Table 1) and it is endothermic by 27.6 kcal/mol (see Scheme 2 and Figure 1). All the intermediates and transition states shown in Scheme 2 were further verified at Coupled Cluster level of theory.

Table 1: Barriers of Oxidation of hydrazine

<table>
<thead>
<tr>
<th>Hydrazine + ( ^3\text{O}_2 )</th>
<th>CCSD(T)/6-311++G**//CCSD D(6-311++G**)</th>
<th>CCSD(T) (CPCM=water)/6-311++G**//CCSD D(6-311++G**)</th>
<th>CCSD(T) (CPCM=water)/aug-cc-pvtz//CCSD(6-311++G**)</th>
<th>CCSD(T) (CPCM=water)/aug-cc-pvqz//CCSD(6-311++G**)</th>
</tr>
</thead>
<tbody>
<tr>
<td>INT1</td>
<td>58.8</td>
<td>35.6</td>
<td>28.8</td>
<td>28.6</td>
</tr>
<tr>
<td>TS(_{1-2})</td>
<td>53.6</td>
<td>30.8</td>
<td>25.3</td>
<td>25.3</td>
</tr>
<tr>
<td>INT2</td>
<td>47.0</td>
<td>28.3</td>
<td>23.7</td>
<td>23.7</td>
</tr>
<tr>
<td>TS(_{2-3})</td>
<td>51.0 ( cis=32.8 ) ( trans=30.9 )</td>
<td>( cis=28.2 ) ( trans=26.6 )</td>
<td>( cis=7.2 ) ( trans=9.99 )</td>
<td>( cis=7.7 ) ( trans=10.4 )</td>
</tr>
<tr>
<td>Diazene + ( \text{H}_2\text{O}_2 )</td>
<td>-5.1 ( cis= -5.6 ) ( trans=9.0 )</td>
<td>( cis= -7.2 ) ( trans=9.99 )</td>
<td>( cis= -7.7 ) ( trans=10.4 )</td>
<td></td>
</tr>
</tbody>
</table>

The Formation of INT1 is essentially by the transfer of electron from N end of hydrazine to dioxygen and hence can be viewed as a peroxide. The general chemical intuition indicates towards the possibility of a proton transfer in INT1. Indeed INT1 was found to undergo a proton transfer via transition state TS\(_{1-2}\) to form INT2 (see Figure 1). The located transition state TS\(_{1-2}\) was found to be only 1.6 kcal/mol in total energy above INT1. Upon consideration of thermodynamic corrections to enthalpy TS\(_{1-2}\) lies slightly below INT1. This indicates towards the facilenes of the proton transfer to occur. The dimethyl hydrazines have similar barriers for formation of analogues of INT1 and are 21.9 kcal/mol and 24.7 kcal/mol for UDMH and SDMH.
respectively. The barriers for transition state for the transfer of proton transfers in the corresponding INT1 were similarly low and led to the formation of the corresponding INT2 analogues (see Scheme 2 and Figure 3).

**Figure 3.**

- **a.** Optimized geometry of INT1 between 1,2 dimethyl hydrazine (SDMH) and O₂. Important bond lengths are shown in Å.
- **b.** Optimized geometry of TS₁₂ between 1,2 dimethyl hydrazine (SDMH) and O₂. Important bond lengths are shown in Å.
- **c.** Optimized geometry of INT1 between 1,1 dimethyl (UDMH) hydrazine and O₂. Important bond lengths are shown in Å.
Chapter 3 (b) Optimization of TS$_{12}$ between 1,1 dimethyl hydrazine (UDMH) and O$_2$. Important bond lengths are shown in Å.

INT2 was found to have exceptionally long bond distances between the adjacent N and O atoms (see Figure 2) upon optimization. Two isomeric forms of INT2 were optimized and they were found to be almost iso-energetic with the later predicted to be slightly more stabilized than the former by 1.1 kcal/mol. While the typical N-O double bond distance is around 1.21 Å (as in HNO molecule) and N-O single bond distance is around 1.45 Å (as in hydroxylamine), to our utter surprise th exceptionally long N-O bonds of 2.13 Å and 2.47 Å, see (Figure 2) for INT2 was observed. The INT2 analogs of SDMH and UDMH also displayed similarly elongated N-O bond lengths and were in same range as those of INT2 for Hydrazine (see Figure 4).

Figure 4. a. Optimized geometry of INT2 between 1,2 dimethyl hydrazine (SDMH) and O$_2$. Important bond lengths are shown in Å. b. Optimized geometry of INT2 between 1,1 dimethyl hydrazine (UDMH) and O$_2$. Important bond lengths are shown in Å.
The unusually elongated N-O bond distances in INT2 of hydrazine and methyl congeners warranted us to investigate the nature of interaction and inspect the MOs, (see Figure 1 for HOMO and LUMO of Hydrazine and Figures 5 for the other relevant molecular orbitals).

Figure 5: Important MOs for 4c-2e bond for the case of INT2 for hydrazine and O₂.
The HOMO and LUMO clearly shows the interaction to be a 4 centre 2 electron bond. INT2 was also investigated with AIM and the analysis shows clear bond paths with bond critical points between the N(1)-O(1) and N(2)-O(2) (please see Figure 6).

Figure 6. Figure depicting the critical points and bond paths of INT2 obtained from AIM analysis. The indices of the critical point. (3,-1) refer to bond critical point and (3,+1) refer to as ring critical point. Please refer to manual of Multiwfn program suite for details. The lines are bond paths.

are bond paths.

The inspection of HOMO reveals that though one of the oxygen, O(1), though having satisfied its valence by bond to one H and O₂, also bonds to the N(1). 4c-2e bonds are typically characterized by presence of very long bond distances between the interacting units.[10(a)] The dissociation energy of INT2 into radicaloid species, OOH and NH₂NH was computed to be 7.99 kcal/mol with ωB97XD, 11.1 kcal/mol with M062X functional, 14.5 Kcal/mol with B2PLYPD and 10.2 kcal/mol in CCSD(T) level of theory, in water (CPCM), and is consistent with the experimentally estimated
dissociation energy for [TCNE₂]²⁻, 9-10 kcal/mol.[11,12] M06-2x functional shows the highest degree of agreement with the CCSD(T) computed value for the dissociation energy of INT2 which is considered to be the gold standard in quantum chemical techniques for single reference regime. General intuition indicates for the wavefunction of such species, having very bond distance interaction, to be fraught with multiconfigurational character. Keeping in mind the aforementioned point we had investigated INT2 thorough using CASSCF based methods with a varying active space and INT2 was found to be consistently have single-reference wavefunction. Further investigations of the HOMO-LUMO energies reveals significant gap between them, implying that stability gained from 4c-2e bond to be substantial. Despite the fact that static quantum chemical studies with implicit solvation also confirmed univocally the formation of a 4c-2e bonded intermediate, we conducted CPMD simulations on the singlet surface to account for the presence of bulk solvent and the inclusion of thermal effects [15,16]. The optimized geometry of INT1 was taken and solvated with 52 explicit water molecules contained in a periodic box of 12.020×12.020×12.020 Å³ dimension. The CPMD simulation revealed that sfter about 1.88 pico seconds (ps) the transfer of proton from N1 to O1 was initiated and the transfer was totally complete within a few femtoseconds (see Figure 7(a)). However the transferred proton remained hydrogen bonded to N1 while remaining coordinated to O1. This short lived intermediate was characterized by a very small NOH bond angle and the presence of H-N H bonding interaction. This intermediate which we call INT1' with OH proton, hydrogen bonded to N undergoes a sliding motion of the H around 3.63 ps and finally undergoes a rupture of the O-H---N
hydrogen bond to form INT2 i.e. the (4c-2e bonded intermediate), which we earlier obtained using static quantum chemical techniques. In the condensed phase, comparison of respective NOH bond angles enables us to distinguish between INT2 from INT1 and INT1' (see Figure 7(b)).

Figure 7: a) Snapshots from the simulation of the first proton transfer and formation of INT2 from INT1. b) Differences in structural parameters for INT1, INT1', and INT2. c) Plot of NOH bond angle vs simulation steps. d) Histogram for the thermal distribution of NOH bond angle in INT2 after its formation. e) Plot of NH bond distance vs simulation steps.

The presence of H bonding in between O and H in INT1 and H and N in INT1' forces the NOH bond angle to be acute angled with a value of only ~ 20°. However in stark
contrast, INT2 (a 4c-2e intermediate) which has no H bonding interaction possess an NOH bond angle close to 90°. The plot for the change in NOH angle starting from INT1 against time progression as obtained from the CPMD simulation is provided in Figure 2(c). Figure 2(c) clearly points toward a distinct increase in NOH bond angle around 3.63 ps which marks the formation of the 4c-2e intermediate. Following the formation of INT2, around 4.35 ps, the NOH bond angle was sampled for about 6.3 ps. The sampled data for NOH angle was plotted as a histogram and fitted to a Gaussian distribution (see Figure 2(d)). A sharp well fitted Gaussian centered around 90° (angle) was obtained. The sharpness of the fitted Gaussian indicates that once INT2 is formed its stability prevents it to revert back to the H bonded INT1'. Thus the formation of INT2 from INT1 was observed to occur via short lived H bonded INT1' which was missing from the static quantum chemical computation and hence gives a CPMD provides a greater insight that earlier obtained. Similar sampling of other bond parameters, such as the N-H distance (see Figure 2(e)) and NHO bond angle (see Figure 8) and plotting them with respect to time evolution, also clearly unanimously confirms the above mentioned observations. INT2 incidentally is a case of 4c-2e bonded intermediate which forms in a natural occurring reaction i.e. the aerial oxidation of hydrazine.
Figure 8. Plot of NHO bond angle vs the simulation step/20 showing three distinct intermediates. Both static and the dynamic computations reveal that INT2 exhibit significantly elongated N-O bond distances, ranging from 2.5 Å to 2.4 Å. 4c-2e bonded have been implicated to be aromatic though no conclusive and extensive study on this subject have ever been reported.[17] To further establish INT2 as a 4c-2e bonded species we decided to investigate the aromaticity of INT2. As we have earlier
observed via AIM computation, the four membered ring formed the two Ns and two Os exhibit a ring critical point i.e. of order (3, +1). Ring critical points are a typical indicators of aromatic systems, though not very convincing evidence can be drawn out of it. So the most popular aromaticity index Nucleus Independent Chemical Shift (NICS)[18] studies have been carried out at M062X/6-31++G**, B3LYP/6-31++g** and MP2/6-31++g** levels of theory. The NICSZZ values were plotted along x, y and z directions at varying distances ranging from -3 Å to +3 Å, originating from a certain point of reference which we took as the centre of mass of the molecule (see Fig 9).

![Figure 9. Reference frame and atomic coordinates of INT2 for NICS calculation along X, Y and Z direction at B3LYP/6-31++G**, M062X/6-31++G** and MP2/6-31++G** level of theory for comparison.](image-url)
The NICSZZ value was found to fall gradually from the origin along the +x and -x coordinate, reaching the minima around the region where the N-N bond of INT2 exists and then gradually increases. The value of NICSZZ component along the x axis goes below -110 ppm, and provides convincing proof that INT2 is indeed very much aromatic. The NICSZZ value along the +y and -y coordinate was observed to decrease around the region of the elongated N-O σ-bonding of INT2. The NICSZZ component along the z axis attains a minima at the center of the molecular plane of INT2 (see Figure 9). The plots provide convincing evidence for INT2 to be an aromatic species. Similar NICS investigation for dimethyl analogues reveals their aromatic nature (see Figure 10).
Figure 10. a) Reference frame and atomic coordinates of \textbf{INT2}$_{UDMH}$ for NICS calculation along X, Y and Z direction at M062X/6-31++G** level of theory. b) Reference frame and atomic coordinates of \textbf{INT2}$_{SDMH}$ for NICS calculation along X, Y and Z direction at M062X/6-31++G** level of theory.

To further confirm our findings, from NICS regarding the aromatic nature of INT2 and dimethyl analogues, we resorted to employing the recently developed Magnetically Induced Current Density (MICD) methodology. MICD provides not only a sound framework for quantification of aromaticity index but also visualization of the ring currents associated with aromaticity and have proved its worth by making correct predictions in many a instances where NICS have indicated erroneous results.[19] Magnetically Induced Current Density (MICD) was computed using
The induced current densities were computed using DFT (B3LYP functional). \textit{Dalton} 2011. \textit{Dalton} 2011. aug-cc-pVDZ and Def2-TZVP basis set were used for computation which have been shown to give excellent results for magnetizabilities using Gauge Invariant Atomic Orbitals (GIAOs). To obtain the current densities, we have first performed response calculations at the DFT level using GIAOs, with the perturbation operator being a magnetic dipole operator placed perpendicular to the plane in which the current density is computed. The response vector is used to construct the necessary AO density matrices for the calculation of the induced current.

Induced ring-current susceptibilities were integrated using a 2-dimensional Gauss–Lobatto quadrature grid. The plane of integration was chosen perpendicular to the molecular plane, extending from 6 bohr above to 6 bohr below and outward of the ring center. This integration plane was subdivided in 20 tiles, and each tile was integrated to polynomial order 6. The streamline plots were obtained using the program PyNGL.

\textit{INT2} along with its dimethyl analogues were investigated using the aforementioned technique. The numerically integrated ring current value for \textit{INT2} has found to be high negative with a value of -12.20 nA/T (clockwise ring current) when the current was integrated along N(2)-O(2) long range bond, at B3LYP/6-31++G** level of theory, indicating that \textit{INT2} to be indeed aromatic.[19(c)] \textit{Benzene} which is considered to be the hallmark example of aromaticity was found have the numerically integrated ring current value of 13.5 nA/T at the same level of theory. \textit{INT2} being asymmetrical, the current susceptibility was measured through each bond by integrating across each one of them. We found that all the current integration values were consistently
corresponding to clockwise current, suggesting INT2 is aromatic through all the four relevant bonds. (see Table 1).

Table 1: Induced Ring Current Susceptibility (in nA/T) in INT2 in different planes at different levels of theory.

<table>
<thead>
<tr>
<th>Level of Theory</th>
<th>(+)XZplane (Z= -8.0 to +8.0) (X=0.0 to +8.0) \ (y-component)</th>
<th>(-)XZplane (Z= -8.0 to +8.0) (X=0.0 to -8.0) \ (y-component)</th>
<th>+YZplane (Z= -8.0 to +8.0) (Y=0.0 to +8.0) \ (x-component)</th>
<th>-YZplane (Z= -8.0 to +8.0) (Y=0.0 to -8.0) \ (x-component)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP/aug-cc-pVDZ</td>
<td>-13.81</td>
<td>9.43</td>
<td>11.95</td>
<td>-11.89</td>
</tr>
<tr>
<td>B3LYP/6-31++G**</td>
<td>-14.43</td>
<td>+9.26</td>
<td>+11.57</td>
<td>-12.20</td>
</tr>
</tbody>
</table>

The plots clearly show the presence of prominent ring currents traveling, in a clockwise direction.
We used static quantum chemical computations along with molecular dynamics simulation to probe the mechanistic pathways leading to formation of product from INT2. The possibility of formation of cis and trans di-imine and H$_2$O$_2$ from INT2 the possibility have been explored. Transition state TS$_{2-3c}$ and TS$_{2-3t}$ were located using DFT computations for the second hydrogen transfer to occur from the other end of N$_2$H$_3$ moiety. The barrier for the transfer of second hydrogen leading to the formation of diazene (cis and trans) and H$_2$O$_2$ was computed to be 3.0 kcal/mol and 1.7 kcal/mol w.r.t INT2 (see Scheme 1). To further ascertain the findings from
static computations and to include temperature and explicit solvent effects, we carried out a CPMD simulation using the previous protocol, within a box of 52 water molecules to understand the fate of INT2. Agreeably, we found out the exact event of the crucial proton transfer, leading to the formation of hydrogen peroxide. INT2 was found to be stable for about 10 ps. We sampled the two NO bond lengths throughout the trajectory and using the data histograms were plotted (see Figure 12(a)). The histogram for each pair N-O atoms was individually fitted to a Gaussian distribution function. The equilibrium bond distances obtained from the fitted Gaussian distribution function turned out to be 2.4 Å for O(1)N(1) and 2.3 Å for O(2)N(2) bond with standard deviations σ O(2)N(2) = 0.16 and σ O(1)N(1) = 0.19 which is excellent agreement to the value obtained from optimization of INT2 using different static quantum chemical techniques.
Having carried out the CPMD simulation for 24.5 more ps, on 24.0 ps we observed that, as computed using quantum chemical techniques, a second proton shift in INT2 happens via TS$_{2-3}$, to form trans-diazine and hydrogen peroxide (see Figure 12(b)). We could only simulate the event of formation for trans diazine and hydrogen peroxide, but the formation of cis diazine can also be simulated with a different set of initial

Scheme 2). However, the transition state leading to the formation of trans-azomethane isomer could not be optimized. The possibility for transfer of methyl groups was
rejected as we found out the transition states to be forbiddingly high in static computations (73.2 kcal/mol). Upon considering UDMH, we realized that the possibility for the transfer of hydrogen from the other end to be impossible because there were no hydrogens left on the reactive end. Transfer of Methyl group was found to proceed through a forbiddingly high barrier of 45.0 kcal/mol, thus making the process unlikely. The dissociation of INT2 remained as the only possible channel for any reaction to occur. INT2 analogue of UDMH was found to dissociate into OOH· radical and (CH₃)₂N-NH· radical. Using CPMD simulations as performed for earlier mentioned cases, we also observed the dissociation of INT2 analogue of UDMH. After performing the simulation for 4.2 ps, INT2 was found to dissociate into OOH· and (CH₃)₂N-NH· radicals (please see Figure 13).

![Figure 14](image)

**Figure 14.** a) Optimized geometry of INT3 between 1,1 dimethyl hydrazine (UDMH) and O₂. Important bond lengths are shown in Å. b) Optimized geometry of TS_{3-4} between 1,1 dimethyl hydrazine (UDMH) and O₂. Important bond lengths are shown in Å.
Radicals are naturally expected to recombine to form \( \text{INT3}_{\text{UDMH}} \). The joining of the radicals leading to formation of \( \text{INT3}_{\text{UDMH}} \) was found to be exoergic by 4.8 kcal/mol (see Figure 14). \( \text{INT3}_{\text{UDMH}} \) containing a peroxide bond is labile towards dissociation into \( \text{OH}^- \) and protonated form of NDMA via \( \text{TS}_{3-4\text{UDMH}} \). The dissociation of peroxide bond was found to proceed by surmounting a free energy barrier of 8 kcal/mol (see Scheme 1 and Figure 14). The protonated form NDMA can easily transfer a proton to \( \text{OH}^- \) either directly or via proton shuttle owing to the aqueous medium the reaction proceeds in. However the dissociation of \( \text{INT3}_{\text{UDMH}} \) into radical species rather the aforementioned ionic species was found to highly exoergic process.

The key point to be noted here is that molecular dynamics simulations performed on the 4c-2e based intermediates were being able to exactly match either the products which are observed experimentally or were able to predict the formation of key radicals, as in the case of UDMH, which could explain the observed gamut of products detected experimentally.[20] Thus the mentioned computation further establishes that the oxidation of hydrazines and its methylated analogues by molecular oxygen propagates through 4c-2e intermediates.

3(b).4 Summary

In summary we have discovered a unique pathway for dioxygen facilitated oxidation which involves a 4c-2e intermediate, which throws open the possibility that 4c-2e type bonding may not be limited to exotic molecular species after all and also warrants investigation of other oxidation reactions by dioxygen where similar pathways may operate. We have also investigated the nature of 4c-2e electron bonded intermediate using different bonding analysis notably being the Atoms in Molecules.
The aromaticity of 4c-2e bonded species have been investigated thoroughly using MICD and NICS techniques. The current density plots clearly depict streamline plot of current densities across all four atoms involved in the 4c-2e bond, thus establishing on a further mote the presence of four center two electron long range bonding interactions.

References


