

Molecular Machines as Light Emitters :

A Porphyrin-Diacetylene System

Nitin Kumar Singh

*A dissertation submitted for the partial fulfilment of
BS-MS dual degree in Science*



Indian Institute of Science Education and Research Mohali
April 2015

Certificate of Examination

This is to certify that the dissertation titled **Molecular machines as Light Emitters : A Porphyrin-Diacetylene system** submitted by **Mr. Nitin Kumar Singh (Reg. No.MS10089)** for the partial fulfillment of BS-MS dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

Professor K. S. Viswanathan

Dr. K. R. Shamasundar

Dr. P. Balanarayan
(Supervisor)

Declaration

The work presented in this dissertation has been carried out by me with Dr. P. Balanarayan at the Indian Institute of Science Education and Research Mohali. This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

Nitin Kumar Singh
(Candidate)

Dated: April 24, 2015

In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. P. Balanarayan
(Supervisor)

Acknowledgement

I would like to express my gratitude to my advisor Dr. P. Balanarayan for his support, patience and encouragement throughout my project. I would also like to express thanks to my project committee members Professor K. S. Vishwanathan and Dr. K. R. Shamasundar for reading drafts of this dissertation and providing many valuable comments that improved contents of this dissertation. I am also grateful to my colleagues Deep Raj, Geetananda, Prashant, Purna and Rupali and my friends Rajat and Irfana for helping me throughout the project. My deepest gratitude to my parents for their constant support and love in my life. I would also like to thank IISER Mohali for providing me the adequate facilities and Department of Science and Technology, India for providing INSPIRE scholarship throughout my academic program.

List of Figures

Figure 1 Structural changes in azobenzene.	2
Figure 2 Different structures of porphyrin-diacetylene system.	7
Figure 3 Inversion plot	9
Figure 4 Light emission comparison.....	11
Figure 5 Insertion plot.....	13
Figure 6 Different structures on PES.....	13
Figure 7 Insertion plot at various field strength	14

List of Tables

Table 1 Energies of Porphyrin ring and diacetylene	8
Table 2 Energies of bent and planar structures	10
Table 3 Energies with respect to Electric field strength.	11

CONTENTS

List of Figures	i
List of Tables	ii
Abstract	iv
Chapter 1 Introduction	1
1.1 Chemistry of porphyrin ring and diacetylene	1
1.2 Molecular machines	2
1.3 Light emitting molecules.....	3
1.4 Plan of thesis	4
1.5 References	5
Chapter 2 Electronic Structure Calculations and Inferences	6
2.1 Methodology and computational details	6
2.2 Results and discussion	6
2.3 Barrier for inversion of the porphyrin-diacetylene	8
2.4 Comparing the light emitted by porphyrin-diacetylene system with ammonia .	9
2.5 Barrier for diacetylene insertion in porphyrin.....	10
2.6 Conclusions	12
2.7 References	15
Appendix	16

Abstract

A molecular inclusion complex of a diacetylene and porphyrin ring is chosen as a model to check if it can be a potential light emitter as in the case of an ammonia molecule. In this work, it is shown that a supramolecular complex of diacetylene threaded porphyrin is a stable minimum with a very high dipole moment of 4.45 Debye at B3LYP/6-311+g(d,p). Although the system is thermodynamically unfavorable, there are remote possibilities of kinetic trapping in a well of depth 11.4 kcal/mol. The barrier for insertion was calculated to be 110.29 kcal/mol. The neutral species corresponding to the same structure has a higher dipole moment and similar potential energy surface (PES) characteristics.

Chapter 1

Introduction

1.1 Chemistry of porphyrin ring and diacetylene

Porphyrin ring is a bio-molecule, found in nature in chlorophyll and haemoglobin. It consists of four subunits of pyrrole rings connected by methine bridges (also called methene or methyne). The porphyrin system has 26 pi electrons and therefore by Hückel's rule, it is aromatic in character. Macromolecules built up by porphyrin have intense absorption bands in the visible region and porphyrin itself is purple in color. Porphyrin binds to metals ions of charge +2 or +3 to form complexes. These ligands are generally bound to iron, magnesium, and cobalt in the biological systems. A porphyrin without the metal is like a base. The porphyrin-metal complexes form a square planar structure. A large amount of literature on metal-porphyrin complexes is available¹, these are called metalloporphyrin. Porphyrins and metalloporphyrins also provide a synthetic base for material's chemistry. Transition metal-porphyrin complexes that have metal-carbon σ bonds are prepared by metathetical reactions¹ (Reactions where compounds exchange parts). Highly nucleophilic metal(I) porphyrin anions (M=Fe, Co, Rh, and Ir) react with halides to form metal(III) porphyrin alkyls. The Studies on stereo-chemical and kinetic properties have also provided the S_N2 character of these metal alkylations². The four nitrogen atoms in porphyrin ring are the reason for the basic character of porphyrin.

Diacetylene is expected to form a weakly interacting species with porphyrin ring in its cavity. The two hydrogen atoms at the ends of diacetylene are acidic in character and easy replacement is possible³. Thus, they are used in polymerization reactions.

1.2 Molecular machines

Molecular machines are supramolecular assemblies that on application of a stimulus undergo structural changes and perform work. Rotaxanes⁴ are a molecular combination of a molecular axle and cyclic macro ring on it. This ring weakly interacts with the axle, and the ring can rotate as well as slide along its axle. Rotaxanes are manipulated through chemical and photochemical inputs. These systems are made to work like switches. Similarly, another example is azobenzene⁵ which in the presence of light changes its form from trans to cis and behaves as switches (Fig.1).

Molecular machines are classified on the basis of various characteristics such as kind of energy supplied, kind of motion they can perform, and the ability for cyclic repetitive motions. These are accompanied by changes in physical and chemical properties via rearrangements of molecular counterparts.

For some molecular machines to work, a constant source of energy is required. The energy to the chemical system is fed through a chemical reaction. Molecular machines work using inputs of chemical energy, for which a constant source of reactant in the form of fuel is to be provided⁴

Many chemical reactions happen as a result of thermal activation or mixing the reactants. When a molecular machine works by thermal activation, it needs addition of reagents in its working cycle at each step because added reagents play a vital role in chemical energy inputs. Anyways such kind of inputs are helpful, but also such additions will also lead to accumulation of by products and eliminating these by products are not easy. Actually, the

best way to make a molecular machine work is by feeding through electrons and protons. With appropriately chosen photo-chemically or electrochemically driven reactions, it is possible to design interesting molecular machines.

In this work, we try to design an example of a molecular motor which produces light by A.C. driving.

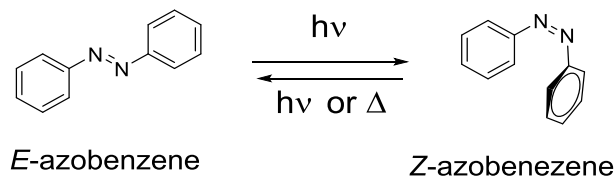


Figure 1 Structural changes in azobenzene.

1.3 Light emitting molecules

An example of a light emitting device is the ammonia MASER (Microwave amplification for stimulated emission of radiation). Ammonia has a bent structure, basically a pyramidal structure. The reason for its bent structure is the presence of lone-pairs on the nitrogen atom and thus lone pair-lone pair repulsion is greater than the bond pair-lone pair repulsion and hence a bent pyramidal structure is obtained. Ammonia has a dipole moment of 1.7 Debye. Starting from a initial geometry i.e. bent in one direction, if its bonds, angles and dihedral are changed in such a way that its energy increases, reaches a maximum (which would be a planar geometry) and then again bends in other direction, inversion can be achieved. The energy barrier for this system is 2078 cm^{-1} and a dipole moment of 1.7 D.

A popular device called MASER based on the ammonia inversion phenomenon has been made. Thus, here ammonia is used to emit light (in the range of microwave) performing a certain task. There are other bigger molecular assemblies which are not light emitters but are used to perform certain tasks. So, these are called molecular machines which find applications in the fields of nanoscience and biochemistry. They are synthetically challenging to prepare and are very task specific. Weak interactions of components, ability to repeat the specific motion, responding to the stimulus provided, and short time scales are some of the basic requirements for molecular assemblies to behave as a molecular machine.

In this project, it is asked whether this proposed molecular machine porphyrin-diacetylene can be prepared and what kind of light is emitted and harmonics generated by such a system.

In MASER, the basic principle involved is called stimulated emission proposed by Einstein in 1917. Consider a two level system, and initially take all electrons/atoms/molecules to be in the ground level (state 1), when irradiated with light some of them will absorb energy and jump up to the excited level (state 2). It will not stay there forever, if it comes down without any external influence it is called spontaneous emission and if it interacts with electromagnetic wave at certain frequency, the process is called stimulated emission.

In the theory developed about MASER, ammonia is considered to be in two states $|1\rangle$ and $|2\rangle$. At any instant, its state is described as a linear combination of the two available states, depicted by probability of coefficients of C_1 and C_2 and the probability is given by

$$|C_2(t)|^2 = \sin^2 \frac{At}{\hbar}$$

The idea of a MASER is to, first find a way to separate molecules in state $|1\rangle$ and $|2\rangle$. Then the molecules in the higher state (say $|1\rangle$) are passed through a cavity which has a resonant frequency equal to that of splitting (24000 megacycles in the case of ammonia MASER). The molecules deliver energy to the cavity and leave the cavity in the state $|2\rangle$. Each molecule that makes a transition will deliver the energy $E = E_I - E_{II}$ to the cavity.

The very first step of separating states is done through the application of direct electric field. Then the molecules in the higher state are fully separated and passed through a cavity having a time varying electric field. Ammonia has an intrinsic dipole moment, the separation of energy states is dependent on the dipole and the electric field applied which is given by the following equations

$$E_I = E_0 + A + \frac{\mu^2 \mathcal{E}^2}{2A}$$

$$E_{II} = E_0 - A - \frac{\mu^2 \mathcal{E}^2}{2A}$$

where E_0 – ground state energy, A – barrier, μ – dipole moment, $\mathcal{E}^2 = \mathcal{E} \cdot \mathcal{E}$, that is the square of electric field, it is also called the coefficient of polarizability of the molecule. Energy of molecules in the electric field are proportional to \mathcal{E}^2 . Ammonia has high polarizability because of small value of A in the denominator⁶.

1.4 Plan of thesis

Calculations on charged and neutral porphyrin-diacetylene complex will be performed. Different structures of the same will be analyzed and dipole moment, energies, and stability will be looked through. These calculations will help in knowing if the complex has features required for potential light emitter. Also various barriers associated with the inversion of complex and insertion of diacetylene in porphyrin will be calculated. Based on the

knowledge of geometries and barriers, potential energy surface will be calculated for generating inversion as well as insertion PES. The insertion PES will give information regarding barriers and tells about thermodynamic stability. Based on this information, it will be predicted whether physical insertion is possible or not. Also the inversion PES will give information regarding inversion barriers and this potential can further be used to calculate the harmonics generated. Back of the envelope calculations are performed to compare the light generated by ammonia and porphyrin-diacetylene system.

1.5 References

1. P. J. Brothers, and J. P. Collma *Acc. Chem. Res.* **19**, 209, (1986).
2. P. Fauvet, M. Gaudemer, A. Boucly, and P. Devynck, *J. J. Organomet. Chem.* **120**, 439, (1976).
3. J. Olmsted and M. Strand *J. Phys. Chem.* **87**, 4790, (1983).
4. S. Silvi, M. Venturi and Alberto Credi *J. Mater. Chem.* **19**, 2279, (2009)
5. W. R. Browne, B. L. Feringa, *Nature nanotechnology* 1, 1, (2006)
6. The Feynman Lectures on PHYSICS. **Volume 3**.

Chapter 2

Electronic Structure Calculations and Inferences

In this work, a supramolecular inclusion complex of porphyrin dianion with diacetylene is examined. Electronic structure calculations have been performed followed by geometry optimization to find structures. The methodology and computational details for this are elaborated in the next section.

2.1 Methodology and computational details

All the calculations have been performed using the *Gaussian 09*¹ suite of packages. The model chemistry used was at the density functional level. The popular functional of Becke-3 parameter exchange with Lee-Yang-Parr correlation functional has been used here. After a number of calculations on the monomers, the basis 6-311+g(d,p) was found to be suitable for these systems, finding a balance between computational time and accuracy. A Hessian evaluation has been performed for characterizing the nature of the geometries on the potential energy surface (PES). Wherever relevant intrinsic reaction coordinate (IRC) calculations have been done to examine the barrier heights.

2.2 Results and discussion

A novel structural complex has been found for porphyrin dianion and diacetylene system. This involves a diacetylene inserted into the porphyrin-ring system. The porphyrin ring stabilizes in a bent form at 0.31 Angstrom away from the center C-C single bond of diacetylene. The porphyrin ring bends to an angle of ~ 30 degree with the perpendicular to

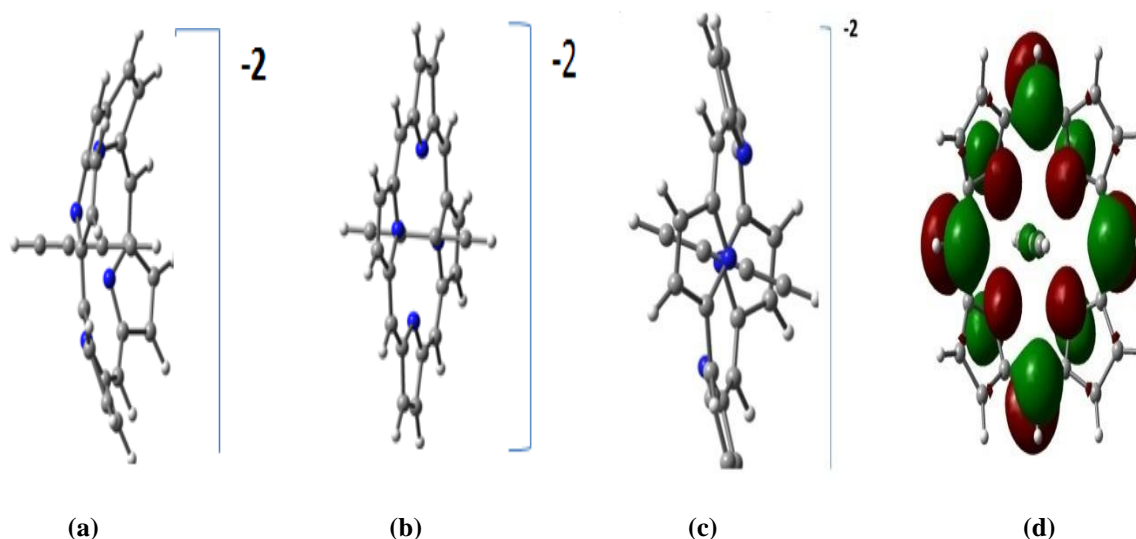


Figure 2 Different structures of porphyrin-diacetylene system.

plane of diacetylene. The geometry for this inclusive complex has been given in Fig. 2(a). What is even more surprising is the presence of a very high dipole moment of 4.5 Debye in the bent structure. Looking at the highest occupied molecular orbital (HOMO) of bent minimum in Fig. 2(d), it becomes clear that most of the charge is accumulated on the porphyrin ring. Electronic distribution on the pyrrole ring depicts a small dipole moments and sum all such dipole moments make dipole moment of the complex high.

However this structure, in spite of being a minimum on the PES, is not thermodynamically stable since its energy is greater than that of separated porphyrin dianion and diacetylene.

From Table 1 and Table 2, the barrier for insertion is 79.41 kcal/mol for the dianion complex. This shows that it is thermodynamically unstable. Similarly, the calculations for the neutral complex was done, again a bent minimum was found. In both the cases the structures were confirmed to be minima on the PES space, with all positive eigenvalues for the Hessian matrix. In the case of neutral complex too, there exists a very high dipole moment of 5.22 Debye. So, both the dianion complex and neutral complex are minima on their respective PES, but for both are unstable with respect to separated components.

Yet another geometry exists for the porphyrin-diacetylene inclusion complex. This is a puckerd structure (Fig. 2(c)) where one pair of adjacent pyrrole rings are bent in one

Table 1 Energies of Porphyrin ring and diacetylene

Compound	(q,S) [#]	$\Delta E(\text{kcal/mol})$	HOMO(a.u.)	LUMO(a.u.)
Porphyrin-ring	0,1	61.33	-0.20324	-0.16919
	-2,1	0.00	0.06874	0.16060
	0,3	61.03	-0.20225, - 0.22484	-0.09552,- 0.24044
	-2,3	29.50	0.11397, 0.04447	0.15196, 0.11132
Diacetylene	0,1	0.00	-0.27515	-0.04242
	2,1	633.48	-0.78913	-0.73740

[#] (q,S) stands for charge and multiplicity respectively. HOMO stands for highest occupied molecular orbital and LUMO stands for lowest occupied molecular orbital

direction and the other is bent in opposite direction. This conformer does not have a net dipole moment. Also, a planar geometry which lies exactly at the center of C-C bond and dipole moment of this is zero. This is a transition state geometry (Fig. 2(b)) which has three imaginary frequency of which one at -63.48 cm^{-1} corresponds to the bending mode. Therefore, it becomes evident that bent minimum geometry can be obtained by moving along this normal mode.

The complex has a bent minimum geometry and planar geometry. So, the flipping from bend in one direction to a bend in opposite direction will have dipole moments also changing directions, and in the presence of oscillating electric field the complex can also show similar behavior to that of ammonia MASER.

2.3 Barrier for inversion of the porphyrin-diacetylene

The barrier is obtained by doing a constrained optimization. Starting from the planar geometry and bending the porphyrin ring by changing the dihedral angles in the z-matrix (refer appendix) constrained optimization is done. The dihedrals are kept constant while optimizing. Further, energy of each geometry with respect to the bending angle is plotted.

The barrier obtained here is 8.64 kcal/mol (Fig. 3), The energy difference between the bent minimum and planar transition state is 11.4 kcal/mol. More over the same barrier in the case of ammonia inversion plot is 5.94 kcal/mol.

2.4 Comparing the light emitted by porphyrin-diacetylene system with ammonia

The first step in MASER¹, is the separation of molecules to state 1 and state 2 in the presence of electric field. The energy separation of the states in the presence of electric field is given by

$$E_D = A + \frac{\mu^2 \mathcal{E}^2}{2A}$$

where, A-barrier height, μ -dipole moment, \mathcal{E} -electric field, E_D -energy difference of states. Now, once these states are separated into state 1 and state 2, the state with higher energy (say state 1) is passed through a resonant cavity in the presence of oscillating electric field. Here the molecule stays for a time period T and the transition from state 1 to state 2 takes place only when frequency of the energy splitting of two states is nearly equal to the frequency of the field. So, this is called the transition probability.

$$P(I \rightarrow II) = \left(\frac{2\pi}{\hbar^2}\right) \mu^2 \mathcal{E}_0^2 T$$

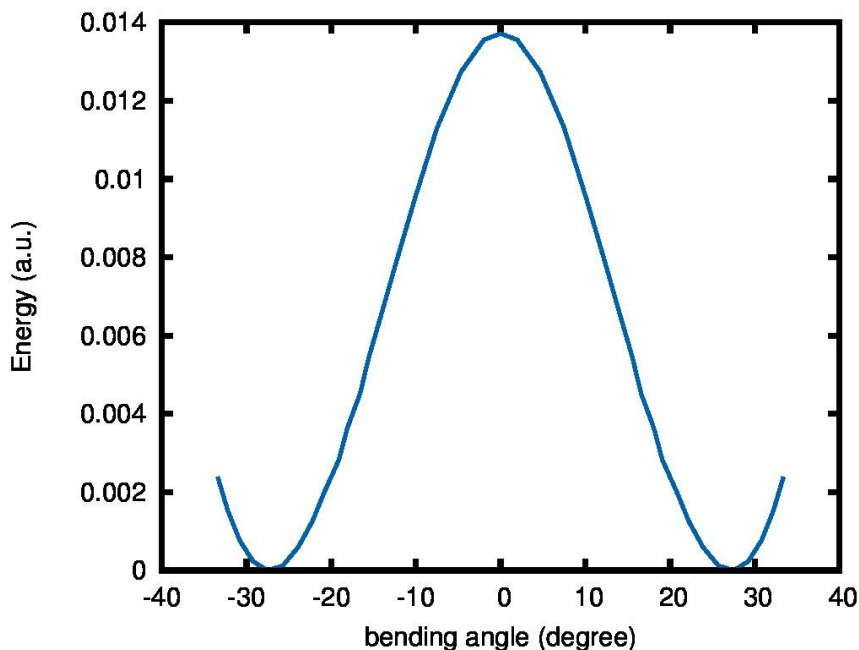


Figure 3 Inversion plot

porphyrin-diacetylene system at B3LYP/6-311+G(d,p). Note that is not the actual irc plot rather it is the bending angle versus the energy of each optimised geometry. The minimum bending angle is at 29.24 degree and -29.24 degree.

Here, it shows that the transition probability is more in the case of the system with higher dipole. Back of the envelope calculations for the light emitted is calculated. (Fig. 4)

2.5 Barrier for diacetylene insertion in porphyrin

The insertion curve is obtained by performing a constrained optimization on the system.

A z-matrix was constructed such that the distance between the centers of porphyrin and diacetylene remains constant, also the diacetylene being perpendicular to the porphyrin ring. Various changes in the geometry, mostly in bending angles of porphyrin are observed. A local minimum is observed at geometry where the distance between the two centers of ring and diacetylene is 4.3 angstrom. Initially the energy decreases by 16.06 kcal/mol (Fig. 5). This shows stabilizing interactions between porphyrin ring and diacetylene. Further, it is observed that a high barrier is developed when the distance between the two decreases and it is 110.29 kcal/mol. This implies that it is thermodynamically not a favorable reaction.

There is a high insertion barrier for diacetylene to be inserted into porphyrin. The system cannot be prepared by physical insertion. It has been reported in literature³, in the

Table 2 Energies of bent and planar structures

Complex	(q,S) [#]	$\Delta E(\text{kcal/mol})$	HOMO(a.u.)	LOMO(a.u.)	Dipole
Bent-local minimum	0,1	64.26	-0.20401	-0.15462	5.22
	-2,1	0.00	0.05724	0.15139	4.45
	0,3	71.61	-0.20452, -0.20077	-0.10105, -0.17229	5.28
	-2,3	26.20	0.10344, 0.04389	0.14452, 0.10047	3.92
Planar- transition state	0,1	70.54	-0.18836	-0.17330	0.00
	-2,1	0.00	0.06451	0.14991	0.00

[#] (q,S) stands for charge and multiplicity respectively. HOMO stands for highest occupied molecular orbital and LUMO stands for lowest occupied molecular orbital.

Table 3 Energies with respect to Electric field strength.

Field (V/nm)	$E_{\text{porphyrin}}+E_{\text{diacetylene}}$ (a.u.)	E_{complex} (a.u.)	$\Delta E(\text{kcal/mol})$
0.00	-1142.04753	-1141.92097	79.41767
5.14	-1141.95992	-1141.95113	5.92369
10.28	-1141.99320	-1142.02749	-21.51732

presence of electric field porphyrin related reactions become more selective. In the presence of electric field the electronic properties of porphyrin-diacetylene system can change, and there are chances of electric field decreasing the barrier or even making the reaction more feasible.

From Table 3, it is observed that with increasing field strength the energies decrease. So, it happens that after certain strength of electric field the energy of fragments is greater than that of complex. Therefore, the insertion can become feasible. At an electric field of about 10.28 V/nm the sum of fragments becomes less than the complex.

Hence, Fig. 7 depicts the insertion at various strengths of electric field. It is observed that with increasing field the respective energy at each geometry decreases and also the barrier increases. It is also noticed that the energy of the minimum (geometry 4 Fig. 6) is decreasing and the difference of this minimum with respect to the separated components is

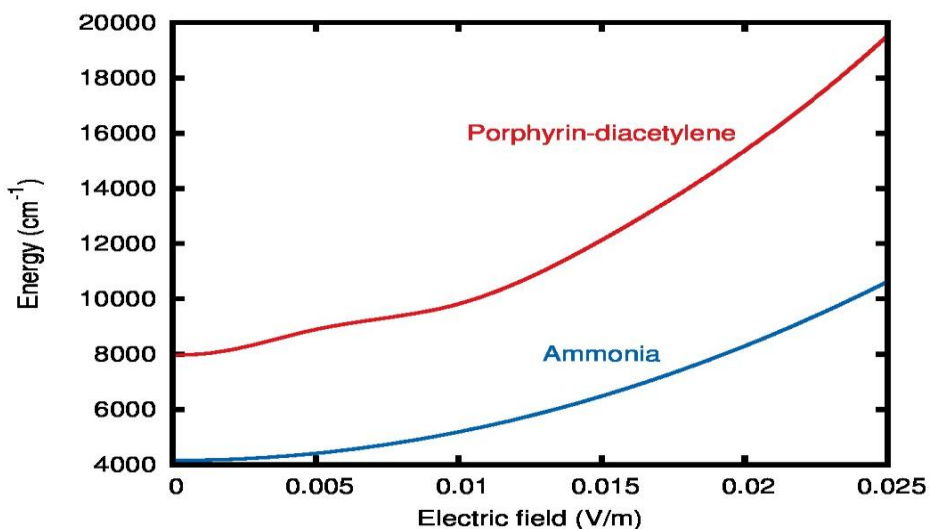


Figure 4 Light emission comparison

also decreasing, thus it may be concluded that at a higher electric field it may happen that energy of minimum (at geometry 4 Fig. 6) is less than sum of fragments.

It is worth while mentioning here that the sum of diacetylene dication and porphyrin dianion is greater than neutral bent complex, thus such insertion is possible if a diacetylene dication is prepared, However, the double ionization energy of 633.48 kcal/mol. This is thermodynamically unstable. It has been reported⁴ that a similar compound $C_4H_3^{+/+2}$ is known to be generated through the process of electron-ionization in the field of mass-spectrometry. In the same reference, a positive proton affinity of 1.50 eV=34.59 kcal/mol is also mentioned. Also, in another article⁵, structural stability calculations have been performed which mention their common appearance in mass spectrometry.

2.6 Conclusions

The complex, porphyrin-diacetylene is a potential light emitter. High dipole moment and bent minimum in the neutral and charged complex are key features of the complex. Both the neutral and charged complex have bent minimum but thermodynamically unfavorable. The planar structure is a transition state and one of imaginary frequency corresponds to the bending mode which will lead to the bent minimum if followed. This confirms a double well potential present for the system analogous to ammonia system. This potential can later be used to generate the harmonics associated with the system. The synthesis is problematic for this system because of high insertion barrier. A different approach is proposed. In the presence of direct electric field energies of sum of fragments decreases and after certain strength of electric field insertion becomes feasible. Also, it is proposed that diacetylene dication and porphyrin dianion can form the neutral complex without any barrier, but the only concern remains here is the formation of diacetylene dication which is not favorable. Primitive calculations shows that this porphyrin-diacetylene emits light with higher energy.

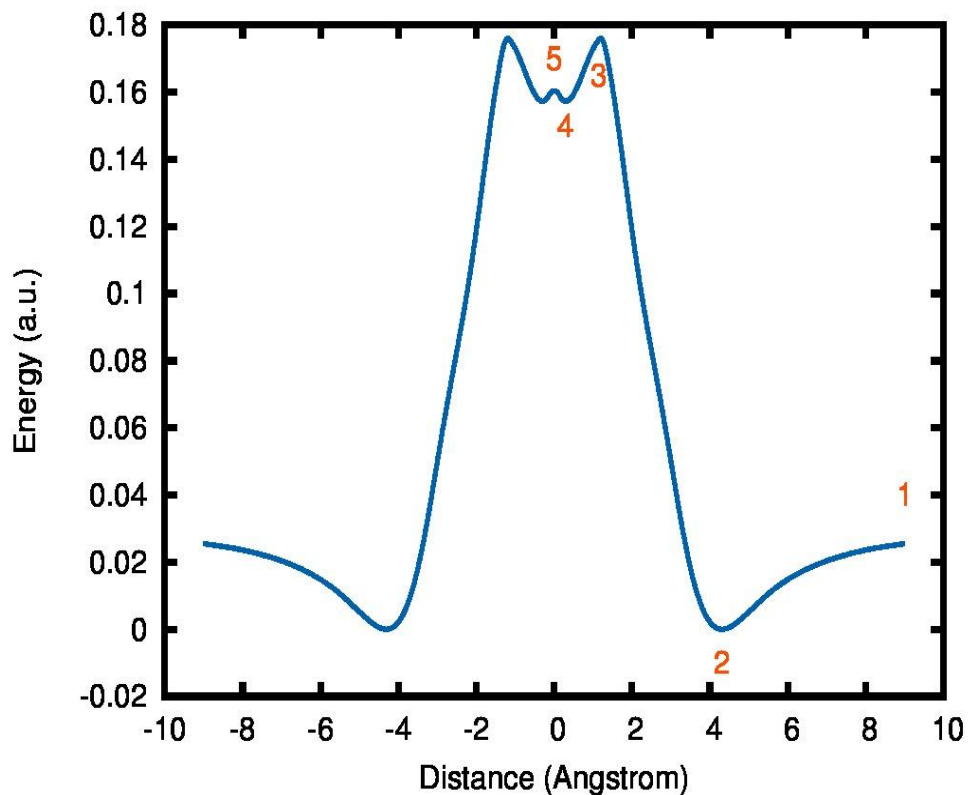


Figure 5 Insertion plot

Physical insertion barriers of diacetylene-porphyrin system. The calculations are performed in method and basis are B3LYP/6-311+g(d,p). The notations 1,2,3,4,5 are the critical geometries in the plot. Their respective figures are shown in figure 6.

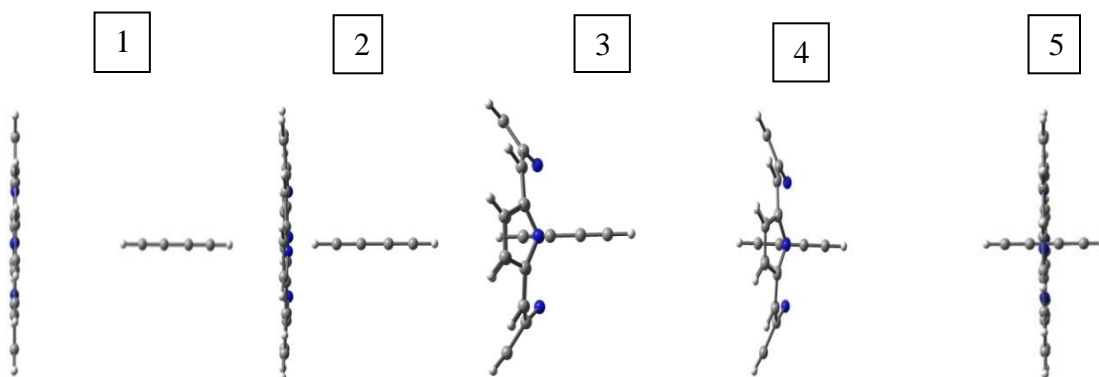


Figure 6 Different structures on PES

Depicts the geometries at various points on the PES. A Z-matrix was constructed and thus distance between diacetylene and porphyrin was decreased at each step in units of 0.1 and then optimized. The method and basis used are B3LYP/6-311+g(d,p). Please note that the minimum bent and planar geometries are not having the same energies previously discussed.

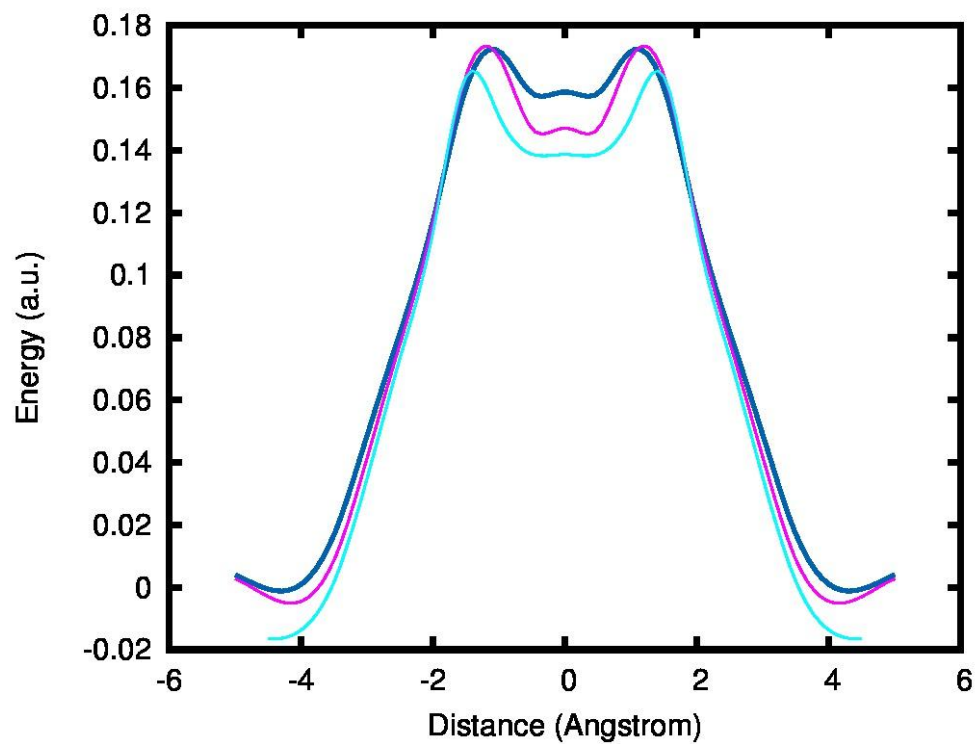


Figure 7 Insertion plot at various field strength

Insertion barriers with changing electric field strengths of 0.00, 2.57, 7.71 V/nm respectively. The barriers involved are 110.29, 112.03, 114.18 kcal/mol respectively.

2.7 References

1. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
2. Feynman Lecture on PHYSICS *Volume 3*.
3. C. F. Gorin *J. Am. Chem. Soc.* **11**, 257, (2013).
4. D. Schroder, J. Loos, H. Schwarz, R. Thissen, J. Roithova, and Z. Hermen, *International Journal of Mass Spectrometry* **230**, 113, (2008).
5. K. Lammerstma, J. A. Pople, P. v R Schleyer, *J. Am. Chem. Soc.* **108**, 7, (1986).

Appendix

Z-Matrix constructed for doing the insertion and inversion calculations

X1						
X2	1	3.0000				
C	1	R01	2	90.0000		
C	1	R01	2	90.0000	3	180.0000
X3	3	3.0000	1	90.0000	2	0.000000
X4	4	3.0000	1	90.0000	2	0.000000
C	3	R2	5	90.0000	1	-180.0000
C	4	R2	6	90.0000	1	180.0000
X5	7	3.0000	3	90.0000	5	0.000000
X6	8	3.0000	4	90.0000	6	0.000000
H	7	R3	9	90.0000	3	-180.0000
H	8	R3	10	90.0000	4	180.0000
X7	1	1.7000	2	90.0000	5	180.0000
X6	13	3.423145	1	90.0000	2	0.000000
X7	13	3.423145	1	90.0000	14	90.00000
X8	13	3.423145	1	90.0000	15	90.00000
X9	13	3.423145	1	90.0000	16	90.00000
N	13	R4	1	90.0000	2	0.000000
N	13	R4	1	90.0000	18	90.00000
N	13	R4	1	90.0000	19	90.00000
N	13	R4	1	90.0000	20	90.00000
C	14	R5	18	A1	1	D1
C	22	R6	18	A2	13	D2

C	23	R6	22	A3	13	D3
C	24	R6	23	A3	22	0.000000
C	15	R5	19	A1	1	D1
C	26	R6	19	A2	13	D2
C	27	R6	26	A3	13	D3
C	28	R6	27	A3	26	0.000000
C	16	R5	20	A1	1	D1
C	30	R6	20	A2	13	D2
C	31	R6	30	A3	13	D3
C	32	R6	31	A3	30	0.000000
C	17	R5	21	A1	1	D1
C	34	R6	21	A2	13	D2
C	35	R6	34	A3	13	D3
C	36	R6	35	A3	34	0.000000
C	22	R7	18	A4	23	D4
C	34	R7	21	A4	35	D4
C	30	R7	20	A4	31	D4
C	26	R7	19	A4	27	D4
H	38	R8	22	A5	29	D5
H	39	R8	34	A5	25	D5
H	40	R8	30	A5	37	D5
H	41	R8	26	A5	33	D5
H	27	R9	26	A6	19	180.0000
H	28	R9	29	A6	19	-180.000
H	23	R9	22	A6	18	180.0000
H	24	R9	25	A6	18	-180.000
H	35	R9	34	A6	21	180.0000
H	36	R9	37	A6	21	-180.000
H	31	R9	30	A6	20	180.0000
H	32	R9	33	A6	20	-180.000

Variables

R01 = 0.7000

R2 = 1.2000

R3 = 0.9000

R4 = 2.22315

R5 = 1.20000

R6 = 1.41068

R7 = 1.50768

R8 = 1.08618

R9 = 1.08618

A1 = 72.0000

A2 = 107.99984

A3 = 108.00000

A4 = 125.32517

A5 = 114.01768

A6 = 125.63785

D1 = 90.0000

D2 = 180.000

D3 = 0.00000

D4 = 180.000

D5 = 180.000

It was the distance of dummy atom X7 is the one changed in each geometry which performing insertion and optimization calculations. Also, the dihedral angles was kept changed order to bent the porphyrin ring and they were kept constant while optimizing.

- 1. Standard Orientations of few important geometries. All the calculations have been performed on Gaussian 09 with method/basis = B3LYP/6-311+G(D,P)**

Porphyrin-ring with charge/multiplicity=0/1

C 0.68037200 4.28659400 0.00000000

C	-0.68037200	4.28659400	0.00000000
C	-1.08020300	2.88178800	0.00000000
N	0.00000000	2.06898200	0.00000000
H	1.34362800	5.14022500	0.00000000
H	-1.34362800	5.14022500	0.00000000
C	1.08020300	-2.88178800	0.00000000
C	0.68037200	-4.28659400	0.00000000
C	-0.68037200	-4.28659400	0.00000000
N	0.00000000	-2.06898200	0.00000000
H	1.34362800	-5.14022500	0.00000000
H	-1.34362800	-5.14022500	0.00000000
C	2.88178800	-1.08020300	0.00000000
C	4.28659400	-0.68037200	0.00000000
C	4.28659400	0.68037200	0.00000000
C	2.88178800	1.08020300	0.00000000
N	2.06898200	0.00000000	0.00000000
H	5.14022500	-1.34362800	0.00000000
H	5.14022500	1.34362800	0.00000000
C	-2.88178800	1.08020300	0.00000000
C	-4.28659400	0.68037200	0.00000000
C	-4.28659400	-0.68037200	0.00000000
C	-2.88178800	-1.08020300	0.00000000
N	-2.06898200	0.00000000	0.00000000
H	-5.14022500	1.34362800	0.00000000
H	-5.14022500	-1.34362800	0.00000000
C	2.40521000	-2.40521000	0.00000000
C	2.40521000	2.40521000	0.00000000
C	-2.40521000	2.40521000	0.00000000
C	1.08020300	2.88178800	0.00000000
C	-2.40521000	-2.40521000	0.00000000

C	-1.08020300	-2.88178800	0.00000000
H	3.17461300	-3.17461300	0.00000000
H	-3.17461300	-3.17461300	0.00000000
H	-3.17461300	3.17461300	0.00000000
H	3.17461300	3.17461300	0.00000000

Porphyrin-ring with charge/multiplicity=-2/1

C	0.68354700	4.29522400	0.00000000
C	-0.68354700	4.29522400	0.00000000
C	-1.09048100	2.88382800	0.00000000
N	0.00000000	2.08903000	0.00000000
H	1.34478500	5.15613900	0.00000000
H	-1.34478500	5.15613900	0.00000000
C	1.09048100	-2.88382800	0.00000000
C	0.68354700	-4.29522400	0.00000000
C	-0.68354700	-4.29522400	0.00000000
N	0.00000000	-2.08903000	0.00000000
H	1.34478500	-5.15613900	0.00000000
H	-1.34478500	-5.15613900	0.00000000
C	2.88382800	-1.09048100	0.00000000
C	4.29522400	-0.68354700	0.00000000
C	4.29522400	0.68354700	0.00000000
C	2.88382800	1.09048100	0.00000000
N	2.08903000	0.00000000	0.00000000
H	5.15613900	-1.34478500	0.00000000
H	5.15613900	1.34478500	0.00000000
C	-2.88382800	1.09048100	0.00000000
C	-4.29522400	0.68354700	0.00000000
C	-4.29522400	-0.68354700	0.00000000
C	-2.88382800	-1.09048100	0.00000000
N	-2.08903000	0.00000000	0.00000000

H	-5.15613900	1.34478500	0.00000000
H	-5.15613900	-1.34478500	0.00000000
C	2.42538800	-2.42538800	0.00000000
C	2.42538800	2.42538800	0.00000000
C	-2.42538800	2.42538800	0.00000000
C	1.09048100	2.88382800	0.00000000
C	-2.42538800	-2.42538800	0.00000000
C	-1.09048100	-2.88382800	0.00000000
H	3.19590600	-3.19590600	0.00000000
H	-3.19590600	-3.19590600	0.00000000
H	-3.19590600	3.19590600	0.00000000
H	3.19590600	3.19590600	0.00000000

Diacetylene with charge multiplicity = 0/1

C	0.00000000	0.00000000	0.68248400
C	0.00000000	0.00000000	1.88953800
C	0.00000000	0.00000000	-0.68248400
C	0.00000000	0.00000000	-1.88953800
H	0.00000000	0.00000000	-2.95202900
H	0.00000000	0.00000000	2.95202900

Diacetylene with charge multiplicity = +2/1

C	0.00000000	0.00000000	0.65046000
C	0.00000000	0.00000000	1.92243400
C	0.00000000	0.00000000	-0.65046000
C	0.00000000	0.00000000	-1.92243400
H	0.00000000	0.00000000	-3.02014100
H	0.00000000	0.00000000	3.02014100

Porphyrin-diacetylene bent system with charge/multiplicity=0/1

C	0.68037200	4.28659400	0.00000000
C	-0.68037200	4.28659400	0.00000000

C	-1.08020300	2.88178800	0.00000000
N	0.00000000	2.06898200	0.00000000
H	1.34362800	5.14022500	0.00000000
H	-1.34362800	5.14022500	0.00000000
C	1.08020300	-2.88178800	0.00000000
C	0.68037200	-4.28659400	0.00000000
C	-0.68037200	-4.28659400	0.00000000
N	0.00000000	-2.06898200	0.00000000
H	1.34362800	-5.14022500	0.00000000
H	-1.34362800	-5.14022500	0.00000000
C	2.88178800	-1.08020300	0.00000000
C	4.28659400	-0.68037200	0.00000000
C	4.28659400	0.68037200	0.00000000
C	2.88178800	1.08020300	0.00000000
N	2.06898200	0.00000000	0.00000000
H	5.14022500	-1.34362800	0.00000000
H	5.14022500	1.34362800	0.00000000
C	-2.88178800	1.08020300	0.00000000
C	-4.28659400	0.68037200	0.00000000
C	-4.28659400	-0.68037200	0.00000000
C	-2.88178800	-1.08020300	0.00000000
N	-2.06898200	0.00000000	0.00000000
H	-5.14022500	1.34362800	0.00000000
H	-5.14022500	-1.34362800	0.00000000
C	2.40521000	-2.40521000	0.00000000
C	2.40521000	2.40521000	0.00000000
C	-2.40521000	2.40521000	0.00000000
C	1.08020300	2.88178800	0.00000000
C	-2.40521000	-2.40521000	0.00000000
C	-1.08020300	-2.88178800	0.00000000

H	3.17461300	-3.17461300	0.00000000
H	-3.17461300	-3.17461300	0.00000000
H	-3.17461300	3.17461300	0.00000000
H	3.17461300	3.17461300	0.00000000

Porphyrin-diacetylene bent system with charge/multiplicity=-2/1

C	0.68354700	4.29522400	0.00000000
C	-0.68354700	4.29522400	0.00000000
C	-1.09048100	2.88382800	0.00000000
N	0.00000000	2.08903000	0.00000000
H	1.34478500	5.15613900	0.00000000
H	-1.34478500	5.15613900	0.00000000
C	1.09048100	-2.88382800	0.00000000
C	0.68354700	-4.29522400	0.00000000
C	-0.68354700	-4.29522400	0.00000000
N	0.00000000	-2.08903000	0.00000000
H	1.34478500	-5.15613900	0.00000000
H	-1.34478500	-5.15613900	0.00000000
C	2.88382800	-1.09048100	0.00000000
C	4.29522400	-0.68354700	0.00000000
C	4.29522400	0.68354700	0.00000000
C	2.88382800	1.09048100	0.00000000
N	2.08903000	0.00000000	0.00000000
H	5.15613900	-1.34478500	0.00000000
H	5.15613900	1.34478500	0.00000000
C	-2.88382800	1.09048100	0.00000000
C	-4.29522400	0.68354700	0.00000000
C	-4.29522400	-0.68354700	0.00000000
C	-2.88382800	-1.09048100	0.00000000
N	-2.08903000	0.00000000	0.00000000
H	-5.15613900	1.34478500	0.00000000

H	-5.15613900	-1.34478500	0.00000000
C	2.42538800	-2.42538800	0.00000000
C	2.42538800	2.42538800	0.00000000
C	-2.42538800	2.42538800	0.00000000
C	1.09048100	2.88382800	0.00000000
C	-2.42538800	-2.42538800	0.00000000
C	-1.09048100	-2.88382800	0.00000000
H	3.19590600	-3.19590600	0.00000000
H	-3.19590600	-3.19590600	0.00000000
H	-3.19590600	3.19590600	0.00000000
H	3.19590600	3.19590600	0.00000000

Porphyrin-diacetylene planar system with charge/multiplicity=0/1

C	0.68387000	4.38749400	0.00000000
C	-0.68387000	4.38749400	0.00000000
C	-1.10881600	2.97779300	0.00000000
N	0.00000000	2.21978200	0.00000000
H	1.32916700	5.25542400	0.00000000
H	-1.32916700	5.25542400	0.00000000
C	1.10881600	-2.97779300	0.00000000
C	0.68387000	-4.38749400	0.00000000
C	-0.68387000	-4.38749400	0.00000000
N	0.00000000	-2.21978200	0.00000000
H	1.32916700	-5.25542400	0.00000000
H	-1.32916700	-5.25542400	0.00000000
C	2.97779300	-1.10881600	0.00000000
C	4.38749400	-0.68387000	0.00000000
C	4.38749400	0.68387000	0.00000000
C	2.97779300	1.10881600	0.00000000
N	2.21978200	0.00000000	0.00000000
H	5.25542400	-1.32916700	0.00000000

H	5.25542400	1.32916700	0.00000000
C	-2.97779300	1.10881600	0.00000000
C	-4.38749400	0.68387000	0.00000000
C	-4.38749400	-0.68387000	0.00000000
C	-2.97779300	-1.10881600	0.00000000
N	-2.21978200	0.00000000	0.00000000
H	-5.25542400	1.32916700	0.00000000
H	-5.25542400	-1.32916700	0.00000000
C	2.43786200	-2.43786200	0.00000000
C	2.43786200	2.43786200	0.00000000
C	-2.43786200	2.43786200	0.00000000
C	1.10881600	2.97779300	0.00000000
C	-2.43786200	-2.43786200	0.00000000
C	-1.10881600	-2.97779300	0.00000000
H	3.20819000	-3.20819000	0.00000000
H	-3.20819000	-3.20819000	0.00000000
H	-3.20819000	3.20819000	0.00000000
H	3.20819000	3.20819000	0.00000000
C	0.00000000	0.00000000	0.70951200
C	0.00000000	0.00000000	1.92059600
C	0.00000000	0.00000000	-0.70951200
C	0.00000000	0.00000000	-1.92059600
H	0.00000000	0.00000000	-2.98105800
H	0.00000000	0.00000000	2.98105800

Porphyrin-diacetylene planar system with charge/multiplicity=-2/1

C	0.68387000	4.38749400	0.00000000
C	-0.68387000	4.38749400	0.00000000
C	-1.10881600	2.97779300	0.00000000
N	0.00000000	2.21978200	0.00000000
H	1.32916700	5.25542400	0.00000000

H	-1.32916700	5.25542400	0.00000000
C	1.10881600	-2.97779300	0.00000000
C	0.68387000	-4.38749400	0.00000000
C	-0.68387000	-4.38749400	0.00000000
N	0.00000000	-2.21978200	0.00000000
H	1.32916700	-5.25542400	0.00000000
H	-1.32916700	-5.25542400	0.00000000
C	2.97779300	-1.10881600	0.00000000
C	4.38749400	-0.68387000	0.00000000
C	4.38749400	0.68387000	0.00000000
C	2.97779300	1.10881600	0.00000000
N	2.21978200	0.00000000	0.00000000
H	5.25542400	-1.32916700	0.00000000
H	5.25542400	1.32916700	0.00000000
C	-2.97779300	1.10881600	0.00000000
C	-4.38749400	0.68387000	0.00000000
C	-4.38749400	-0.68387000	0.00000000
C	-2.97779300	-1.10881600	0.00000000
N	-2.21978200	0.00000000	0.00000000
H	-5.25542400	1.32916700	0.00000000
H	-5.25542400	-1.32916700	0.00000000
C	2.43786200	-2.43786200	0.00000000
C	2.43786200	2.43786200	0.00000000
C	-2.43786200	2.43786200	0.00000000
C	1.10881600	2.97779300	0.00000000
C	-2.43786200	-2.43786200	0.00000000
C	-1.10881600	-2.97779300	0.00000000
H	3.20819000	-3.20819000	0.00000000
H	-3.20819000	-3.20819000	0.00000000
H	-3.20819000	3.20819000	0.00000000

H	3.20819000	3.20819000	0.00000000
C	0.00000000	0.00000000	0.70951200
C	0.00000000	0.00000000	1.92059600
C	0.00000000	0.00000000	-0.70951200
C	0.00000000	0.00000000	-1.92059600
H	0.00000000	0.00000000	-2.98105800
H	0.00000000	0.00000000	2.98105800