A DFT and AIM study of the interactions of pyridine and pyrazine with alkali hydrides. Identification of dihydrogen bonds involving aromatic C-H hydrogen

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The interactions of pyridine (py) and pyrazine (pz) with LiH, NaH and KH are studied by DFT at the B3LYP/6-311++g(2d,p) level. The interaction energies corrected for BSSE lie in the range -86.7 to -38.8 kJ mol^{-1}. Dihydrogen bonds are observed only for the py-KH and pz-KH systems with distances 2.27 and 2.17 Å respectively. AIM analyses show presence of bond critical points, associated with an electron density of 0.011-0.013. Our calculations on the ammonia borane dimer, where presence of dihydrogen bond is authentic, at the same level of theory reveal that the electron density at the bond critical points of the dihydrogen bonds (of calculated lengths 2.03-2.05 Å) is 0.015.

The result of the interaction between a proton and a hydride is exothermic generation of dihydrogen. The reaction LiH + HCl = LiCl + H$_2$ has a heat of reaction of -234.7 kJ mol^{-1} in the gas phase[1]. But if somehow the charges on the concerned H atoms can be reduced by controlling the electronic properties of the atoms to which they are attached, then an H$^{\delta+}$…H$^{\delta-}$ type interaction can be stabilized. A good example is the intermolecular B-H…H-N interaction found in the crystal structure[2,3] of H$_3$B-NH$_3$ where H atoms bound to B bear δ- charge and those bound to N δ+. The first unequivocal recognition of H…H interaction was however made independently by Crabtree and co-workers[4] and Morris and co-workers[5] in some Ir hydride complexes in 1994. It has been named as "dihydrogen bonding" by Crabtree and co-workers in 1996[6]. Such dihydrogen bonding has now been recognized experimentally and theoretically

in many other systems of the type M-H…H-X where M is less electronegative than H, e.g. Li, Ga etc. and X more electronegative than H, e.g. O, N etc[7-11]. A feature of the compounds containing dihydrogen bonds is that they release H$_2$ quite easily[12-14]. For example, some alkyl substituted amine boranes start evolving H$_2$ at room temperature in tetrahydrofuran in presence of a suitable catalyst[13]. Thus, such compounds are very important from the fuel cell point of view. Very recently it has been proposed that formation of dihydrogen bond is important in the biological activity of monoiron hydrogenases[15]. Herein, we describe a combination of some aromatic compounds and alkali hydrides as a new class of materials having dihydrogen bonds. Despite a lot of activity in the field, aromatics have not been used to generate such materials.

Computational details

The DFT calculations were performed using B3LYP functional with an all-electron 6-311++G(2d,p) basis set within the Gaussian 03W suite of programs[16]. The inputs were created by GaussView. BSSE corrections to the interaction energies were done by using the counterpoise method available in Gaussian 03W. AIM calculations were performed by using AIM 2000 (version 2.0) program[17]. For AIM calculations, the required wave functions were generated by Gaussian 03W.

Results and discussion

Among the aromatics, we have chosen pyridine (py) and pyrazine (pz). The B3LYP/6-311++g (2d,p) calculations show that the H atoms in py bear a positive charge (Mulliken) of 0.14 and those in pz, a charge of 0.15. Since in alkali hydrides H atoms are negatively charged, we reckoned that their interactions with py and pz might give rise to dihydrogen bonds. Accordingly we have studied the interactions of LiH, NaH and KH with py and pz by DFT at the B3LYP/6-311++g(2d,p) level. The global energy minima structures obtained in individual cases are described in Fig. 1 and the corresponding interaction energies ΔE corrected for BSSE are given in Table 1. Selected bond angles and bond lengths are given in Table 2.
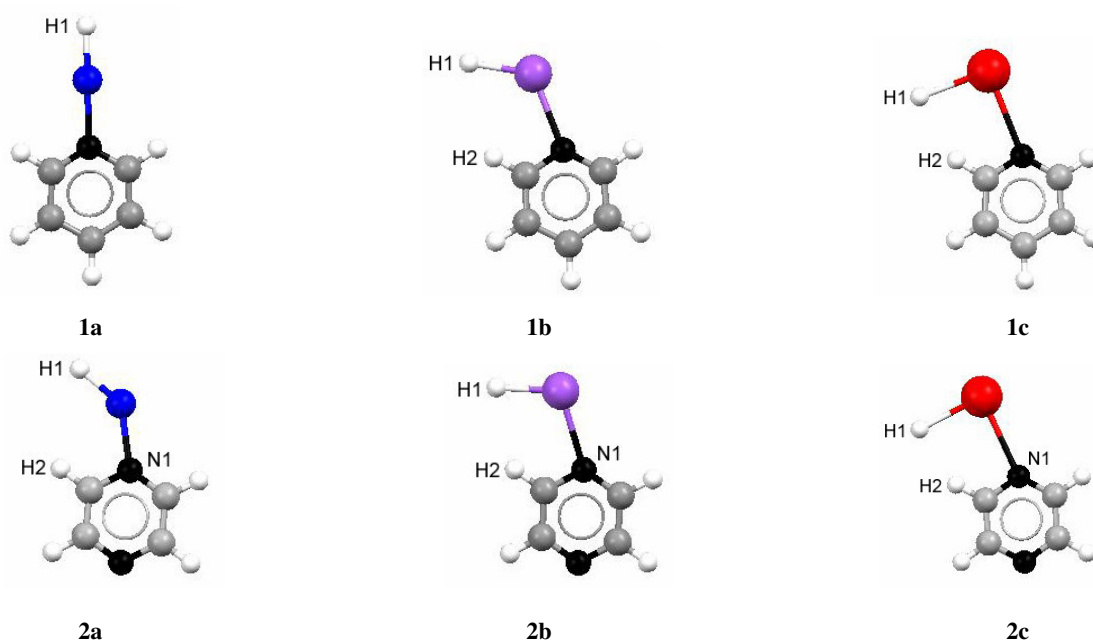
Fig. 1— Ball-and-stick representations of the global energy minima structures as obtained from B3LYP/6-311++g(2d,p) calculations for the interactions of py and pz with LiH, NaH and KH. [**1a**, py and LiH; **1b**, py and NaH; **1c**, py and KH; **2a**, pz and LiH; **2b**, pz and NaH; **2c**, pz and KH. Colour code: white, H; grey, C; black, N; blue, Li; purple, Na; red, K].

Table 1— Interaction energy (ΔE) for the interactions of py and pz with LiH, NaH and KH

System [a]	ΔE (kJ mol^{-1})	BSSE correction	Corr. ΔE (kJ mol^{-1})
py-LiH (**1a**)	-88.9	2.2	-86.7
py-NaH (**1b**)	-53.9	2.8	-51.1
py-KH (**1c**)	-43.9	1.3	-42.6
pz-LiH (**2a**)	-76.6	1.9	-74.7
pz-NaH (**2b**)	-46.6	2.7	-43.9
Pz-KH (**2c**)	-40.1	1.3	-38.8

[a]The numbers given within parentheses refer to Fig. 1

Table 2— Selected bond distances, bond angles and Mulliken charges

	Bond distances (Å)		Bond angles (°)		Mulliken charges	
1a	N-Li	2.02	N-Li-H1	180.0	N	0.10
	Li-H1	1.62			Li	0.08
					H1	0.35
1b	N-Na	2.43	N-Na-H1	120.7	N	-0.31
	Na-H1	1.92			Na	0.25
	H1-H2	2.90			H1	-0.42
					H2	0.10
1c	N-K	2.84	N-K-H1	91.3	N	-0.42
	K-H1	2.30			K	0.58
	H1-H2	2.27			H1	-0.53
					H2	0.01
2a	N1-Li	2.02	N1-Li-H1	138.3	N1	-0.05
	Li-H1	1.62			Li	0.13
	H1-H2	3.05			H1	-0.36
					H2	0.15
2b	N1-Na	2.46	N1-Na-H1	109.2	N1	-0.26
	Na-H1	1.93			Na	0.26
	H1-H2	2.52			H1	-0.40
					H2	0.03
2c	N1-K	2.88	N1-K-H1	87.4	N1	-0.35
	K-H1	2.29			K	0.55
	H1-H2	2.17			H1	-0.51
					H2	-0.02

The interactions of py and pz with LiH, NaH and KH are found to be quite exothermic. The corrected ΔE values for py or pz follow the order: LiH > NaH > KH. The angle N-M′-H (M′: an alkali metal) becomes more acute in that order, bringing the hydride H closer to a ring H atom. As per Pauling, the van der Waals' radius of H is 1.0 Å (ref. 18). However, very recently, Truhlar and co-workers have recommended a value of 1.2 Å as the van der Waals' radius of H for the identification of dihydrogen bonds[19]. This means that if the distance between two H atoms is less than 2.4 Å, one can expect a dihydrogen bond between them. By this criterion, from Table 2 we find that a dihydrogen bond is possible only when KH interacts with py or pz; an H…H distance in **1c** is 2.27 Å and that in **2c** 2.17 Å (Table 2). Since the H…H distance in **2c** is shorter than that in **1c**, it is reasonable to expect that the dihydrogen bond in **2c** is stronger than that in **1c**.

In Bader's theory of atoms-in-molecule (AIM), existence of a bond critical point between two interacting atoms ensures chemical bonding between them[20]. Accordingly, we have done AIM analyses for **1c** and **2c**. The molecular graphs generated by AIM calculations are shown in Fig. 2. Bond critical points are observed between H1 and H2 in **1c** and **2c** in Fig. 2 with electron density ρ at the respective bond critical points of 0.011 and 0.013. Incidentally, the ρ values at the bond critical points for the K-N bonds in **1c** and **2c** are 0.016 and 0.014 respectively.

To calibrate our method, we have carried out AIM analyses in H_3N-BH_3 dimer where existence of dihydrogen bonds should be authentic. The structure of the ammonia-borane dimer optimized at the B3LYP/6-311++g(2d,p) level is given in Fig. 3(a). The dihydrogen bonds have the distances in the range 2.03-2.05 Å. The dihydrogen bond distances are accurately known in the crystals of H_3N-BH_3 from neutron diffraction[3]; the shorter one matches quite well with the theoretically determined ones in H_3N-BH_3 dimer (Fig. 3). Earlier Meng et al.[21] have optimized the structure of the H_3N-BH_3 dimer using B3LYP at a somewhat lower basis set, 6-311++g(d,p). Two of their dihydrogen distances (2.24, 1.90, 1.96 and 2.13) are unusually short. However, Meng et al. have not carried out any AIM analyses. AIM analyses in the present study show that H1, H5 and H6 in Fig. 3(a) have a common bond critical point with $\rho = 0.015$. Similarly, H2, H3 and H4 in Fig. 3(a) also have a common bond critical point with the same ρ value. This vindicates that the dihydrogen bonds observed theoretically in py-KH and pz-KH systems are real.

Thus here we have shown that aromatic C-H hydrogen atoms are potential in forming a dihydrogen bonds. In this context we mention that earlier it has been found that alkenic and alkyl H atoms are capable of forming dihydrogen bonds with borane H atoms.[22-24]

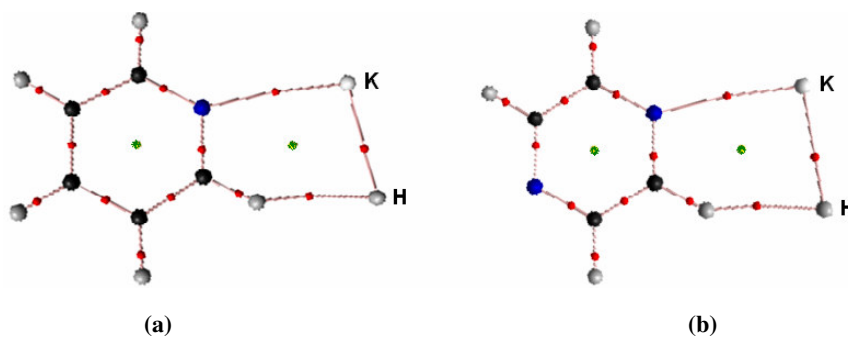**(a)**   **(b)**

Fig. 2— Molecular graphs of (a) pyridine-KH complex and (b) pyrazine-KH complex as obtained from AIM calculations. [Colour code: black, C; blue, N; grey, H, red, bond critical point; green, ring critical point].

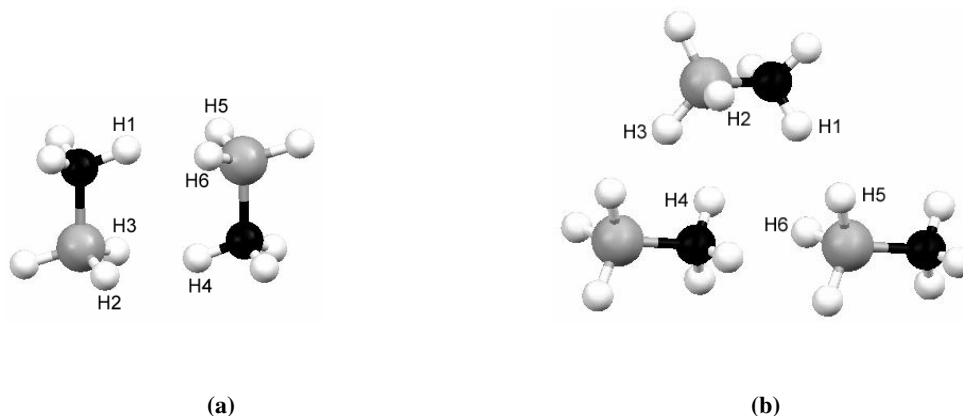**(a)**   **(b)**

Fig. 3 — (a) Global energy minima structure of ammonia borane dimer as obtained from the B3LYP/6-311++g(2d,p) calculations. [Dihydrogen bond distances (Å): H1-H5 2.05, H1-H6 2.04, H2-H4 2.03 and H3-H4 2.05]. (b) A portion of the neutron diffraction structure of ammonia borane showing the dihydrogen bonds. [Distances (Å): H1-H6 2.02, H1-H5 2.22, H2-H4 2.02 and H3-H4 2.22. Colour code: black, N; grey, B; white, H].

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