A Prebiotic Surface Catalyzed Photochemically Activated Synthesis of Corrin Derivatives: A and B Monomers

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Abstract: - Alkynes such as but-2-ynimine, propyne and ethyne form weak charge-transfer, η^2 -alkynyl complexes, with surface catalysts such as Mg.porphin in which the alkynyl group is positively charged and the porphin has a negative charge. The enthalpy changes are -0.040, -0.002 and -0.018 h, respectively. However, if the adduct is excited to a higher energy state it may migrate to form a weak charge transfer bond with the nitrogen atom of an adjacent pyrrole unit. If the catalyst, Mg.porphin accepts two adducts they may have opposite charges. The di-adduct complexes may bond leading to high energy products in which the orientation is determined by the exciting radiation. Subsequent reactions with nucleophiles such as cyanoacetylene and methyl cyanide anions may give derivatives of pyrroline that can oligomerize to tetramers that can cyclise to corrin derivatives.

The reactions have been shown to be feasible from the overall enthalpy changes in the ZKE approximation at the HF and MP2 /6-31G* level.

Key-Words: Mg.porphin , but-2-ynimine, propyne, ethyne, corrin derivatives.

1 Introduction

Vitamin B12, cobalamin [1]. is a highly conjugated cyclic chromophoric molecule containing the corrin structure [2] chelating a cobalt ion which may be present in oxidation states 1,2 or 3. The cobalt ion may also accept coordination from deoxyadenosyl, cyanide, hydroxide ions, water and dimethylbenziminazole [3,4]. It is an essential vitamin to prevent pernicious anaemia [5] where it acts as a cofactor to form holoenzymes from the adenosylcobalamin dependent isomerases, the methyl cobalamin dependent methyl transferases and dehalogenases [3]. In the action of the isomerases a hydrogen atom is transferred from the substrate to an adjacent atom site. In the methyl transfer reactions a methyl group coordinated to the cobalt ion is transferred to an acceptor. In anaerobic dehalogenation it facilitates reductive dehalogenation in which a bound chorine atom forms hydrogen chloride.

The biosynthesis of the active vitamin has been achieved from the amino laevulic acid [5]. Neither animals or plants can manufacture B12, just microoranisms [5]

From a prebiotic perspective [6] it is desirable if the reactant molecules formed spontaneously from a supposed prebiotic atmosphere to be inevitably present. It has often been held that the atmosphere of the Earth was originally mildly reducing [5,7] implying the presence of concentrations of carbon monoxide, ammonia, water and hydrogen. It is also supposed that alkynes such as acetylene [8,9] were present as found on Titan, a moon of Saturn. It has also been demonstrated that porphin may act as a catalyst for the formation of sugars [10] and polyenes [11].

This paper proposes a model for the surface catalytic photochemically activated formation of the corrin structure from the gases, propyne, ethyne, hydrogen cyanide and hydrogen with the surface catalyst, magnesium porphin . Experimental gaseous mixture subjected to discharge have been shown to produce biomolecules [12].

2 Problem Formulation

The computations tabulated in this paper used the GAUSSIAN98 [13] commercial package. The standard calculations at the HF and MP2 levels including zero-point energy corrections (HF) [14], together with scaling [15], using the same basis set, 6-31G*, are as previously published [6]. Enthalpy changes at the MP2 level not including scaled zero point energies are designated as $\Delta H_{(MP2)}$. The charge transfer complexes are less stable when calculated at the Hartree Fock level [14].

If the combined energy of the products is less than the combined energy of the reactants it may show that the reaction is also likely to be spontaneous at higher temperatures. This paper uses the atomic unit of energy, the hartree [13].
1h = 627.5095 $kcal.mol^{-1}$.
1h = $4.3597482 \times 10^{-18}$ J

3 Problem Solution

3.1 Total energies (hartrees)

Molecules that are present interstitially and in planets [16,17] are here taken to be the initial reactant molecules: propyne, ethyne and hydrogen cyanide, where the formation of the but-2-yne nitrile and but-2-ynimine (cis) may be produced by atmospheric free radical or ionic reactions [17].

$CH_3\text{-}C \equiv C\text{-}H + H\text{-}CN \rightarrow CH_3\text{-}C \equiv C\text{-}CN + H_2$ [1]

$\Delta H = -0.00816$ h

$CH_3\text{-}C\equiv C\text{-}CN + H_2 \rightarrow CH_3\text{-}C\equiv C\text{-}CH{=}NH$ (cis) [2]

$\Delta H = 0.00444$ h

Further reactants are taken to be cyanoacetylene [16] and methyl cyanide [17], also formed atmospherically by the reactions,

$H\text{-}C \equiv C\text{-}H + H\text{-}CN \rightarrow H\text{-}C \equiv C\text{-}CN + H_2$ [3]

$\Delta H = -0.00382$ h

$CH_4 + H\text{-}CN \rightarrow CH_3\text{-}CN + H_2$ [4]

$\Delta H = 0.00307$ h

It is also assumed that the environment was mildly alkaline due to the presence of ammonia in the reducing atmosphere, so that the anions may be formed according to the equations,

$H\text{-}C \equiv C\text{-}CN + OH^- \rightarrow NC\text{-}C \equiv C^- + H_2O$ [5]

$\Delta H = -0.09794$ h

$CH_3\text{-}CN + OH^- \rightarrow NC\text{-}CH_2^- + H_2O$ [6]

$\Delta H = -0.04799$ h

Mg.porphin is a powerful catalyst able to form charge transfer complexes with a number of different kinds of molecules [18].

With propyne the Mg.porphin is positively charged +0.073 [11].

Mg.porphin + propyne → Mg. propyne.porphin

$\Delta H = -0.00209$ h [7]

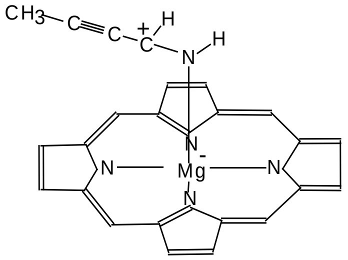
However, it is also possible for the propyne to migrate to bond with a pyrrole nitrogen atom to form a high energy complex [11].

Mg.propyne.porphin → Mg.porphin.propyne

$\Delta H = 0.01862$ h [8]

The catalyst also forms a weak charge transfer complex with but-2-ynimine where the ligand is positively charged (0.07) and the porphin has a negative charge, as shown,

Mg.porphin + $HN{=}CH\text{-}C\equiv C\text{-}CH_3 \rightarrow$ Mg.1,N-but-2-ynimin-1-yl.porphin [9]



Mg.1,N-but-2-ynimin-1-yl.porphin (cis) (1)

$\Delta H = -0.04014$ h

Mg.porphin may also form an adduct with acetylene [19],

$\Delta H = -0.01807$ h

The data for the total energies and zero point energies for the HF and MP2/6-31G* equilibrium geometries for these molecules and others involved in the synthesis are given in Table.1.

Table 1
MP2 /6-31G* total energies and zero point energies (hartrees) for the respective equilibrium geometries

Molecule	MP2 hartree	ZPE (HF) hartree
Mg.1,N-but-2-ynimin-1-yl.porphin (cis) (1)	-1394.57494	0.37950

3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-methenyl Δ^1- pyrroline^{+1} $C_{11}H_{12}N_3^+$ Monomer A (2)	-585.94178	0.173521
3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-ethenyl Δ^1- pyrroline^{+1} $C_{12}H_{10}N_3^+$ Monomer B (3)	-625.12035	0.20245
$C_{10}H_9N_2^+$ Monomer C (4)	-493.95240	0.17420
$C_{12}H_{10}N_3^+$ Monomer D (5)	-625.12956	0.20389
Mg.1,N-but-2ynimin-1yl.porphin.N-ethynyl (6)	-1471.64654	0.40450
Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-propenimin-1-yl.porphin.(7)	-1471.48430	0.40111
Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-cyanoethynyl propenimin-1-yl.porphin^{-1} (8)	-1640.24330	0.42825
Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-cyanoethynyl propanimin-1-yl.porphin (9)	-1640.84952	0.42920
Mg.1,N-2-cyanoethynyl-3-cyanomethanyl -3-methyl-pent-N4-ynyl.porphin^{-1} (10)	-1772.57046	0.48282
Mg.1,N-3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-methynyl Δ^1-NH-pyrrolin-1yl.porphin^{-1}(11)	-1772.43600	0.47996
Mg.1,N-3-cyanoethynyl-4-cyanomethanyl -4-methyl-5-methenyl Δ^1-NH-pyrrolin-1-yl.porphin (12)	-1771.64001	0.48033
Mg.1,N-3-cyanoethynyl-4-cyanomethanyl -4-methyl-5-methenyl Δ^1-N-pyrrolin-1-yl.porphin^{+1} (13)	-1771.17348	0.46260
but-2-yne nitrile	-208.25777	0.05963
but-2-ynimine	-209.41044	0.08479
Mg.porphin	-1185.12250	0.29262
Mg.OH.porphin^{-1}	-1260.79369	0.29802
propyne	-116.24181	0.06010
ethyne	-77.06679	0.02945
H-C ≡ C-CN	-169.07910	0.02976
$NC\text{-}C \equiv C^-$	-168.49375	0.01711
CH_3-CN	-132.33825	0.04840
$NC\text{-}CH_2^-$	-131.70120	0.03278
H-CN	-93.15894	0.01593
CH_4	-40.33255	0.04778
H_2	-1.14414	0.01059
OH^-	-75.51314	0.00885
H_2O	-76.19685	0.02298

3.2 The overall stoichiometry for the formation of the four monomers that oligomerize to corrin derivatives.

Although Mg.porphin is here taken as the catalyst for the reaction, the overall stoichiometry for the synthesis of corrin derivatives from but-2-ynimine, propyne, ethyne, methyl cyanide and cyanoacetylene can be represented as follows, where the final hydrogenation and hydrolysis present in the vitamin B12 structure is yet to occur.

The monomer that forms ring A [2] is formed as follows:

$H\text{-}C \equiv CH + CH_3\text{-}C \equiv C\text{-}CH{=}NH + NC\text{-}C \equiv C^- + NC\text{-}CH_2^- + 3H^+ \rightarrow C_{11}H_8N_3^+ + 2H_2$
Monomer A (2) Fig.1 [10]

$\Delta H = -1.53068$ h

The monomer that forms ring B [2] is formed as follows:

$CH_3\text{-}C \equiv CH + CH_3\text{-}C \equiv C\text{-}CH{=}NH + NC\text{-}C \equiv C^- + NC\text{-}CH_2^- + 3H^+ \rightarrow C_{12}H_{10}N_3^+ + 2H_2$
Monomer B (3) Fig.1 [11]

$\Delta H = -1.54041$ h

The monomer that forms ring C [2] is formed as follows:

$CH_3\text{-}C \equiv CH + CH_3\text{-}C \equiv C\text{-}CH{=}NH + NC\text{-}C \equiv C^- + 2H^+ \rightarrow C_{10}H_9N_2^+ + H_2$
Monomer C (4) Fig.1 [12]

$\Delta H = -0.93026$ h

The monomer that forms ring D [2] is formed as follows:

$CH_3\text{-}C \equiv CH + CH_3\text{-}C \equiv C\text{-}CH{=}NH + NC\text{-}C \equiv C^- + NC\text{-}CH_2^- + 3H+ \rightarrow C_{12}H_{10}N_3^+ + 2H_2$
Monomer D (5) Fig.1 [13]

$\Delta H = -1.54369$ h

The enthalpy changes are negative indicating that there may be energetically favourable routes to the formation of each of these monomers from these reactants.

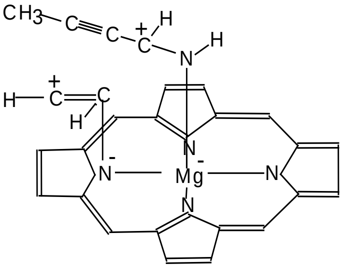
The intermediates by which the stoichiometric reactions may have occurred are as follows:

3.3 The Formation of monomer A.

3.3.1. The formation of the Mg.1,N-but-2-ynimin-1-yl.porphin.N-ethynyl

But-2-ynimine forms a weak charge transfer complex with the Mg ion of the catalyst Mg.porphin, whilst ethyne forms a weak van der Waals adduct centered on a pyrrole nitrogen atom. The charges on the two adducts are different. The but-2-ynimine adduct carries a positive charge, calculated as 0.080, whilst the ethyne is negative sharing electrons with the pyrrole-N atom with a calculated charge of -0.011, giving the catalyst a net positive charge 0.069. When the catalyst is excited with UV radiation an in-plane electronic transition occurs in which the magnetic vector of the radiation is perpendicular to the ring causing rotation of the positively charged adduct [11]. It is postulated that when the magnetic vector is pointing upwards towards the observer this is more effective in causing rotation than when the adduct is forced to the catalyst surface, and a high energy complex is formed, as shown,

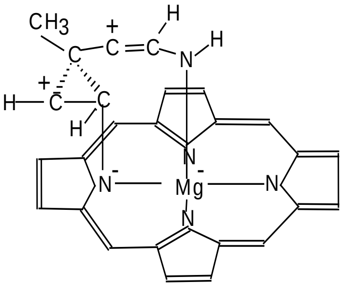
Mg.porphin + CH_3-C ≡ C-CH-NH + H-C ≡ C-H → [14]



Mg.1,N-but-2-ynimin-1-yl.porphin.N-ethynyl (6)

$$\Delta H = -0.04890 \text{ h}$$

which subsequently bonds,



Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-propenimin-1-yl.porphin (7)

$$\Delta H = 0.15922 \text{ h}$$

As the enthalpy change is appreciable and positive it is postulated that this occurs by electromagnetic excitation where the first excitation of these very weak complexes requires about 0.21 h. The activation energy to form the complex was calculated as 0.114 h at HF accuracy, with the activation energy for the reverse reaction being 0.014 h.

The high energy di-adduct complex is then susceptible to nucleophilic attack by numerous molecules in various sequences of reactions. Here the reactions given are those that lead to the stereospecificity depicted in Fig.1 for a corrin derivative with similar stereochemistry to that found in Vitamin B12 [2].

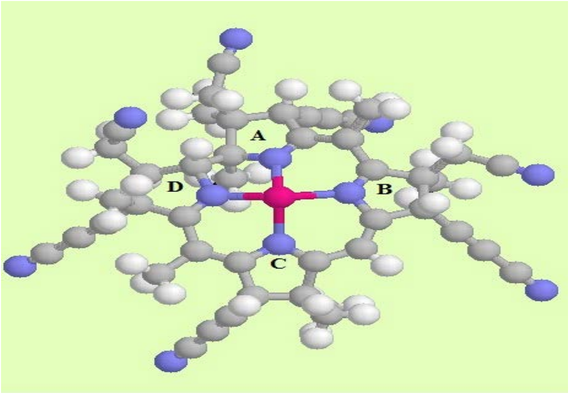
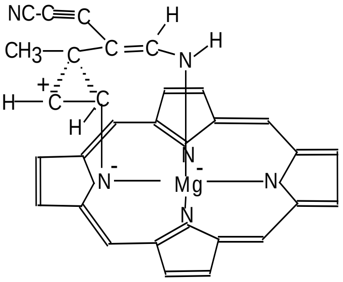


Fig.1. The designation of the corrin rings as recommended by IUPAC [2].

3.3.2. The formation of the Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-cyanoethynyl propenimin-1-yl.porphin^{-1}

The high energy complex is subject to nucleophilic reaction with the cyanoacetylene anion,

Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-propenimin-1-yl.porphin + NC-C ≡ C^- →



Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-cyanoethynyl propenimin-1-yl.porphin^{-1} (8)

[15]

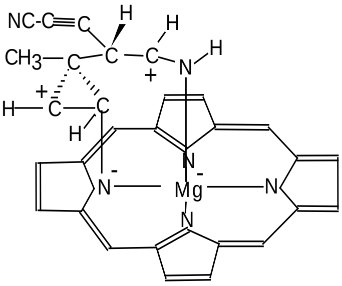
No activation energy is recorded for this addition.

$\Delta H = -0.25634$ h

3.3.3. The formation of Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-cyanoethynyl propanimin-1-yl.porphin

The negatively charged adduct may easily react with a proton in an energetic reaction where it is assumed that it preferentially attacks from above the adduct surface,

Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-cyanoethynyl propenimin-1-yl.porphin^{-1}
+ H^+ →



Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-cyanoethynyl propanimin-1-yl.porphin (9) [16]

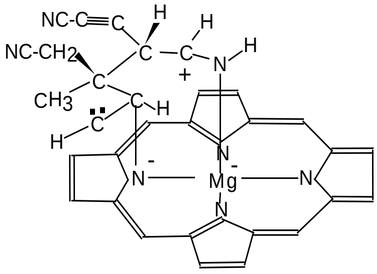
$\Delta H = -0.60537$ h

No activation energy was recorded for this hydrogen ion addition.

3.3.4. The formation of Mg.1,N-2-cyanoethynyl-3-cyanomethanyl-3-methyl-pent-N4-ynyl.porphin

The strong nucleophile, cyanomethyl anion, formal charge C1 -0.74, N3 -0.69) can open up the complex to form the diadduct, Mg.1,N-2-cyanoethynyl-3-cyanomethanyl-3-methyl-pent-N4-ynyl.porphin. where attack is assumed to be from above the surface of the catalyst,

Mg.1,N-2-(1-methyl cyclopropenyl)-2-cyanoethynyl propanimin-1-yl.porphin + $NC\text{-}CH_2^-$ →

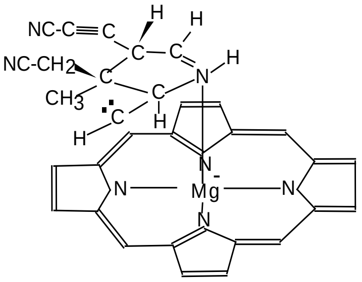


Mg.1,N-2-cyanoethynyl-3-cyanomethanyl-3-methyl-pent-N4-ynyl.porphin^{-1} (10) [17]

$\Delta H = 0.00120$ h

3.3.5. The formation of Mg.1,N-3-cyanoethynyl-4-cyanomethanyl -4-methyl-5-methynyl Δ^1-NH-pyrrolin-1-yl.porphin^{-1} [1]

The Mg.1,N-2-cyanoethynyl-3-cyanomethanyl-3-methyl-pent-N4-ynyl.porphin^{-1} may easily cyclize,



Mg.1,N-3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-methynyl Δ^1-NH-pyrrolin-1-yl.porphin^{-1} (11) [18]

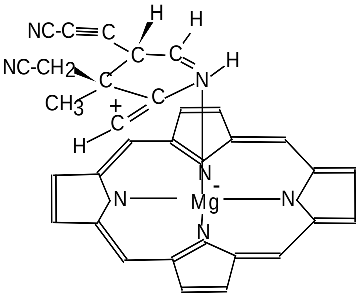
The activation energy was calculated as 0.162 h with the reverse reaction activation energy as 0.048 h at HF level of accuracy.

$\Delta H = 0.13193$ h

3.3.6 The formation of Mg.1,N-3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-methenyl Δ^1-NH-pyrrolin-1-yl.porphin.

With Mg.1,N-3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-methynyl Δ^1-NH-pyrrolin-1-yl.porphin^{-1} the addition of a proton results in the elimination of hydrogen gas in an energetically favourable reaction,

Mg.1,N-3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-methenyl Δ^1-NH-pyrrolin-1-yl.porphin^{-1} + H^+ → H_2 +



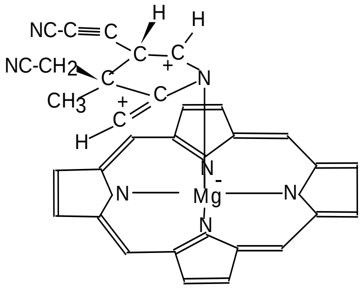
Mg.1,N-3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-methenyl Δ^1-NH-pyrrolin-1-yl. porphin (12) [19]

$\Delta H = -0.36840$ h

3.3.7 The formation of Mg.1,N-3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-methenyl Δ^1-N-pyrrolin-1-yl.porphin$^+$

Further reaction with a proton in an energetically favourable reaction gives a stable pyrroline structure,

Mg.1,N-3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-methenyl Δ^1-NH-pyrrolin-1-yl.porphin + H^+ → H_2 +



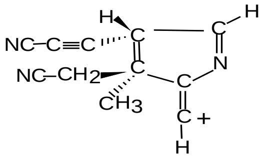
Mg.1,N-3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-methenyl Δ^1-N-pyrrolin-1-yl.porphin$^+$ (13)
[20]

$\Delta H =$ -0.65397 h

3.3.8 The formation of 3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-methenyl Δ^1-pyrroline$^+$

The complex containing a weak charge transfer bond may easily dissociate to give Monomer A and the catalyst in the mildly alkaline medium..

Mg.1,N-3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-methenyl Δ^1-N-pyrrolin-1yl.porphin^{+1} → Mg.porphin +



3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-methenyl Δ^1- pyrroline^{+1} Monomer A (2)
[21]

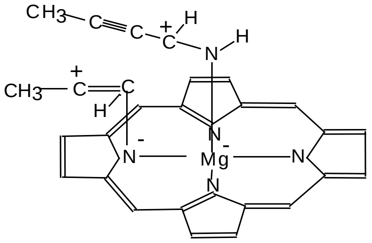
$\Delta H =$ 0.11235 h

3.4 The Formation of monomer B.

3.4.1 The formation of the Mg.1,N-but-2-ynimin-1-yl.porphin.N-propynyl.

A similar weak charge transfer complex may form between but-2-ynimine and the Mg ion of the catalyst Mg.porphin, whilst the propyne forms a weak van der Waals adduct centered on a pyrrole nitrogen atom. The charges on the two adducts are different. Whilst the propyne is marginally negative sharing electrons with the pyrrole-N atom with a calculated charge of -0.013, the but-2ynimine adduct carries a positive charge, calculated as 0.077, giving the catalyst a net positive charge 0.064. When the catalyst is excited with UV radiation an in-plane electronic transition occurs in which the magnetic vector of the radiation is perpendicular to the ring. It is postulated that when the magnetic vector is pointing upwards towards the observer rotation occurs in the anticlockwise direction [11], and this is more effective in causing rotation than when the adduct is forced to the catalyst surface, and a high energy complex is formed, as shown,

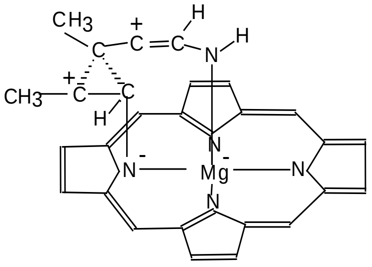
Mg.porphin + CH_3-C≡ C-CH-NH + CH_3-C≡ C-H →



Mg.1,N-but-2-ynimin-1-yl.porphin.N-propynyl (14)
[22]

$\Delta H =$ -0.05094 h

which subsequently bonds,



Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-propenimin-1-yl.porphin (15)

$\Delta H =$ 0.15909 h

The activation energy was calculated as 0.146 h with the activation energy to dissociate the ring as 0.133 h. The adducts carry a net charge of -0.230.

As the enthalpy change is appreciable and positive it is postulated that this occurs by electromagnetic excitation where the first excitation of these very weak complexes requires about 0.21 h.

The high energy di-adduct complex is then susceptible to nucleophilic attack by numerous molecules in various sequences of reactions. Here the reactions given are those that lead to the stereospecificity for ring B depicted in Fig.1 for a corrin derivative with similar stereochemistry to that found in Vitamin B12 [2]

The data for the total energies and zero point energies for the HF and MP2/6-31G* equilibrium geometries for.these molecules and others involved in the synthesis are given in Table.2.

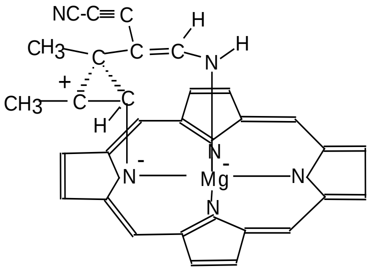
Table 2
MP2 /6-31G* total energies and zero point energies (hartrees) for the respective equilibrium geometries

Molecule	MP2 hartree	ZPE (HF) hartree
Mg.1,N-but-2-ynimin-1-yl.porphin.N-propynyl (14)	-1510.82353	0.43507
Mg.1,N-3-(1-methyl cyclopropen-N2-yl)-2-propenimin-1-yl.porphin (15)	-1510.66357	0.43287
Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-cyanoethynyl propenimin-1-yl.porphin^{-1} (16)	-1679.40291	0.46707
Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-cyanoethynyl propanimin-1-yl.porphin (17)	-1679.90396	0.47850
Mg.1,N-2-cyanoethynyl-3-cyanomethanyl-3-methyl-pent-N4-ethynyl.porphin^{-1} (18)	-1811.73922	0.51275
Mg.1,N-3-cyanoethynyl-4-cyanomethanyl -4-methyl-5-ethynyl Δ^1-NH-pyrrolin-1yl.porphin^{-1} (19)	-1811.79109	0.51530
Mg.1,N-3-cyanoethynyl-4-cyanomethanyl -4-methyl-5-ethenyl Δ^1-NH-pyrrolin-1yl.porphin (20)	-1811.02986	0.49824
Mg.1,N-3-cyanoethynyl-4-cyanomethanyl -4-methyl-5-ethenyl Δ^1-N-pyrrolin-1yl.porphin^{+1}(21)	-1810.32542	0.49206
3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-methenyl Δ^1- pyrroline^{+1} (3)	-625.12035	0.20245

3.4.2. The formation of Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-cyanoethynyl propenimin-N1-yl.porphin.

The high energy complex is subject to nucleophilic reaction with the anion from cyanoacetylene,

Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-propenimin-1-yl.porphin + $NC\text{-}C \equiv C^-$ →



Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-cyanoethynyl propenimin-1-yl.porphin^{-1} (16)
[23]

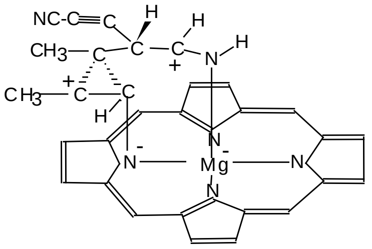
No activation energy is recorded for this addition. The net charge on the adducts was -0.475.

$$\Delta H = -0.23039 \text{ h}$$

3.4.3. The formation of Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-cyanoethynyl propanimin-N1-yl.porphin

The negatively charged adduct may easily react with a proton in an energetic reaction where it is assumed that it preferentially attacks from above the adduct surface,

Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-cyanoethynyl propenimin-1-yl.porphin^{-1} + H^+ →



Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-cyanoethynyl propanimin-1-yl.porphin (17)
[24]

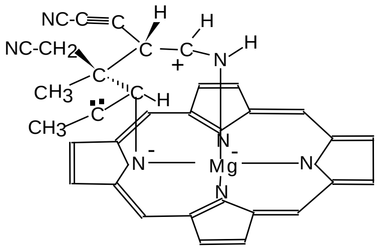
$$\Delta H = -0.49088 \text{ h}$$

No activation energy was recorded for this proton addition. The net charge on the adducts was 0.323.

3.4.4. The formation of Mg.1,N-2-cyanoethynyl-3-cyanomethany-3-methyl-pent-N4-ethynyl.porphin

The strong nucleophile, cyanomethyl anion can open up the complex to form the diadduct, Mg.1,N-2-cyanoethynyl-3-cyanomethanyl-3-methyl-pent-N4-ynyl.porphin^{-1}.

Mg.1,N-2-(1-methyl cyclopropen-N2-yl)-2-cyanoethynyl propanimin-1-yl.porphin + $NC\text{-}CH_2^{-1}$ →

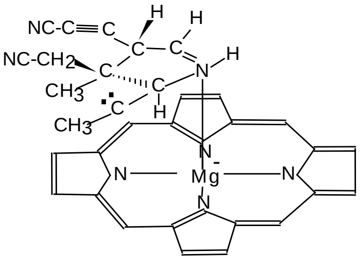


Mg.1,N-2-cyanoethynyl-3-cyanomethanyl -3-methyl-pent-N4-ethynyl.porphin^{-1} (18) [25]

$\Delta H = -0.13276$ h

3.4.5. The formation of Mg.1,N-3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-ethynyl Δ^1-NH-pyrrolin-1-yl.porphin^{-1}.

The Mg.1,N-2-cyanoethynyl-3-cyanomethanyl -3-methyl-pent-N4-ynyl.porphin may easily cyclize,



Mg.1,N-3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-ethynyl Δ^1-NH-pyrrolin-1-yl.porphin^{-1} (19) [26]

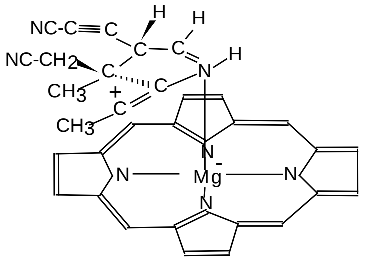
The activation energy was calculated as 0.084 h with 0.115 for the reverse reaction at HF level of accuracy.

$\Delta H = -0.04960$ h

3.4.6 The formation of Mg.1,N-3-cyanoethynyl-4-cyanomethanyl -4-methyl-5-ethenyl Δ^1-NH-pyrrolin-1-yl.

The addition of a proton to the Mg.1,N-3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-methynyl Δ^1-NH-pyrrolin-1-yl.porphin^{-1} results in the elimination of hydrogen gas in an energetically favourable reaction,

Mg.1,N-3-cyanoethynyl-4-cyanomethanyl)-4-methyl-5-ethenyl Δ^1-NH-pyrrolin-1-yl.porphin^{-1} + $H^+ \rightarrow H_2$ +



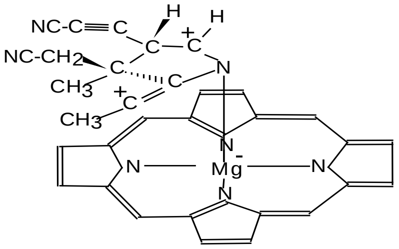
Mg.1,N-3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-ethenyl Δ^1-NH-pyrrolin-1-yl.porphin (20) [27]

$\Delta H = -0.38867$ h

3.4.7 The formation of Mg.1,N-3-cyanoethynyl-4-cyanomethanyl -4-methyl-5-ethenyl Δ^1-N-pyrrolin-1-yl.porphin^{+1}

Further reaction with a proton in an energetically favourable reaction gives a stable pyrroline structure,

Mg.1,N-3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-ethenyl Δ^1-NH-pyrrolin-1-yl.porphin + $H^+ \rightarrow H_2$ +



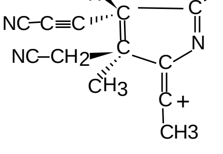
Mg.1,N-3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-ethenyl Δ^1-N-pyrrolin-1yl.porphin^{+1} (21) [28]

$\Delta H = -0.43576$ h

3.4.8 The formation of 3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-ethenyl Δ^1-pyrroline^{+1}

The complex containing a weak charge transfer bond may easily dissociate to give Monomer B and the catalyst.

Mg.1,N-3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-ethenyl Δ^1-N-pyrrolin-1-yl.porphin^{+1} $\rightarrow$ Mg.porphin +



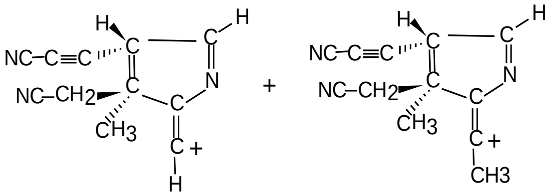
3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-ethenyl Δ^1- pyrroline^{+1} (3) [29]

$\Delta H = +0.08524$ h

It cleaves from the catalyst in the mildly alkaline environment.

4. Conclusion

The synthesis of Monomers A and B as depicted here is predicated on the formation of weak complexes calculated as charge transfer and van der Waals, which may be orientated to form stereospecific di-adducts by the magnetic field of exciting radiation. The monomers A and B are highly reactive and may easily engage in dimerization with an activation energy of 0.157 h, as shown,



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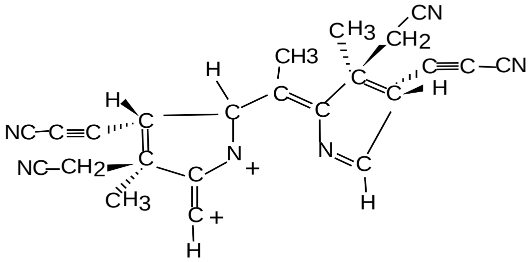
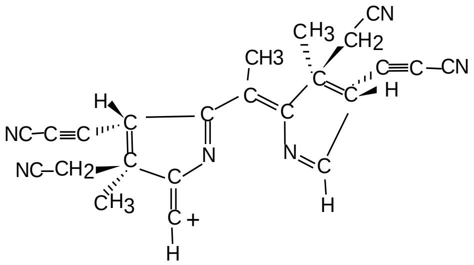


with the subsequent elimination of a proton in the mildly alkaline medium to form a corrin derivative further stabilized by ions such as Mg^{++}.



1-(3-cyanoethynyl-4-cyanomethanyl-4-methyl-5-methenyl Δ1- pyrroline-2yl)-1'-(3-cyanoethynyl-4-cyanomethanyl-4-methyl- Δ1- pyrrolin-5yl) -1-methyl methene^{+}

The enthalpy change was calculated as -0.52798 h.

Further work at a higher accuracy may alter the values given here.

5 Acknowledgements

Appreciation is expressed for the advice and support given to this project by Professor Curt Wentrup of the University of Queensland.

Appreciation is also expressed to the National Computing Infrastructure facility supported by the Australian Government (grant NCI-MAS g01) and QCIF, and the assistance of Mr.D.Green, H.Hartig, M.Hankel and M.Nicholls.

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