Theoretical Investigation of Intermolecular Dihydrogen Bonds in C₂H₂···HM and C₂H₄···HM (M = Li, Na and K) Complexes: A DFT and *ab initio* Study

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This study aims to investigate the dihydrogen bond formation in ethyne (C_2H_2) and ethene (C_2H_4) with alkali metal hydrides (HM; M = Li, Na and K) complexes using density functional theory (DFT) and *ab initio* methods. It mainly focuses on the comparison of the performances of different functionals of DFT and *ab initio* method on the intermolecular dihydrogen bonded complexes. The geometrical parameter and energy values agree with the formation of dihydrogen bonds in the complexes. Among the ethyne and ethene complexes, the smallest dihydrogen bond distance was formed by C_2H_2···HK and C_2H_4···HK, respectively. The C_2H_2 is found to form better dihydrogen bond (DHB) with alkali metal hydrides than C_2H_4. Among all the functionals, M06L was observed to predict shortest H···H bond distance, while M062X the longest. Natural bond orbital (NBO), quantum theory of atom in molecules (QTAIM) along with molecular electrostatic potential (MEP) analysis further confirms the dihydrogen bond formation.

Keywords: Alkali hydrides, Dihydrogen bond, Density functional theory, Hybrid functionals.

INTRODUCTION

During the last few decades, several researchers [1,2] have focussed their attention in the study of non-covalent interaction due to their significant effect in hydrogen storage, biological process, molecular recognition, crystal engineering, catalytic process and material chemistry. Of the various non-covalent interactions, hydrogen bond and dihydrogen bond (DHB) are the most fascinated subject of investigation [3]. The dihydrogen bond is an electrostatic interaction formed between two different hydrogen atoms that have opposite charges. That is, one acts as a proton donor and other as a proton acceptor causing them to electrostatically interact with each other, provided that their intermolecular separation should be less than the van der Waals radii of both the hydrogen atoms summed up together [4,5]. It is designated as X-H···H-M where 'X' represents hydrocarbon and 'M' represents the metal to which the hydrogen is bonded. These interactions are formed due to the close approach of hydridic hydrogen and protonic hydrogen causing a charge separation which results in an attractive pull. The existence of DHB has been proved in the literature [6-8]. All these factors were governed

by the property of hydrogen atom to exist in H⁺ or H⁻ state that makes them attractive electrostatically in a molecule [9].

Many experimental and theoretical studies in identifying the DHB formation are found in the literature [10-12]. Yao & Ren [11] studied the dihydrogen bond formation between HB=BH and HM (M = Li, Na, K, BeH, MgH or CaH) complexes, to check whether B-H can be the proton donor or not in the system formed. Cybulski *et al.* [12] have reported the formation of several dihydrogen bonded complexes such as $LiH···H_2$, $LiH···CH_4$, $LiH···C_2H_2$, $LiH···C_2H_6$ in the gas phase and identified that density functional theory (DFT) gives an accurate result for the interaction energy and spin-spin coupling constant than coupled cluster (CCSD). Lu *et al.* [13] studied the dihydrogen bond (DHB) in CaH_2···HY (Y = CH_3, C_2H_3, C_2H, CN and NC) complexes and identified both linear and bent structures using B3LYP and MP2 methods. Alkorta *et al.* [14] while studying the weak interaction in different complexes using *ab initio* method at different basis sets identified DHB in few complexes along with X-H···σ interactions.

Ethyne (C_2H_2) and ethene (C_2H_4) are found to be the derivatives of unsaturated hydrocarbons with importance in indus-

tries as raw materials and as an energy sources [15]. Several studies on the dihydrogen bond interactions between alkali metal hydrides and proton donors are reported because of their importance in high volumetric and gravimetric capacities [10-12,16]. Hence, in this study we have focused on the study of DHB formation between hydrocarbons (C_2H_2 and C_2H_4) and alkali metal hydrides (M = Li, Na and K). A benchmark study of density functional theory (DFT) and *ab initio* methods was performed in order to identify the best appropriate method for dihydrogen bonded interaction. Comparison of the impact of different functionals on these DHB complexes is necessary as it will aid the researchers in selecting the functional/methods to better understand the behaviour and properties of various DHB systems.

COMPUTATIONAL METHODS

In this study, a systematic theoretical investigation of the dihydrogen bonded complexes formed by C_2H_2 and C_2H_4 with HM (M = Li, Na and K) was performed using stand-alone hybrid functionals in density functional theory (DFT) and *ab initio* methods. Several DFT functionals were selected *e.g.* PBEPBE [17], B3LYP [18], B3PW91 [19], CAM-B3LYP [20], LC-BLYP [21], HSEH1PBE [22], M062X [23], M06L [24], ωB97XD [25] and *ab initio* methods [26-28] (MP2, MP3 and CCSD) employed along with the 6-311++G** basis set. The vibrational analysis confirmed all the structures to have no imaginary frequencies and hence to occupy the local minima. Interaction energy (ΔE^C) gives the information about how the system energy varies when the individual structures combine to form a complex. ΔE^C requires few corrections, which normally includes the influence of the functional of nearby compounds expressed as basis set superposition error (BSSE) which was corrected using Boys & Bernardi method called the counterpoise correction [29], given by the following equation:

$$\Delta E^C = E_{AB} - E_A - E_B + BSSE \qquad (1)$$

where E_{AB} is the energy of the dihydrogen bonded complex, E_A and E_B are the energies of individually optimized hydrocarbon and metal hydride, respectively.

The strength of dihydrogen bonds were analyzed in terms of electron density distribution and population for all the selected

functionals using the quantum theory of atoms in molecules (QTAIM) [30] and natural bond orbital (NBO) analysis [31,32], respectively. This will provide a proper knowledge about the atomic level behavior of the DHB systems. Additionally, to know the nature of H···H interaction, we also carried out charge analysis using molecular electrostatic potential (MEP) by M06L method [2]. All the structures were constructed using Chemcraft [33] software and the calculations were performed by Gaussian 09 program package [34].

RESULTS AND DISCUSSION

Structural parameters: The isolated complexes of C_2H_2 and C_2H_4 with HM (M=Li, Na and K) were optimized using various DFT and *ab initio* methods and are listed in Table-1. All the structures were optimized at B3LYP level of theory and are depicted in Fig. 1. Since, the geometrical structures obtained from other potentials are almost similar to B3LYP, are not shown. Dihydrogen bonds play a major role in the geometry of the molecules and the H···H bond distance is what administers all the properties of these molecules. The H···H bond distance varies for all the complexes in the range of 1.835-2.528 Å (Table-1) with the change in the functional. The structural difference in C_2H_2 and C_2H_4 causes the dihydrogen bond distance to vary for the same metal hydride, making it incomparable with each other. In the case of C_2H_2 involving complexes, the functional predicts the DHB distance to be in the range of 1.835-2.116 Å. The bond distance varies with the interacting metal hydrides in the order of C_2H_2···HK < C_2H_2···HNa < C_2H_2···HLi for most of the functionals. This implies that better dihydrogen bond is formed for K-H bonded hydrocarbons than Na-H and Li-H. The functional also shows different bond distance in each of the cases such that it varies in the order of M06L < PBEPBE < HSEH1PBE < B3PW91 < LC-BLYP < B3LYP < CAM-B3LYP < ωB97XD < M062X < MP2 < MP3 < CCSD as clearly observed from Fig. 2.

Similarly, the DHB distance varies in the case of C_2H_4 complexes are in the range of 2.173-2.528 Å. The order of bond distance for C_2H_4 with metal hydrides is similar to C_2H_2 geometry predicting K-H to be the most stable alkali metal hydride. However, among the other two, Na-H is found to have better bonding than Li-H. C_2H_4 with Li-H has its bond distance

TABLE-1
DIHYDROGEN BOND DISTANCE (Å) OF ALL THE COMPLEXES OPTIMIZED USING DIFFERENT HYBRID FUNCTIONALS AT 6-311++G** BASIS SET

Functionals	C_2H_2···HLi	C_2H_2···HNa	C_2H_2···HK	C_2H_4···HLi	C_2H_4···HNa	C_2H_4···HK
PBEPBE	1.921	1.921	1.882	2.247	2.227	2.195
B3LYP	2.010	2.013	1.974	2.398	2.388	2.337
B3PW91	1.987	1.984	1.934	2.400	2.396	2.309
CAM-B3LYP	2.012	2.014	1.975	2.363	2.361	2.311
HSEH1PBE	1.943	1.945	1.909	2.267	2.255	2.217
LC-BLYP	2.006	2.005	1.970	2.307	2.306	2.272
M062X	2.022	2.023	1.984	2.528	2.506	2.426
M06L	1.884	1.867	1.835	2.245	2.222	2.173
ωB97XD	2.022	2.020	1.962	2.322	2.303	2.275
MP2	2.049	2.042	1.983	2.405	2.388	2.322
MP3	2.076	2.078	2.011	2.423	2.412	2.338
CCSD	2.104	2.116	2.041	2.471	2.473	2.383
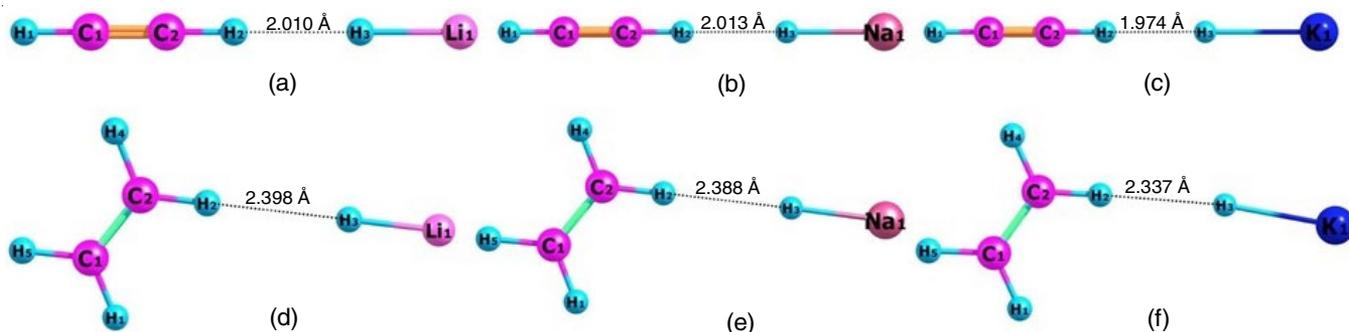
Fig. 1. Optimized structures of (a) C₂H₂···HLi, (b) C₂H₂···HNa, (c) C₂H₂···HK, (d) C₂H₄···HLi, (e) C₂H₄···HNa and (f) C₂H₄···HK at B3LYP/6-311++G** level of theory
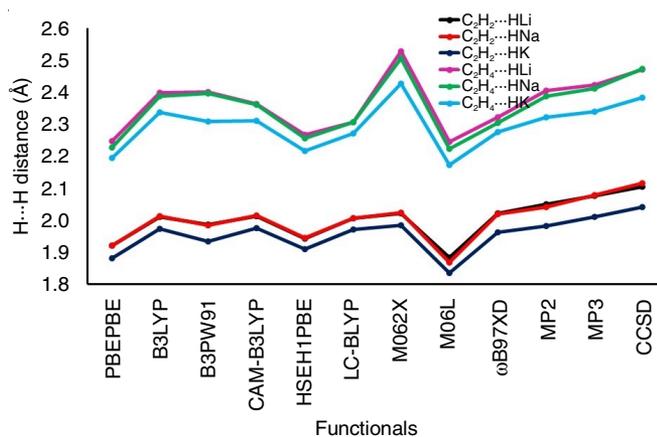

Fig. 2. Graphical representation of DHB distance versus various functionals of all the complexes

ranging from 2.245-2.528 Å which is in the order of M06L < PBEPBE < HSEH1PBE < LC-BLYP < ωB97XD < CAM-B3LYP < B3LYP < B3PW91 < MP2 < MP3 < CCSD < M062X. C₂H₄ with NaH has its bond distance ranging from 2.222-2.506 Å which is in the order of M06L < PBEPBE < HSEH1PBE < ωB97XD < LC-BLYP < CAM-B3LYP < B3LYP < MP2 < B3PW91 < MP3 < CCSD < M062X. The C₂H₄ with KH has its bond distance ranging from 2.173-2.426 Å, which is in the order of M06L < PBEPBE < HSEH1PBE < LC-BLYP < ωB97XD < B3PW91 < CAM-B3LYP < MP2 < B3LYP < MP3 < CCSD < M062X.

Among the functional M062X predicts the largest DHB distance for all the complexes and it seems to be comparatively high (2.426-2.528 Å) for C₂H₄···HM complexes. From the DHB distance, it is understood that C₂H₂ shows more tendencies to form a better dihydrogen bond with alkali metal hydrides than C₂H₄. Few changes are also noted in the bond distance of hydrogen due to complexing which further proves the effect of dihydrogen bond interaction on a system.

Interaction energy: The BSSE corrected interaction energies of the complexes are shown in Table-2. From the energy values, we recognize that the dihydrogen bond formation very much depends on the interacting molecule (ie., alkali metals). Under different functionals, C₂H₂ and C₂H₄ with alkali metal hydrides exhibit different values in their ΔE^C. For C₂H₂···HLi and C₂H₂···HNa, the ΔE^C ranges from -2.604 to -4.367 kcal/mol in the order HSEH1PBE > LC-BLYP > M06L > wB97XD > wB97XD > PBEPBE > M062X > MP2 > CAM-B3LYP > B3LYP > B3PW91 > MP3 > CCSD, and -3.250 to -4.832 kcal/mol in the order M06L > wB97XD > HSEH1PBE > LC-BLYP > M062X > PBEPBE > MP2 > CAM-B3LYP > MP3 > B3LYP > B3PW91 > CCSD respectively. In case of C₂H₂···HK the ΔE^C ranges from -4.016 to -5.924 kcal/mol where the ΔE^C shown by the functional are in the order of M06L > LC-BLYP > HSEH1PBE > wB97XD > M062X > PBEPBE > MP2 > CAM-B3LYP > B3PW91 > B3LYP > MP3 > CCSD. C₂H₄ has ΔE^C ranging from -0.195 to -1.618 kcal/mol, -0.853 to -1.733 kcal/mol and -0.502 to -2.309 kcal/mol for C₂H₄···HLi, C₂H₄···HNa

TABLE-2
BSSE CORRECTED INTERACTION ENERGY (ΔE^C, kcal/mol) OF ALL THE COMPLEXES OPTIMIZED USING DIFFERENT FUNCTIONALS

Functionals	C₂H₂···HLi	C₂H₂···HNa	C₂H₂···HK	C₂H₄···HLi	C₂H₄···HNa	C₂H₄···HK
PBEPBE	-4.148	-4.060	-5.296	-1.073	-1.625	-2.309
B3LYP	-3.571	-3.521	-4.587	-1.054	-1.030	-1.355
B3PW91	-3.432	-3.583	-4.682	-0.796	-0.853	-1.231
CAM-B3LYP	-3.810	-3.884	-4.938	-1.236	-1.267	-1.644
HSEH1PBE	-4.367	-4.398	-5.502	-1.544	-1.594	-2.034
LC-BLYP	-4.316	-4.381	-5.521	-1.549	-1.637	-2.115
M062X	-4.011	-4.147	-5.304	-1.618	-1.733	-2.204
M06L	-4.280	-4.832	-5.924	-1.142	-1.694	-2.159
ωB97XD	-4.161	-4.474	-5.459	-1.513	-1.668	-2.008
MP2	-3.903	-3.891	-5.271	-1.255	-0.879	-1.719
MP3	-3.219	-3.847	-4.173	-1.431	-1.450	-1.632
CCSD	-2.604	-3.250	-4.016	-0.195	-0.860	-0.502

and $C_2H_4 \cdots HK$, respectively and each of the functional follow different order. Both the hydrocarbons (C_2H_2 and C_2H_4) show the interaction energy (ΔE^C) ranges to be in the order of KH > NaH > LiH for all the alkali metal hydrides among which KH interacted complexes have more interaction thereby signifying to be the most stable DHB complexes.

Vibrational frequencies: The selected vibrational frequencies (cm⁻¹) and corresponding intensities (km mol⁻¹) of the monomers and their complexes are listed in Tables 3 and 4. The H···H stretching frequencies of the complexes are in the range of 60 to 150 cm⁻¹ for all levels of theory and indicated the formation of DHB interactions. Datka & Kukulska-Zajac

TABLE-3
SELECTED VIBRATIONAL MODES (cm⁻¹) AND CORRESPONDING INTENSITIES (km/mol)
OF THE ISOLATED MONOMERS OBTAINED AT DIFFERENT FUNCTIONALS

Structures	PBEPBE	B3LYP	B3PW91	CAM-B3LYP	HSEH1PBE	LC-BLYP	M062X	M06L	ωB97XD	MP2	MP3	CCSD
C-H of C_2H_2	3453	3520	3528	3535	3538	3554	3542	3494	3529	3546	3570	3535
C-H of C_2H_4	3074	3136	3147	3161	3159	3192	3165	3139	3160	3192	3197	3171
Li-H	1366	1408	1395	1425	1398	1447	1424	1378	1348	1432	1427	1407
	(146)	(180)	(195)	(203)	(187)	(228)	(213)	(229)	(240)	(222)	(208)	(177)
Na-H	1136	1167	1158	1196	1160	1226	1195	1117	1100	1182	1179	1150
	(175)	(219)	(246)	(275)	(233)	(322)	(283)	(298)	(337)	(304)	(281)	(210)
K-H	953	975	976	999	982	1025	986	1014	1016	1012	1007	977
	(369)	(434)	(478)	(511)	(455)	(556)	(473)	(530)	(551)	(540)	(503)	(383)

TABLE-4
CALCULATED FREQUENCIES (cm⁻¹) AND CORRESPONDING INTENSITIES (km/mol)
OF THE COMPLEXES OBTAINED AT DIFFERENT FUNCTIONALS

Complexes		PBEPBE	B3LYP	B3PW91	CAM-B3LYP	HSEH1PBE	LC-BLYP
$C_2H_2 \cdots HLi$	H···H	146 (1)	136	135	139	148	145
	C-H	3163 (588)	3282 (461)	3269 (486)	3305 (433)	3269 (508)	3326 (423)
	Li-H	1424 (320)	1458 (339)	1444 (373)	1475 (356)	1457 (359)	1503 (377)
$C_2H_2 \cdots HNa$	H···H	100 (0)	94	113 (24)	97	101	102
	C-H	3151 (739)	3272 (583)	3250 (634)	3292 (539)	3112 (36)	3179 (17)
	Na-H	1200 (370)	1224 (409)	1143 (503)	1254 (469)	1227 (439)	1289 (514)
$C_2H_2 \cdots HK$	H···H	93	88	91	91	95	95
	C-H	3073 (1059)	3210 (800)	3176 (857)	3232 (703)	3182 (874)	3252 (645)
	K-H	1038 (674)	1050 (720)	1055 (794)	1076 (782)	1070 (753)	1105 (804)
$C_2H_4 \cdots HLi$	H···H	103 (9)	84 (12)	79 (14)	93 (10)	104 (11)	107 (8)
	C-H	3028 (36)	3123 (18)	3132 (19)	3148 (17)	3144 (20)	3180 (15)
	Li-H	1389 (207)	1427 (244)	1411 (267)	1446 (266)	1422 (254)	1474 (282)
$C_2H_4 \cdots HNa$	H···H	79 (8)	61 (14)	61 (14)	70 (10)	79 (10)	81 (8)
	C-H	3022 (43)	3132 (23)	3132 (23)	3147 (20)	3143 (23)	3179 (17)
	Na-H	1163 (242)	1176 (337)	1176 (337)	1220 (357)	1189 (313)	1260 (124)
$C_2H_4 \cdots HK$	H···H	82 (23)	70 (39)	70 (41)	76 (34)	83 (31)	85 (11)
	C-H	3002 (95)	3118 (29)	3127 (29)	3142 (26)	3139 (29)	3174 (21)
	K-H	991 (471)	1004 (551)	1007 (605)	1031 (625)	1023 (562)	1060 (658)
Complexes		M062X	M06L	ωB97XD	MP2	MP3	CCSD
$C_2H_2 \cdots HLi$	H···H	138	164 (1)	137	135	133	129
	C-H	3297 (425)	3208 (626)	3291 (443)	3350 (377)	3379 (339)	3359 (321)
	Li-H	1474 (376)	1450 (454)	1434 (370)	1477 (370)	1477 (347)	1457 (313)
$C_2H_2 \cdots HNa$	H···H	97	114 (0)	94	95	93	89
	C-H	3147 (15)	3167 (822)	3145 (23)	3328 (493)	3363 (442)	3328 (493)
	Na-H	1253 (487)	1189 (564)	1214 (465)	1227 (501)	1226 (474)	1200 (402)
$C_2H_2 \cdots HK$	H···H	106 (44)	102 (0)	95	92	92	88
	C-H	3253 (659)	3101 (1027)	3215 (691)	3267 (659)	3307 (589)	3298 (596)
	K-H	1094 (737)	1108 (905)	1110 (819)	1073 (812)	1067 (769)	1043 (670)
$C_2H_4 \cdots HLi$	H···H	113 (0)	114 (41)	21 (29)	91 (23)	89 (26)	84 (23)
	C-H	3149 (11)	3127 (19)	3149 (20)	3189 (14)	3186 (13)	3162 (12)
	Li-H	1453 (243)	1419 (278)	1419 (300)	1451 (283)	1450(265)	1429 (232)
$C_2H_4 \cdots HNa$	H···H	93 (35)	102 (2)	97 (0)	71 (27)	70 (32)	122 (3)
	C-H	3147 (15)	3096 (56)	3145 (23)	3179 (18)	3184 (17)	3075 (27)
	Na-H	1245 (202)	1157 (379)	1201 (410)	1199 (388)	1197 (362)	1213 (292)
$C_2H_4 \cdots HK$	H···H	89 (5)	95 (3)	89 (57)	36 (128)	36 (110)	34 (123)
	C-H	3139 (22)	3075 (102)	3139 (28)	3148 (36)	3156 (29)	3156 (25)
	K-H	1044 (503)	1098 (633)	1039 (649)	1027 (628)	1020 (589)	995 (497)

[35] experimentally studied the alkenes family and found C-H stretching vibrations to be in the range of 3100-3000 cm⁻¹. Singh *et al*. [36] theoretically reported dihydrogen bonds between C_2H_2 and borane trimethylamine complexes and observed that the C-H stretching vibrations are in the range of 3400-3100 cm⁻¹ [36]. In present case, the C-H stretching vibrations of Li-H complexes are in the range of 3379-3028 cm⁻¹ for all the levels which is decreased by -46 to -167 cm⁻¹ from their respective monomers. Similarly, C-H bonds of Na-H and K-H complexes are red-shifted by -4 to -207 cm⁻¹ and -18 to -263 cm⁻¹, respectively from their corresponding monomers and matched well with the earlier reported results [35-37]. The isolated Li-H stretching frequencies are in the range of 1447-1348 cm⁻¹ which upon complexation increased by 23-56 cm⁻¹ resulting in a blue shift. Similarly, Na-H and K-H involving complexes of Na-H and K-H stretching frequencies are also blue shifted from the corresponding monomer.

Natural bond orbital (NBO) analysis: The natural bond orbitals (NBO) analysis was performed to examine the delocalization interaction between occupied Lewis type NBO orbitals (lone pair or bonding) to unoccupied non-Lewis type NBO orbitals (Rydberg or anti-bonding) orbitals. It corresponds to a donor-acceptor interaction explaining intra- and intermolecular interactions [38,39]. To gain a better understanding into the nature, the NBO calculations were carried out at different functionals with 6-311++G** basis set. In all complexes, electron exchange was observed between two molecules causing the formation of dihydrogen bond. The stabilization energy (E(2)) (kcal/mol) that defines the strength of donor-acceptor interaction is listed in Table-5, along with the energy splitting of donor and acceptor orbitals ($E_j - E_i$) and the element of Fock matrix ($F_{i,j}$) describing their interaction. The stabilization energy E(2) of the complexes are found to be in the range of 0.56-11.11 kcal/mol. Among all the complexes, more E(2) is observed for C_2H_2···HK complex which has the smallest DHB distance and more interaction energy. Among the functionals, M06L and M062X give the maximum and least E(2) values for all C_2H_4 complexes making the latter not appropriate.

QTAIM analysis: From the quantum theory of atom in molecules (QTAIM) analysis, topological parameters such as electron density (ρ), Laplacian of electron density ($\nabla^2\rho$) and dipole moment (D) are tabulated in Table-6. Dipole moment varies for different molecular combination with different functional groups. Normally, more the dipole moment, more is its stability, but in present case for a specific molecular combination different functionals gives different values of dipole moment and the least value among these denotes better dihydrogen bonding. Dipole moment being charge dependent depends highly on the structure of the molecule; hence in present studies, it exhibits the changes based on the complexes. For C_2H_2···HLi, dipole moment varies from 6.609 to 7.467 D, and for C_2H_2···HNa and C_2H_2···HK it varies from 6.470 to 8.498 D and 6.457 to 10.09 D, respectively. In case of C_2H_4, the dipole moment for Li-H, Na-H and K-H interacted complexes varies from 5.449 to 7.031 D,

TABLE-5
NBO PARAMETERS OF THE COMPLEXES CALCULATED AT DIFFERENT FUNCTIONALS WITH 6-311++G** BASIS SET

Complexes		PBEPBE	B3LYP	B3PW91	CAM-B3LYP	HSEH1PBE	LC-BLYP
C_2H_2···HLi	Donor(i)	H3-Li1	H3-Li1	H3-Li1	H3-Li1	H3-Li1	H3-Li1
	Acceptor(j)	C2-H2	C2-H2	C2-H2	C2-H2	C2-H2	C2-H2
	E(2)	7.01	5.73	6.33	6.44	6.91	7.20
	E(j) – E(i)	0.62	0.72	0.71	0.85	0.71	0.97
	F(i,j)	0.059	0.057	0.060	0.066	0.063	0.075
C_2H_2···HNa	Donor(i)	H3-Na1	H3-Na1	H3-Na1	H3-Na1	H3-Na1	H3-Na1
	Acceptor(j)	C2-H2	C2-H2	C2-H2	C2-H2	C2-H2	C2-H2
	E(2)	6.98	5.83	6.72	6.84	7.16	7.97
	E(j) – E(i)	0.61	0.71	0.70	0.83	0.70	0.95
	F(i,j)	0.058	0.057	0.061	0.067	0.063	0.078
C_2H_2···HK	Donor(i)	H3-K1	H3-K1	H3-K1	H3-K1	H3-K1	H3-K1
	Acceptor(j)	C2-H2	C2-H2	C2-H2	C2-H2	C2-H2	C2-H2
	E(2)	8.27	7.07	8.35	8.65	8.53	10.23
	E(j) – E(i)	0.59	0.69	0.68	0.81	0.68	0.92
	F(i,j)	0.062	0.062	0.067	0.075	0.068	0.087
C_2H_4···HLi	Donor(i)	H3-Li1	H3-Li1	H3-Li1	H3-Li1	H3-Li1	H3-Li1
	Acceptor(j)	C2-H2	C2-H2	C2-H2	C2-H2	C2-H2	C2-H2
	E(2)	2.85	1.87	1.87	2.13	2.66	2.56
	E(j) – E(i)	0.60	0.70	0.69	0.82	0.69	0.95
	F(i,j)	0.037	0.032	0.032	0.037	0.038	0.044
C_2H_4···HNa	Donor(i)	H3-Na1	H3-Na1	H3-Na1	H3-Na1	H3-Na1	H3-Na1
	Acceptor(j)	C2-H2	C2-H2	C2-H2	C2-H2	C2-H2	C2-H2
	E(2)	2.96	1.92	1.96	2.22	2.80	2.77
	E(j) – E(i)	0.59	0.69	0.68	0.81	0.68	0.93
	F(i,j)	0.037	0.032	0.033	0.038	0.039	0.045
C_2H_4···HK	Donor(i)	H3-K1	H3-K1	H3-K1	H3-K1	H3-K1	H3-K1
	Acceptor(j)	C2-H2	C2-H2	C2-H2	C2-H2	C2-H2	C2-H2
	E(2)	3.43	2.61	2.90	3.15	3.60	3.82
	E(j) – E(i)	0.58	0.67	0.67	0.79	0.66	0.91
	F(i,j)	0.040	0.037	0.039	0.045	0.044	0.053

Complexes		M062X	M06L	ωB97XD	MP2	MP3	CCSD
C$_2$H$_2$···HLi	Donor(i)	H3-Li1	H3-Li1	H3-Li1	H3-Li1	H3-Li1	H3-Li1
	Acceptor(j)	C2-H2	C2-H2	C2-H2	C2-H2	C2-H2	C2-H2
	E(2)	5.88	8.55	7.39	6.20	5.73	5.32
	E(j) − E(i)	0.84	0.61	0.87	1.09	1.09	1.09
	F(i,j)	0.063	0.065	0.072	0.073	0.071	0.068
C$_2$H$_2$···HNa	Donor(i)	H3-Na1	H3-Na1	H3-Na1	H3-Na1	H3-Na1	H3-Na1
	Acceptor(j)	C2-H2	C2-H2	C2-H2	C2-H2	C2-H2	C2-H2
	E(2)	6.37	9.93	8.13	6.89	6.22	5.61
	E(j) − E(i)	0.82	0.59	0.86	1.06	1.06	1.06
	F(i,j)	0.065	0.068	0.074	0.076	0.073	0.069
C$_2$H$_2$···HK	Donor(i)	H3-K1	H3-K1	H3-K1	H3-K1	H3-K1	H3-K1
	Acceptor(j)	C2-H2	C2-H2	C2-H2	C2-H2	C2-H2	C2-H2
	E(2)	7.92	11.11	10.18	9.40	8.71	8.03
	E(j) − E(i)	0.80	0.58	0.84	1.05	1.05	1.04
	F(i,j)	0.071	0.072	0.082	0.089	0.085	0.082
C$_2$H$_4$···HLi	Donor(i)	H3-Li1	H3-Li1	H3-Li1	H3-Li1	H3-Li1	H3-Li1
	Acceptor(j)	C2-H2	C2-H2	C2-H2	C2-H2	C2-H2	C2-H2
	E(2)	0.56	2.44	2.63	1.74	1.64	1.43
	E(j) − E(i)	0.81	0.60	0.86	1.06	1.06	1.05
	F(i,j)	0.019	0.034	0.042	0.038	0.037	0.035
C$_2$H$_4$···HNa	Donor(i)	H3-Na1	H3-Na1	H3-Na1	H3-Na1	H3-Na1	H3-Na1
	Acceptor(j)	C2-H2	C2-H2	C2-H2	C2-H2	C2-H2	C2-H2
	E(2)	0.64	3.35	2.94	2.03	1.89	1.59
	E(j) − E(i)	0.79	0.58	0.84	1.03	1.03	1.03
	F(i,j)	0.020	0.040	0.044	0.041	0.040	0.036
C$_2$H$_4$···HK	Donor(i)	H3-K1	H3-K1	H3-K1	H3-K1	H3-K1	H3-K1
	Acceptor(j)	C2-H2	C2-H2	C2-H2	C2-H2	C2-H2	C2-H2
	E(2)	1.19	3.91	3.80	3.11	3.01	2.63
	E(j) − E(i)	0.78	0.57	0.83	1.01	1.01	1.01
	F(i,j)	0.027	0.042	0.050	0.050	0.049	0.046

TABLE-6
THE ELECTRON DENSITY (ρ, a.u.) AND LAPLACIAN OF ELECTRON DENSITY (∇^2ρ, a.u.) AND DIPOLE
MOMENT (D, debye) OF ALL THE COMPLEXES CALCULATED USING DIFFERENT FUNCTIONALS

Complex		PBEPBE	B3LYP	B3PW91	CAM-B3LYP	HSEH1PBE	LC-BLYP	M062X	M06L	ωB97XD	MP2	MP3	CCSD
C$_2$H$_2$···HLi	D	6.609	6.645	6.746	6.611	6.763	6.745	6.785	7.117	7.467	6.992	6.992	6.992
	ρ	0.0146	0.0121	0.0128	0.0120	0.0139	0.0121	0.0117	0.0159	0.0123	0.0112	0.0105	0.0099
	∇^2ρ	0.1538	0.1645	0.1594	0.1649	0.1602	0.1653	0.1661	0.1614	0.1551	0.1695	0.1707	0.1689
C$_2$H$_2$···HNa	D	6.941	6.470	7.473	7.352	6.712	6.788	6.848	8.498	6.964	8.217	8.217	8.217
	ρ	0.0149	0.0123	0.0132	0.0122	0.0142	0.0124	0.0119	0.0170	0.0127	0.0117	0.0108	0.0100
	∇^2ρ	0.1244	0.1323	0.1288	0.1368	0.1300	0.1410	0.1369	0.1262	0.1254	0.1328	0.1340	0.1309
C$_2$H$_2$···HK	D	8.625	6.457	9.278	9.397	9.148	9.696	9.494	9.960	9.620	10.09	10.09	10.09
	ρ	0.0169	0.0140	0.0153	0.0139	0.0160	0.0140	0.0135	0.0189	0.0144	0.0138	0.0130	0.0121
	∇^2ρ	0.0751	0.0770	0.0770	0.0787	0.0775	0.0800	0.0797	0.0769	0.0759	0.0811	0.0810	0.0789
C$_2$H$_4$···HLi	D	6.203	5.449	6.342	6.331	6.324	6.369	6.331	6.637	7.031	6.590	6.590	6.590
	ρ	0.0084	0.0064	0.0063	0.0068	0.0081	0.0075	0.0059	0.0088	0.0074	0.0063	0.0060	0.0055
	∇^2ρ	0.1525	0.1633	0.1580	0.1641	0.1586	0.1644	0.0138	0.1603	0.1541	0.1680	0.1690	0.1670
C$_2$H$_4$···HNa	D	6.424	5.997	6.264	6.180	6.222	6.375	7.064	7.966	7.500	7.719	7.719	7.719
	ρ	0.0089	0.0066	0.0066	0.0070	0.0085	0.0077	0.0062	0.0094	0.0079	0.0067	0.0063	0.0056
	∇^2ρ	0.1231	0.1310	0.1275	0.1357	0.1285	0.1399	0.0140	0.1248	0.1249	0.1321	0.1328	0.1294
C$_2$H$_4$···HK	D	8.0088	5.9457	8.6834	8.8189	8.5683	9.1599	8.7960	9.3583	9.1443	9.5234	9.5234	9.5234
	ρ	0.0099	0.0077	0.0082	0.0081	0.0096	0.0088	0.0074	0.0108	0.0090	0.0081	0.0079	0.0072
	∇^2ρ	0.0740	0.0760	0.0759	0.0778	0.0763	0.0790	0.0154	0.0759	0.0170	0.0803	0.0801	0.0779

5.997 to 7.966 D and 5.946 to 9.523 D, respectively. Comparing the dipole moment based on the functional, B3LYP provides the least and ωB97XD, M06L provides the maximum values.

The values of electron density and its Laplacian are found to be in the range of 0.0055-0.0189 a.u. and 0.0170-0.1707 a.u. Among all the functionals, M06L gives the best result for

electron density and Laplacian in all the molecular systems. On the other hand, M062X under estimates the values making it unstable for DHB studies. Fig. 3 illustrates a good exponential correlation between the electron density at bond critical point (BCP) and DHB distance of all the complexes. It is clearly observed that the DHB distance decreases as the electron density increases exponentially.

Molecular electrostatic potential (MEP) analysis: The electrostatic potential caused in space by charge distribution is obliged to know the electrophilic and nucleophilic regions in the given molecule. The molecular electrostatic potential affords a visual method to understand the charge distribution of compounds [40,41]. To attain a deeper understanding into the origin of DHB interaction between C_2H_2 and C_2H_4 with HM (Li, Na and K), the analysis of the molecular electrostatic potential has been carried out. Fig. 4 illustrates the molecular electrostatic potential of C_2H_2 and C_2H_4 with alkali metal hydrides (Li, Na and K) complexes calculated at M06L/6-311++G** level of theory. As mentioned above, both electro-

philic and nucleophilic parts were observed on the given complexes wherein red-colour surface represents the nucleophilic region and the blue-colour part denotes the electrophilic region. Thus, the nucleophilic area is indeed located on both sides of the bond (M–H, C=C, and C≡C), whereas electrophilic area is around the ethene and ethyne molecules. Therefore, molecular electrostatic potential confirms the dihydrogen bond formation between C-H and M-H bonds.

Conclusion

A theoretical study on dihydrogen bond in C_2H_2···HM and C_2H_4···HM (M = Li, Na and K) complexes were performed by DFT and *ab initio* methods. The intermolecular dihydrogen bond distances were well in agreement with the van der Waals radii of two hydrogen atoms (2.4 Å). The smallest dihydrogen bond distance and more interaction energy were observed for C_2H_2···HK complex. Among all the functionals, smallest dihydrogen bond distance was observed for M06L functional while the largest for M062X. The vibrational analysis of the
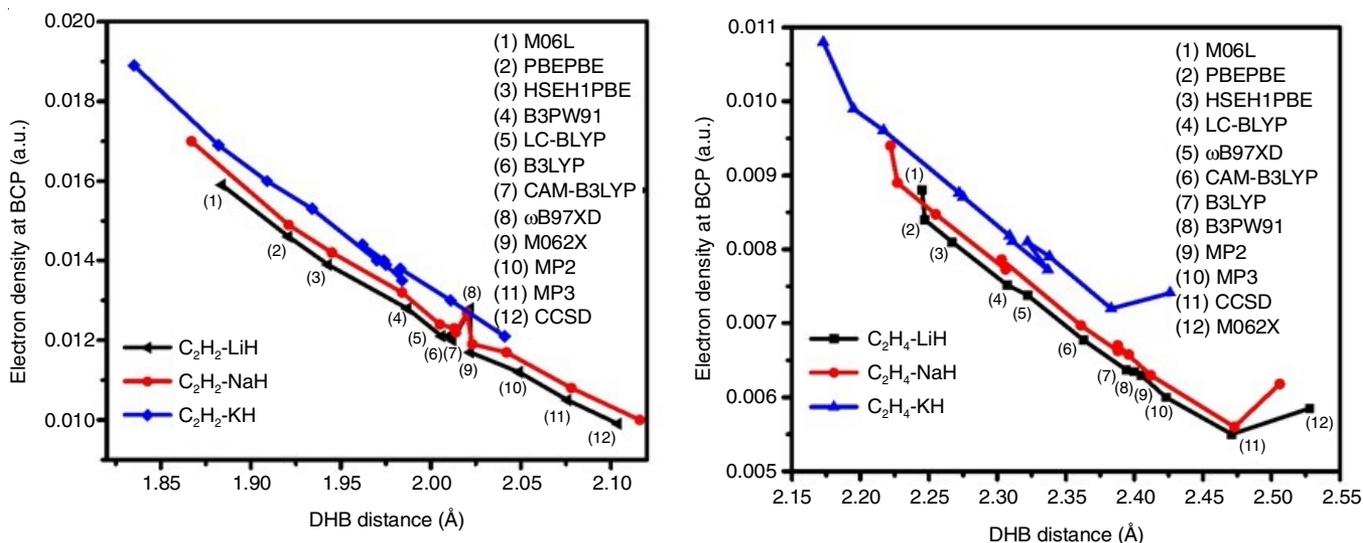

Fig. 3. Dependence of electron density at BCP (a.u.) upon bond distance of H···H interaction
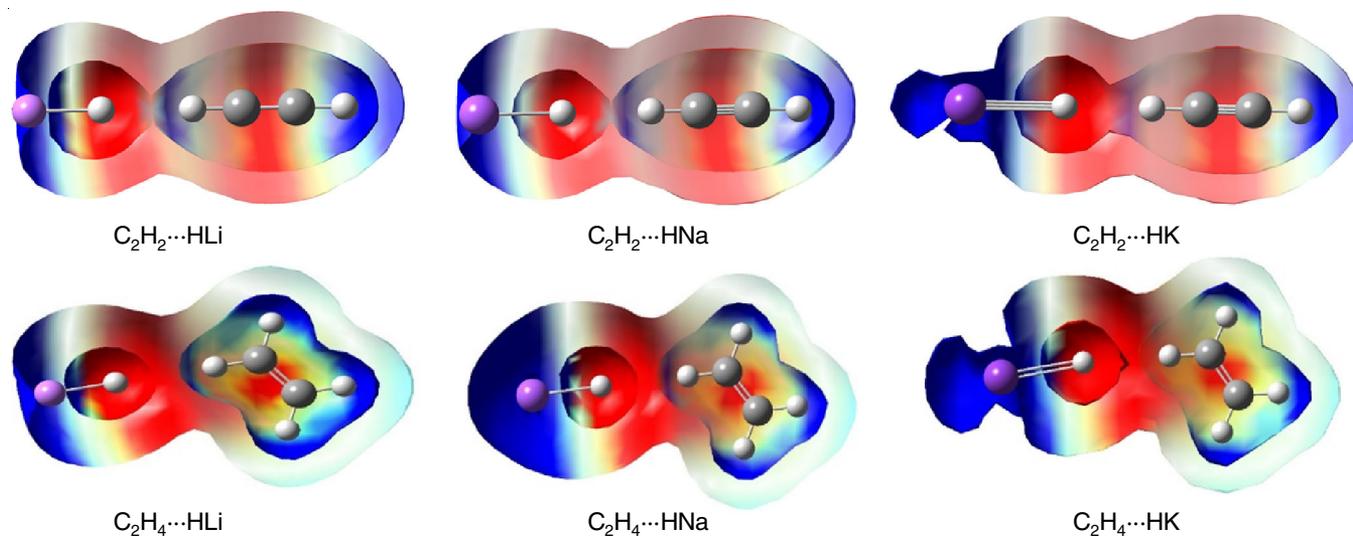

Fig. 4. Molecular electrostatic potential of the complexes obtained at M06L/6-311++G** level of theory

complexes revealed red and blue shift for C-H and M-H bonds. The QTAIM analysis of H···H bond revealed closed shell interactions for all the complexes. The MEP shows that the negative potential sites were around alkali metal hydride while positive potential sites were around the ethene and ethyne molecules. Among all the complexes, it was found that K-H containing complexes are most stable than Li-H and Na-H involved complexes.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. K.S. Sandhya, G.S. Remya and C.H. Suresh, *J. Chem. Sci.*, **130**, 98 (2018);
https://doi.org/10.1007/s12039-018-1498-0
2. P.V. Bijina and C.H. Suresh, *J. Chem. Sci.*, **128**, 1677 (2016);
https://doi.org/10.1007/s12039-016-1162-5
3. N. Zare and A. Zabardasti, *J. Chem. Sci.*, **129**, 1647 (2017);
https://doi.org/10.1007/s12039-017-1377-0
4. S. Wojtulewski and S.J. Grabowski, *J. Mol. Struct.*, **645**, 287 (2003);
https://doi.org/10.1016/S0022-2860(02)00581-1
5. I. Alkorta, K. Zborowski, J. Elguero and M. Solimannejad, *J. Phys. Chem. A*, **110**, 10279 (2006);
https://doi.org/10.1021/jp061481x
6. Y. Li, L. Zhang, S. Du, F. Ren and W. Wang, *Comput. Theor. Chem.*, **977**, 201 (2011);
https://doi.org/10.1016/j.comptc.2011.09.033
7. I. Alkorta, J. Elguero and S.J. Grabowski, *J. Phys. Chem. A*, **112**, 2721 (2008);
https://doi.org/10.1021/jp711387g
8. B.G. Oliveira, *Comput. Theor. Chem.*, **998**, 173 (2012);
https://doi.org/10.1016/j.comptc.2012.07.031
9. Y. Tan, X. Chen, J. Chen, Q. Gu and X. Yu, *J. Mater. Chem. A Mater. Energy Sustain.*, **2**, 15627 (2014);
https://doi.org/10.1039/C4TA02842B
10. R. Custelcean and J.E. Jackson, *Chem. Rev.*, **101**, 1963 (2001);
https://doi.org/10.1021/cr000021b
11. A.Q. Yao and F. De Ren, *Comput. Theor. Chem.*, **963**, 463 (2011);
https://doi.org/10.1016/j.comptc.2010.11.014
12. H. Cybulski, M. Pecul, J. Sadlej and T. Helgaker, *J. Chem. Phys.*, **119**, 5094 (2003);
https://doi.org/10.1063/1.1597633
13. L. Feng, F. Bai, Y. Wu and H. Zhang, *Sci. China Chem.*, **55**, 262 (2012);
https://doi.org/10.1007/s11426-011-4391-y
14. I. Alkorta, J. Elguero, M. Solimannejad and S.J. Grabowski, *J. Phys. Chem. A*, **115**, 201 (2011);
https://doi.org/10.1021/jp1100544
15. T.M. Nunes, I.C.C. Turatti, S. Mateus, F.S. Nascimento, N.P. Lopes and R. Zucchi, *Genet. Mol. Res.*, **8**, 589 (2009);
https://doi.org/10.4238/vol8-2kerr012
16. Y. Guo, G. Xia, Y. Zhu, L. Gao and X. Yu, *Chem. Commun.*, **46**, 2599 (2010);
https://doi.org/10.1039/b924057h
17. J.P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, **77**, 3865 (1996);
https://doi.org/10.1103/PhysRevLett.77.3865
18. A.D. Becke, *J. Chem. Phys.*, **98**, 5648 (1993);
https://doi.org/10.1063/1.464913
19. J.P. Perdew and Y. Wang, *Phys. Rev. B Condens. Matter*, **45**, 13244 (1992);
https://doi.org/10.1103/PhysRevB.45.13244
20. T. Yanai, D. Tew and N. Handy, *Chem. Phys. Lett.*, **393**, 51 (2004);
https://doi.org/10.1016/j.cplett.2004.06.011
21. J. Heyd and G. Scuseria, *J. Chem. Phys.*, **121**, 1187 (2004);
https://doi.org/10.1063/1.1760074
22. H. Iikura, T. Tsuneda, T. Yanai and K. Hirao, *J. Chem. Phys.*, **115**, 3540 (2001);
https://doi.org/10.1063/1.1383587
23. Y. Zhao and D.G. Truhlar, *J. Phys. Chem.*, **110**, 5121 (2006);
https://doi.org/10.1021/jp060231d
24. Y. Zhao and D.G. Truhlar, *Theor. Chem. Acc.*, **120**, 215 (2008);
https://doi.org/10.1007/s00214-007-0310-x
25. J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, **10**, 6615 (2008);
https://doi.org/10.1039/b810189b
26. M. Head-Gordon, J.A. Pople and M.J. Frisch, *Chem. Phys. Lett.*, **153**, 503 (1988);
https://doi.org/10.1016/0009-2614(88)85250-3
27. J.A. Pople, J.S. Binkley and R. Seeger, *Int. J. Quantum Chem.*, **Y-10(Suppl.)**, 1 (1976);
https://doi.org/10.1002/qua.560100802
28. G.D. Purvis III and R.J. Bartlett, *J. Chem. Phys.*, **76**, 1910 (1982);
https://doi.org/10.1063/1.443164
29. S.F. Boys and F. Bernardi, *Mol. Phys.*, **19**, 553 (1970);
https://doi.org/10.1080/00268977000101561
30. R.F.W. Bader, *Chem. Rev.*, **91**, 893 (1991);
https://doi.org/10.1021/cr00005a013
31. P.D. Duraisamy, P. Gopalan and A. Angamuthu, *Chem. Pap.*, **74**, 1609 (2020);
https://doi.org/10.1007/s11696-019-01011-5
32. D. Kaur and R. Kaur, *J. Chem. Sci.*, **127**, 1299 (2015);
https://doi.org/10.1007/s12039-015-0885-z
33. G.A. Zhurko and D.A. Zhurko, Chemcraft: Lite Version Build 08 (Freeware, Available online: http://www. chemcraftprog.com) (2005).
34. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, G.A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A.V. Marenich, J. Bloino, B.G. Janesko, R. Gomperts, B. Mennucci, H.P. Hratchian, J.V. Ortiz, A.F. Izmaylov, J.L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V.G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M.J. Bearpark, J.J. Heyd, E.N. Brothers, K.N. Kudin, V.N. Staroverov, T.A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A.P. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, J.M. Millam, M. Klene, C. Adamo, R. Cammi, J.W. Ochterski, R.L. Martin, K. Morokuma, O. Farkas, J.B. Foresman and D.J. Fox, Gaussian, Inc., Wallingford CT, Gaussian 16, Revision C.01 (2016).
35. J. Datka and E. Kukulska-Zajac, *J. Phys. Chem. B*, **108**, 17760 (2004);
https://doi.org/10.1021/jp0493428
36. P.C. Singh and G.N. Patwari, *Chem. Phys. Lett.*, **419**, 5 (2006);
https://doi.org/10.1016/j.cplett.2005.11.003
37. S. Jeyavijayan, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **136**, 890 (2015);
https://doi.org/10.1016/j.saa.2014.09.110
38. S. Scheiner, *Acc. Chem. Res.*, **46**, 280 (2013);
https://doi.org/10.1021/ar3001316
39. P.D. Duraisamy, P. Gopalan and A. Angamuthu, *Monatsh. Chem.*, **151**, 1569 (2020);
https://doi.org/10.1007/s00706-020-02680-9
40. S.M. Soliman, M.A. M Abu-Youssef, J. Albering and A. El-Faham, *J. Chem. Sci.*, **127**, 2137 (2015);
https://doi.org/10.1007/s12039-015-0976-x
41. A. Barakat, A.M. Al-Majid, M.S. Islam, M. Ali, S.M. Soliman, M.R.H. Siddiqui, H.A. Ghabbour and H.-K. Fun, *J. Chem. Sci.*, **127**, 1547 (2015);
https://doi.org/10.1007/s12039-015-0923-x