Protonation in Hydrocarbons: Allene (C_3H_4), Isobutane (C_4H_{10}), 2-butyne (CH_3CCCH_3), 1, 2-butadiene and 1, 3-butadiene C_4H_6

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Abstract: *It is imperative to note now that experimentally determined Proton Affinities (PAs) do not specify the site of protonation in a molecule (a limitation). Also, assigning only one experimental PA value to a heteronuclear molecule is not ideal as such molecules can have more than one proton afiinity (PA) values. In this current research, the above stated limitations have been fixed for some hydrocarbon molecules (including Allene, CH2CCH2, Isobutane, C4H10, 2-Butyne, CH3CCCH3, 1,2-Butadiene, C4H6, and 1,3-Butadiene, C4H6) using our knowledge of computational chemistry and some eminent and remarkable findings which will go a long way in redefining proton affinity have been made, these are: (i) The most stable protonated analogues are found to be the ones corresponding to the experimentally determined PA values (except in the case of 1,2-butadiene). (ii) PA corresponds to the most stable protonated analogue with the proton attached to the site of less electron density. (ii) "PA corresponds to the most stable protonated analogue with proton attached to the site of higher electron density" (iii) "PA for less stable protonated analogue with proton attached to the site of highest electron density. These are new trends in addition to other known trends.*

Key words: *Proton affinity, protonation, Computational method, Experimental method, hydrocarbons, heteronuclear species, protonated analoguie.*

1. INTRODUCTION

The present world scientific advancement has led to the quest in exploring the interstellar medium (ISM). One of such is the five recent interstellar probes launched by the America's space agency NASA (National Aeronautics and space agency) [1] which is currently in progress with the aim of studying the ISM.[2] A vast number of molecules especially hydrocarbons have been found in the ISM and circumstellar medium [3] with hydrogen been the chief or primary component, [4] most of these occurs as ions, gases or molecules. 80% of the cations have been reported to be made up of protonated molecules, [5, 12] due to the abundant nature of hydrogen in the ISM. Therefore, one way of studying the ISM bores down to uncovering the chemical properties of such interstellar species such as their proton affinity. Proton affinity (PA) can be obtained either experimentally or computationally. Experimentally, PA is obtained using the following procedures: Ion Cyclotron Resonance (ICR), Ion Mobility Spectrometry (IMS), High Pressure Mass Spectroscopy (HPMS), Flame Ion Mass Spectrometry (FIMS), Knudsen Cell Mass Spectrometry (KCMS) and Selected Ion Flow Tubes. [15, 16]

Computationally, PA can be calculated using the Ab-initio methods, molecular mechanics, Density functional methods, chemical dynamics, molecular dynamics, semi-empirical methods and QM/MM. [17] Some of the common Ab-initio methods usually applied in obtaining PA and used in this present work include: HF/6-311++G**, B3LYP/6-311++G**, MP2/6-311++G**, MP2/cc-pVDZ, CCSD/6-311++G**, G4.

Allene (C_3H_4) is a polyene with two double bonds in between two adjacent carbon centres and normallyoccur as pigments in Fucoxanthine and Perdinin. It serves as a ligand in organometallics. [18]

Isobutane (C_4H_{10}) is an isomer of butane usually used as a precursor for isooctane in the refineries and petrochemical industries, [19] also as a refrigerant and as solvents. [20]

2-butyne (CH$_3$CCCH$_3$) also known as crotonylene is an artificially prepared unsaturated hydrocarbon and a member of the alkyne normally used in the synthesis of Hydroquinones that are alkylated (Alkylated hydroquinones) and has a low torsional barrier which makes it of great interest in the field of physical chemistry. [21] 1, 2-butadiene is an isomer of 1, 3-butadiene. Both have the formular C$_4$H$_6$ and are used as monomer in the production of synthetic rubber. [22]

From the understanding that heteronuclear species (e.g. hydrocarbons) can have more than one proton affinity unlike homonuclear species (e.g. H$_2$) which can only have one PA, and also been moved by the finding that only a single proton affinity can until now be determined for a molecules irrespective of the different possible number of sites of protonation and the process been too difficult and at the same time cannot specify the actual site of protonation, And finally, proton affinity is not regular in trend as a new and rare trend in defining PA is possible, thus the aim of this work includes: (i) Using six (6) Ab-initio computational methods to accurately predict the proton affinity of the protonated analogues thereby making it possible for a heteronuclear molecule to have more than one proton affinity. (ii) To specify the best site of protonation in the chosen heteronuclear molecules.(iii)Redefining proton affinity via some new, rare and uncommon trend.

2. METHODOLOGY

Gaussian 09 suite of programs was applied with six Ab-initio computational methods ranging from the Gaussian 04 theory compound method (G4), Moller-Plesset perturbation theory (MP2) at cc-pVDZ basis set, Becke, three-parameter, Lee-Yang-Parr (B3LYP) at 6-311++G** basis set, Moller-Plesset perturbation theory (MP2) at 6-311++G** bais set and the Hartree-Fock (HF) at 6-311++G** were implemented. [23] Preference was placed on these chosen methods based on experience over the years that some methods are more accurate than others and so these methods were carefully selected based on their high performance and accuracy. [5-10]

3. RESULTS AND DISCUSSIONS

3.1. Allene, CH$_2$CCH$_2$

Table1: *PA values for Allene, CH$_2$CCH$_2$*

Method	Proton attached to C2 atom		Proton attached to C1/C3 atom	
	PA (kcal/mol)	Error	PA (kcal/mol)	Error
HF/6-311++G**	197.0129	11.71287	184.3027	-0.99733
B3LYP/6-311++G**	183.8126	-1.48742	177.8148	-7.48515
MP2/6-311++G**	182.7176	-2.58242	173.3238	-11.9762
MP2/cc-pVDZ	185.0795	-0.22047	174.7871	-10.5129
CCSD/6-311++G**	187.4584	2.158414	178.6545	-6.64554
G4	188.4367	3.136701	182.6373	-2.66274
Expt	185.3	NA	185.3	NA

Table2: *Sum of electronic and zero-point Energies for protonated analogues of allene.*

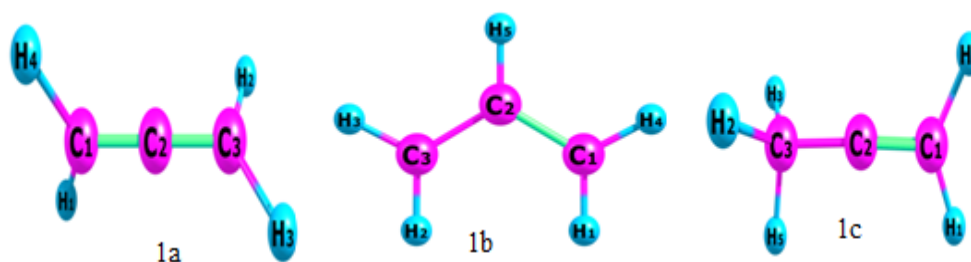| Method	Energy (Hartree/Particle)*	
	C2	C3
HF/6-311++G**	-116.149272	-116.129017
B3LYP/6-311++G**	-116.933485	-116.923927
MP2/6-311++G**	-116.544622	-116.529652
MP2/cc-pVDZ	-116.504493	-116.488091
CCSD/ 6-311++G**	-116.543334	-116.529304
G4	-116.913971	-116.904729

Fig1: *(1a) Optimized geometry of neutral allene, (1b)Geometry for protonation at C2, (1c) Geometry for protonation at C3*

Table 1 presents the calculated PAs of allene CH$_2$CCH$_2$ and its reported experimental value obtained from the NIST website. Table 2 contains the sum of electronic and zero-point energies for the protonated species, their optimized geometries are depicted by fig.1a-c. Allene CH$_2$CCH$_2$ An unsaturated hydrocarbon with three (3) carbon chains and two double bonds has only two possible protonated analogues formed by attaching proton at carbon C2 or C3, Meanwhile, C3 is equivalent to C1 as such similar. The reported observed experimental PA value for allene is 185.3 kcal/mol. Only one value is obtained experimentally and as inappropriate for a heteronuclear specie, also, no specification as to whether the PA value obtained was at C1 or C1/C3. In obtaining this PA values at the two possible site of protonation, we applied six computational methods. The PA value of the protonated analogue which corresponds more to the experimental value and found to be more stable is taken to be the most correct. As shown in table 1, the value 185.0795 kcal/mol predicted by MP2/cc-pVDZ when proton was attached to C2 was outstanding as it corresponds more to the experimental value. As shown in table 1 and 2, the outcome of our calculations reveals that the experimental PA value value of allene corresponds more to the protonated analogue in which the proton is attached to the C2 atom. This protonated analogue is also found to be more stable than the one in which the proton is attached to either the C1 or C3 atom. When proton is attached to C2, -CH$_2$ bears more electron density than C2, therefore, this leaves us with a conjecture that, for allene, "PA corresponds to the most stable protonated analogue with the proton attached to the site of less electron density"

3.2. Isobutane, C4H10

Table 3: *PA values for Isobutane, C$_4$H$_{10}$*

	Proton attached to C1 atom		Proton attached to C4 atom	
Method	PA (kcal/mol)	Error	PA (kcal/mol)	Error
HF/6-311++G**	265.4713	103.4713	138.9388	-23.0612
B3LYP/6-311++G**	170.4705	8.470477	142.626	-19.374
MP2/6-311++G**	154.2889	-7.71111	140.1084	-21.8916
MP2/cc-pVDZ	154.8016	-7.19843	140.6594	-21.3406
CCSD/6-311++G**	163.0245	1.02445	140.8596	-21.1404
G4	172.7	10.70002	145.1975	-16.8025
Expt	162.0	NA	162.0	NA

Table 4: *Sum of electronic and zero-point Energies for protonated analogues of isobutane.*

Method	Energy (Hartree/Particle)*	
	C1	C4
HF/6-311++G**	-157.483706	-157.423757
B3LYP/6-311++G**	-158.647315	-158.602942
MP2/6-311++G**	-158.079165	-158.056567
MP2/cc-pVDZ	-158.015385	-157.992848
CCSD/ 6-311++G**	-158.091406	-158.056084
G4	-158.617529	-158.573701
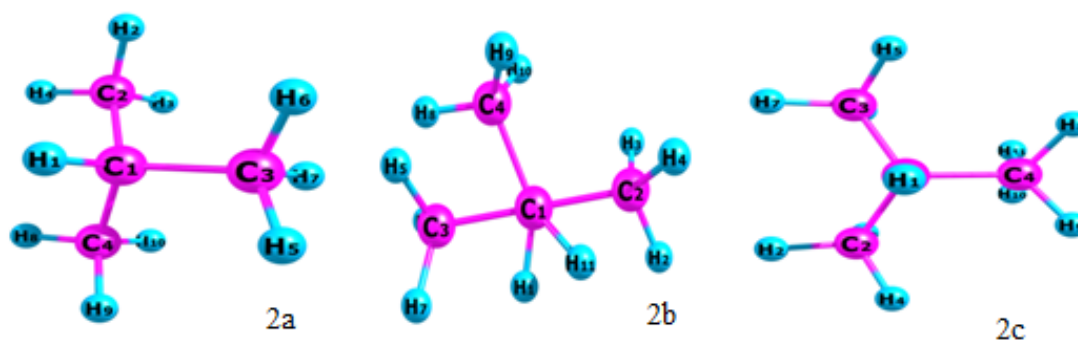
Fig2: *(2a) Optimized geometry of neutral isobutene, (2b) Geometry for protonation at C1, (2c) Geometry for protonation at C4*

As depicted in fig. 2a, isobutane (2-methylpropane, an isomer of butane) is a hydrocarbon with four (4) total hydrogen atoms and ten (10) hydrogen atoms. Unexpectedly, it has only two (2) protonated analogues, one obtained by the attachment of proton to carbon C1 and the other to C2 as shown by fig

2b-c, C2 is equivalent to C3 and C4. Table 3 contains the calculated and the experimental PA values for isobutane and its protonated analogues while table 4 presents the sum of electronic and zero-point energies for the protonated analogues. From NIST, the reported experimental PA value for isobutane is 162.0 kcal/mol. Analysis of the results in table 1 reveals that the best computational method is CCSD/6-311++G** reason been that it recorded the least and minimal error of 1.0245 kcal/mol when proton was attached to C1. The calculated PA values when proton was attached to C1 generally corresponds more to the experimental value than those with C2, C3 or C4. This protonated analogue was also found to be more stable than the others. This deduction is in line with our proposed trend in protonation of allene above which state that "PA corresponds to the most stable protonated analogue with the proton attached to the site of less electron density" this holds true for isobutane on account that the experimentally reported PA for isobutane corresponds more to when proton was attached to C1 which is also more stable (table 2, with the least energy) and C1 still has less electron distribution.

3.3. 2-Butyne, CH3CCCH3

Table 5: *PA values for 2-Butyne, CH₃CCCH₃*

Method	Proton attached to C2 atom		Proton attached to C1/C4 atom	
	PA (kcal/mol)	Error	PA (kcal/mol)	Error
HF/6-311++G**	185.9342	0.534193	129.0693	-56.3307
B3LYP/6-311++G**	182.8167	-2.58327	152.0512	-33.3488
MP2/6-311++G**	172.0273	-13.3727	129.8229	-55.5771
MP2/cc-pVDZ	173.3263	-12.0737	130.8903	-54.5097
CCSD/6-311++G**	181.3094	-4.09055	131.1627	-54.2373
G4	187.9077	2.50771	157.097	-28.303
Expt	185.4	NA	185.4	NA

Table 6: *Sum of electronic and zero-point Energies for protonated analogues of 2-butyne.*

Method	Energy (Hartree/Particle)*	
	C2	C1/4
HF/6-311++G**	-155.157	-155.067
B3LYP/6-311++G**	-156.234	-156.185
MP2/6-311++G**	-155.709	-155.641
MP2/cc-pVDZ	-155.652	-155.584
CCSD/ 6-311++G**	-155.706	-155.626
G4	-156.208	-156.159
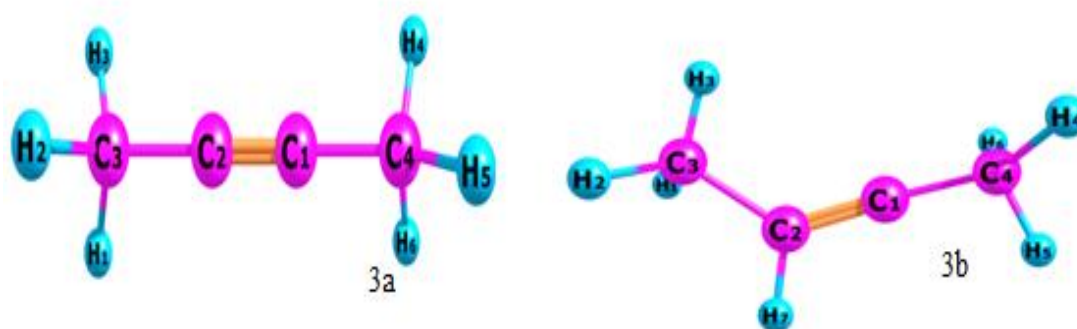
Fig3: (*3a) Optimized geometry for neutral 2-butyne, (3b) Goemetry for protonation at C2*

In 2-butyne, when a proton is attached to the C4, it optimizes to the same structure as when proton is attached to C3 and therefore, C3 is equivalent to C2, likewise C2 to C1. As such, only two protonated analogues are possible for 2-butyne as shown in Fig.3a-b. As reported by NIST and contained in table 5, the observed experimental value for 2-butyne is 185.4 kcal/mol placing our value of 185.9342 kcal/mol obtained when proton is attached to C2 using the Hartree-Fork method at 6-311++G** basis set a priority and best method with a very minimal error of 0.534193 kcal/mol. This protonated analogue (C2) is also found to be more stable as it has the least energy as shown in table 6. Since C2 is a site of higher electron density brought about by the pi-bond electron, this therefore follow the common trend that in 2-butyne, "PA corresponds to the most stable protonated analogue with proton attached to the site of higher electron density.

3.4.1, 2-Butadiene, C4H6

Table 7: *PA values for 1,2-Butadiene, C$_4$H$_6$*

Method	Proton attached to C4 atom		Proton attached to C3 atom		Proton attached to C1 atom		Proton attached to C2 atom	
	PA (kcal/mol)	Error	PA (kcal/mol)	Error	PA (kcal/mol)	Error	PA (kcal/mol)	Error
HF/6-311++G**	191.6226	5.422567	208.4128	22.21284	185.9078	-0.29216	166.5812	-19.6188
B3LYP/6-311++G**	184.8423	-1.35767	198.5572	12.35717	179.6127	-6.58734	159.7915	-26.4085
MP2/6-311++G**	183.4907	-2.70933	194.7676	8.567644	174.9754	-11.2246	153.9714	-32.2286
MP2/cc-pVDZ	184.6547	-1.5453	197.1898	10.98983	176.3502	-9.84976	154.5631	-31.6369
CCSD/6-311++G**	184.9553	-1.24472	199.6365	13.43649	180.35	-5.85001	157.8952	-28.3048
G4	189.8197	3.619732	203.2051	17.00514	184.3435	-1.85654	164.351	-21.849
Expt	186.2	NA	186.2	NA	186.2	NA	186.2	NA

Table 8: *Sum of electronic and zero-point Energies for protonated analogues of 1,2-Butadiene, C$_4$H$_6$.*

Method	Energy (Hartree/Particle)*			
	C4	C3	C1	C2
HF/6-311++G**	-155.157	-155.184	-155.148	-155.117
B3LYP/6-311++G**	-156.235	-156.256	-156.226	-156.195
MP2/6-311++G**	-155.716	-155.734	-155.702	-155.668
MP2/cc-pVDZ	-155.659	-155.679	-155.645	-155.611
CCSD/ 6-311++G**	-155.706	-155.73	-155.699	-155.663
G4	-156.209	-156.23	-156.2	-156.168
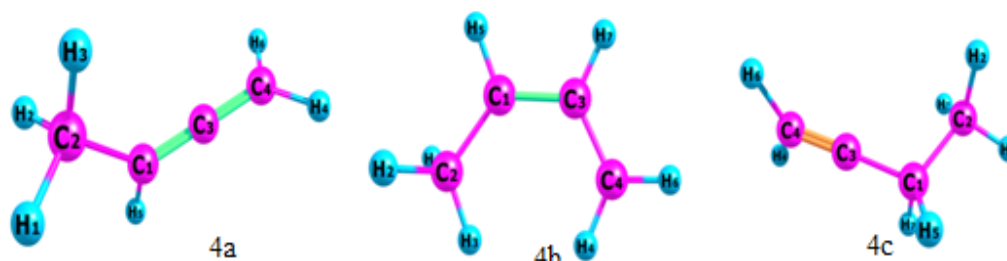
Fig4: *(4a) Optimized geometry for 1, 2-Butadiene, (4b) Geometry for the protonation at C3, (4c) Geometry for the protonation at C1*

A rare trend has to be introduced in elucidating the PA of 1,2-butadiene, thus helping in redefining PA. 1, 2-butadiene is grouped into a rare trend which is "PA for less stable protonated analogue with proton attached to the site of highest electron density"

As expected, 1, 2-butadiene has four (4) possible protonated analogues formed when proton is attached to C1, C2, C3, and C4 respectively. As shown in table 7, out of the six computational methods applied, two methods were noticeable and distinguished; HF/6-311++G** with a superior prediction of the PA of 1,2-biitadiene as 185.9078 kcal/mol (0.29216 kcal/mol error) as against the experimental value of 186.2 kcal/mol while the other second outstanding method is CCSD/ 6-311++G** with a very close prediction of 184.9553 kcal/mol (-1.24472 kcal/mol error), but on the general, the experimental PA value corresponds to the protonated analogue in which the proton is attached to the C4 atom. However, this is not the most stable protonated analogue. The protonated analogue in which the proton is attached to the C3 atom is found to be more stable than all other protonated analogues. This behavior is obvious on account that C3 has an extra pi-bond electron which increases its electron density, thereby holding our assertion true.

3.5.1, 3-Butadiene, C4H6

Table 9: *PA values for 1, 3-Butadiene, C4H6*

Method	Proton attached to C1 atom		Proton attached to C2 atom	
	PA (kcal/mol)	Error	PA (kcal/mol)	Error
HF/6-311++G**	199.0485	11.84851	185.4096	-1.7904
B3LYP/6-311++G**	191.8585	4.65851	181.0685	-6.13152
MP2/6-311++G**	185.451	-1.74899	183.1173	-4.0827
MP2/cc-pVDZ	187.5532	0.353168	183.7693	-3.43071
G4	197.4634	10.26342	187.1566	-0.04342
Expt	187.2	NA	187.2	NA

Table 10: *Sum of electronic and zero-point Energies for protonated analogues of 1,3-Butadiene.*

Method	Energy (Hartree/Particle)*	
	C1	C2
HF/6-311++G**	-155.184	-155.162
B3LYP/6-311++G**	-156.256	-156.239
MP2/6-311++G**	-155.733	-155.730
MP2/cc-pVDZ	-155.679	-155.673
G4	-156.23	-156.213
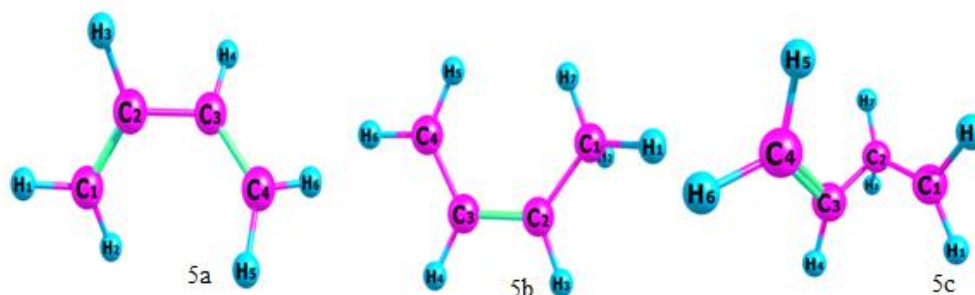
Fig.5: *5a. Optimized geometry of 1, 3-Butadiene. 5b. Geometry for protonation at C1. 5c. Geometry for protonation at C2*

Table 1 contains the calculated PA values of 1,3-butadiene obtained using five different computational methods and the reported experimental value of 187.2 kcal/mol from the NIST. Unexpectedly, 1,3-butadiene has only two (2) protonated analogues due to equivalency, protonation at C4 atom optimizes to similar structure as protonation at C1, therefore C1 and C4 are equivalent whereas C2 and C3 are also equivalent giving rise to two protonated analogues as shown in Fig.5a-c. in general for 1,3-butadiene, the computational method with the best prediction is the G4 method, it recorded a near perfect PA value of 187.1566 kcal/mol (0.04342 kcal/mol error). The experimental PA value corresponds to the protonated analogue in which proton is attached to C1 atom. As shown in table 2, this protonated analogue is also found to be more stable than the one in which proton is attached to C2 atom. Meanwhile, the C2 atom has a higher electron density due to the pi-bond electron while C1 has less electron density. This deduction corresponds with the common PA trend that "PA corresponds more to the most stable protonated analogue with proton attached to the site of less electron density

4. CONCLUSION

The protonation of Allene (C$_3$H$_4$), Isobutane (**C$_4$H$_{10}$**), 2-butyne (CH$_3$CCCH$_3$), 1,2-butadiene and 1,3-butadiene C$_4$H$_6$ have been investigated Using the Ab-initio computational methods. The best method have been ascertained by taking the difernece between the calculated and the experimental values. Generally, MP2/cc-PVDZ, CCSD/6-311++G**, HF/6-311++G** and the G4 method gave the best predictions for the different molecules. The six (6) computational methods indicate the best sites of protonation for the various molleecules via stability checks and follow the trends: (i) The most stable protonated analogues are found to be the ones corresponding to the experimentally determined PA values (except in the case of 1,2-butadiene). (ii) PA corresponds to the most stable protonated analogue with the proton attached to the site of less electron density. (ii) "PA corresponds to the most stable protonated analogue with proton attached to the site of higher electron density" (iii) "PA for less stable protonated analogue with proton attached to the site of highest electron density.

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