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# Naphthylazoimidazole and mercury(II) complexes. Single crystal X-ray structure of 1-ethyl-2-(naphthyl- $\alpha$ -azo)imidazolium hexafluorophosphate

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## Abstract

1-Alkyl-2-(naphthyl-( $\alpha/\beta$ )-azo)imidazole [ $\alpha$ -NaiR (**2**)/ $\beta$ -NaiR (**3**); R = Me (**a**), Et (**b**), CH<sub>2</sub>Ph (**c**)] are N,N'-bidentate chelating ligands. The structure of 1-ethyl-2-(naphthyl- $\alpha$ -azo)imidazolium hexafluorophosphate has been confirmed by single crystal X-ray structure study and shows supramolecular geometry through non-covalent interactions (C–H $\cdots$ F, C–H $\cdots$  $\pi$ ,  $\pi\cdots\pi$ ). Mercury(II) complexes of the formula Hg(NaiR)Cl<sub>2</sub> (**4/5**) have been synthesised and characterised by spectral (IR, UV–Vis and <sup>1</sup>H and <sup>13</sup>C NMR) studies.  $\alpha$ -NaiR has been used to synthesise organomercury derivatives, Hg( $\alpha$ -NaiR–H)Cl (**6**) and the site of mercuration has been supported by charge density calculation using a semi-empirical PM3 technique.

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**Keywords:** Naphthylazoimidazole; H-bonding; Coordination compounds; Organomercuration; X-ray structure

## 1. Introduction

Over the past few years, we have been engaged in the design of molecules of imidazole and have explored their chemistry. Progress in the coordination chemistry [1–15] and analytical application [16,17] of 2-(arylo)imidazoles (**1**) and their derivatives has encouraged us to design newer molecules with poly-aromatic hydrocarbons. In this series, naphthyl was chosen and  $\alpha$ - and  $\beta$ -naphthylamines have been used to synthesise 1-alkyl-2-(naphthyl-( $\alpha/\beta$ )-azo)imidazoles ( $\alpha$ -NaiR (**2**),  $\beta$ -NaiR (**3**)) [18,19]. Our interest has been raised by a crystallographic study of 1-ethyl-2-(naphthyl- $\alpha$ -azo)imidazolium hexafluorophosphate, which has indicated the presence of charge assisted C–H<sup>d+</sup> $\cdots$ F<sup>d-</sup> as well as C–H<sup>d+</sup> $\cdots$ p<sup>d-</sup> hydrogen bonds. The hydrogen bond offers the most efficient and robust noncovalent infrastructure and, for

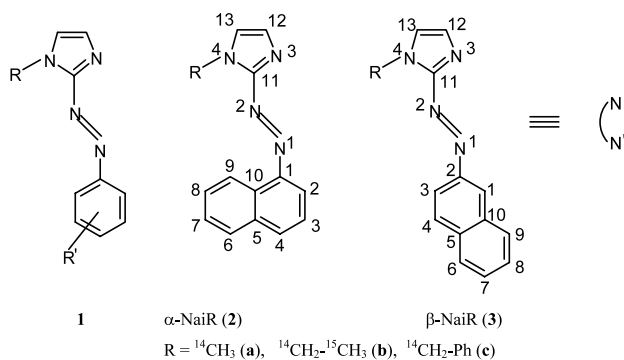
this reason, recently is being used in supramolecular chemistry and crystal engineering [20–23].

The C–H $\cdots$ F interaction may account for the activation of this C–H bond in a metal assisted route. We have observed similar C–H activation of 1-alkyl-2-(naphthyl- $\alpha$ -azo)imidazoles by Pd(OAc)<sub>2</sub> and the cyclopalladated compound has been structurally established [24]. In the field of non-transition organometallics organo-mercury compounds are mostly studied because of their air and moisture stability, and have been used for a transmetallation reaction to synthesise other organometallic compounds that are otherwise impossible to synthesise. Mercury(II) in the form of Hg(OAc)<sup>+</sup>, a potent reagent for the C–H activation process [25–29], is chosen. In this paper, we wish to report the coordination complexes of mercury(II) and 1-alkyl-2-(naphthyl-( $\alpha/\beta$ )-azo)imidazole and the organomercury derivatives of 1-alkyl-2-(naphthyl- $\alpha$ -azo)imidazole along with the x-ray crystal structure of 1-ethyl-2-(naphthyl- $\alpha$ -azo)imidazolium hexafluorophosphate. The complexes have been characterised by spectral studies and site of mercuration has been supported by theoretical (PM3)

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charge density calculation.



## 2. Experimental

### 2.1. Materials

1-Alkyl-2-(naphthyl-( $\alpha/\beta$ )-azo) imidazoles ( $\alpha$ -NaiR (2),  $\beta$ -NaiR (3)) were synthesised by the reported procedure [22,23]. Hg(OAc)<sub>2</sub> was purchased from Lancaster, UK. All other chemicals used were of AR quality and were used as received. The organic solvents were purified and dried by standard methods [24].

### 2.2. Instrumentation

UV–Vis spectra were recorded using a JASCO UV–VIS–NIR V-570 spectrophotometer and IR spectra were obtained from a JASCO FTIR-420 instrument. Microanalyses were collected from a Perkin–Elmer 2400 CHN elemental analyser.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded from Bruker 300 MHz FT-NMR ( $^1\text{H}$ ) and 125 MHz ( $^{13}\text{C}$ ) spectrometers in  $\text{CDCl}_3$  and  $\text{DMSO}-d_6$  solution.

### 2.3. Preparation of coordination complexes

The complexes were prepared by a general procedure and the experimental condition was set up following the previously reported procedure [11]. Detailed synthesis of Hg( $\alpha$ -NaiMe)Cl<sub>2</sub> (4a) is given below.

To a methanol solution of 1-methyl-2-(naphthyl- $\alpha$ -azo)-imidazole ( $\alpha$ -NaiMe, 2a) (0.30 g, 1.27 mmol) was added HgCl<sub>2</sub> (0.36 g, 1.33 mmol) in methanol. The reaction mixture was stirred for 0.5 h. A crimson-red compound precipitated immediately which was filtered, washed with water and methanol.

Hg( $\alpha$ -NaiMe)Cl<sub>2</sub> (4a): Yield 74%; IR (KBr): 1624 (C=N), 1427 (N=N), 352 (Hg–Cl), 280 (Hg–N)  $\text{cm}^{-1}$ . UV–Vis (DMSO) ( $\lambda_{\text{max}}$ , nm, ( $10^{-3}$   $\epsilon$ ,  $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$ ): 424 (16.61), 410 (16.93), 378 (11.44) nm. *Anal.* Found: C, 33.16; H, 2.30; N, 11.10. Calc. for  $\text{C}_{14}\text{H}_{12}\text{N}_4\text{Cl}_2\text{Hg}$ : C,

33.10; H, 2.36; N, 11.03%. Hg( $\alpha$ -NaiEt)Cl<sub>2</sub> (4b): Yield 79%; IR (KBr): 1625 (C=N), 1425 (N=N), 350 (Hg–Cl), 282 (Hg–N)  $\text{cm}^{-1}$ . UV–Vis (DMSO): 424 (28.20), 402 (35.37), 378 (28.07) nm. *Anal.* Found: C, 34.46; H, 2.61; N, 10.70. Calc. for  $\text{C}_{15}\text{H}_{14}\text{N}_4\text{Cl}_2\text{Hg}$ : C, 34.51; H, 2.68; N, 10.74%. Hg( $\alpha$ -NaiCH<sub>2</sub>Ph)Cl<sub>2</sub> (4c): Yield 75%; IR (KBr): 1620 (C=N), 1422 (N=N), 352 (Hg–Cl), 280 (Hg–N)  $\text{cm}^{-1}$ . UV–Vis (DMSO): 435 (18.87), 417 (19.42), 347 (16.39) nm. *Anal.* Found: C, 39.82; H, 2.84; N, 9.72. Calc. for  $\text{C}_{19}\text{H}_{16}\text{N}_4\text{Cl}_2\text{Hg}$ : C, 39.89; H, 2.80; N, 9.80%. Hg( $\beta$ -NaiMe)Cl<sub>2</sub> (5a): Yield 68%; IR (KBr): 1624 (C=N), 1428 (N=N), 355 (Hg–Cl), 285 (Hg–N)  $\text{cm}^{-1}$ . UV–Vis (DMSO): 405 (14.25), 385 (13.67) nm. *Anal.* Found: C, 33.02; H, 2.31; N, 11.10. Calc. for  $\text{C}_{14}\text{H}_{12}\text{N}_4\text{Cl}_2\text{Hg}$ : C, 33.10; H, 2.36; N, 11.03%. Hg( $\beta$ -NaiEt)Cl<sub>2</sub> (5b): Yield 72%; IR (KBr): 1626 (C=N), 1424 (N=N), 354 (Hg–Cl), 284 (Hg–N)  $\text{cm}^{-1}$ . UV–Vis (DMSO): 415 (23.63), 380 (28.89), 365 (26.37) nm. *Anal.* Found: C, 34.45; H, 2.62; N, 10.80. Calc. for  $\text{C}_{15}\text{H}_{14}\text{N}_4\text{Cl}_2\text{Hg}$ : C, 34.51; H, 2.68; N, 10.74%. Hg( $\beta$ -NaiCH<sub>2</sub>Ph)Cl<sub>2</sub> (5c): Yield 78%; IR (KBr): 1630 (C=N), 1426 (N=N), 360 (Hg–Cl), 288 (Hg–N)  $\text{cm}^{-1}$ . UV–Vis (DMSO): 405 (13.25), 390 (11.45), 365 (14.27) nm. *Anal.* Found: C, 39.80; H, 2.84; N, 9.74. Calc. for  $\text{C}_{19}\text{H}_{16}\text{N}_4\text{Cl}_2\text{Hg}$ : C, 39.89; H, 2.80; N, 9.80%.

### 2.4. Synthesis of cyclomercurated compounds, Hg( $\alpha$ -NaiR-H)Cl (6)

Cyclomercurated compounds of  $\alpha$ -NaiR were prepared following a general procedure [25–27]. Detailed synthesis of Hg( $\alpha$ -Nai Me–H)Cl (6a) is given below.

A solution of Hg(OAc)<sub>2</sub> (0.35 g, 1.1 mmol) in dry MeOH (30 ml) was added dropwise to a solution of  $\alpha$ -NaiMe (2a, 0.22 g 0.93 mmol) in the same solvent (30 ml). The mixture was refluxed for 6 h and an orange precipitate was filtered off under the hot conditions. LiCl (5 mmol) was added to the filtrate, warmed for a few minutes and the resulting precipitate was filtered, washed with ether and dried in vacuo. The product was recrystallised from DMSO–MeOH mixture to give Hg( $\alpha$ -NaiMe–H)Cl (6a).

Hg( $\alpha$ -NaiMe–H)Cl (6a): Yield 41%; IR (KBr): 1620 (C=N), 1410 (N=N), 345 (Hg–Cl), 285 (Hg–N)  $\text{cm}^{-1}$ . UV–Vis (DMSO): 422 (18.22), 400 (17.49), 370 (15.37) nm. *Anal.* Found: C, 35.58; H, 2.61; N, 11.80. Calc. for  $\text{C}_{14}\text{H}_{11}\text{N}_4\text{ClHg}$ : C, 35.66; H, 2.55; N, 11.89%. Hg( $\alpha$ -NaiEt–H)Cl (6b): Yield 38%; IR (KBr): 1616 (C=N), 1412 (N=N), 350 (Hg–Cl), 280 (Hg–N)  $\text{cm}^{-1}$ . UV–Vis (DMSO): 428 (16.56), 400 (15.84), 380 (14.90) nm. *Anal.* Found: C, 37.04; H, 2.64; N, 10.50. Calc. for  $\text{C}_{15}\text{H}_{13}\text{N}_4\text{ClHg}$ : C, 37.11; H, 2.68; N, 11.54%. Hg( $\alpha$ -NaiCH<sub>2</sub>Ph–H)Cl (6c): Yield 45%; IR (KBr): 1628 (C=N), 1418 (N=N), 352 (Hg–Cl), 288 (Hg–N)  $\text{cm}^{-1}$ . UV–Vis (DMSO): 440 (18.99), 415 (16.47), 370 (15.69) nm.

*Anal.* Found: C, 42.55; H, 2.74; N, 10.40. Calc. for  $C_{19}H_{15}N_4ClHg$ : C, 42.61; H, 2.80; N, 10.47%.

### 2.5. X-ray crystal structure and analysis

The X-ray quality single crystal of 1-ethyl-2-(naphthyl- $\alpha$ -azo)imidazolium hexafluoro-phosphate ( $\alpha$ -NaiEtH<sup>+</sup>PF<sub>6</sub><sup>−</sup>) was grown by slow evaporation of a methanol–water (1:1 v/v) solution of 1-ethyl-2-(naphthyl- $\alpha$ -azo)imidazole with few drops of HPF<sub>6</sub>. The orange coloured crystal was isolated after 2 weeks of evaporation. The crystal size was 0.25 × 0.20 × 0.10 mm<sup>3</sup>. X-ray diffraction data were collected at 293(2) K with the Siemens SMART CCD using graphite-monochromatized Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Unit cell parameters were determined from least-squares refinement of setting angles with  $2\theta$  in the range 4–56°. Data were corrected for  $L_p$  effects and an empirical absorption correction was applied. A summary of the crystallographic data and structure refinement parameters are given in Table 1. Of 9305 collected reflections, 4125 reflections were unique. The structure was solved by heavy atom methods using SHELX-97 and successive difference Fourier syntheses, and refined with all data on  $F^2$  using SHELXL-97 [29,30]. A weighting scheme based upon  $P = (F_o^2 + 2F_c^2)$  was employed in order to reduce statistical bias. The hydrogen atoms were fixed

geometrically and refined using the riding model. In the final difference Fourier maps the residual maximum and minimum were 0.35 and  $-0.22$  e Å<sup>−3</sup>, respectively. All calculations were carried out using the SHELXS-97 [30], SHELXL-97 [31], ORTEP-3 [32] and PLATON-99 [33] programs.

### 2.6. Electron density calculation

Computations of molecular geometry and energy were made using the PM3 semi-empirical SCF method as implemented in ZINDO [34] version 3. Calculations were made from an optimised geometry of the molecules. Selected conformational data, viz. total energy, binding energy, heats of formation, dipole moments and energies of HOMO and LUMO are listed in Table 5. EHMO calculations were carried out using crystallographic parameters of  $[\alpha\text{-NaiEtH}^+][\text{PF}_6^-]$ .

## 3. Results and discussion

### 3.1. Synthesis

1-Alkyl-2-(naphthyl-( $\alpha/\beta$ -azo)imidazoles [ $\alpha$ -NaiR (2),  $\beta$ -NaiR (3); R = Me (a), Et (b), CH<sub>2</sub>Ph (c)] have been synthesised by the alkylation of the respective naphthylazoimidazoles with alkyl halide in dry THF in the presence of NaH [18,19]. The molecules are characterised by <sup>1</sup>H NMR spectral data. 1-Alkyl-2-(naphthyl- $\beta$ -azo)imidazoles are crystalline solids [18] while analogous  $\alpha$ -naphthyl derivatives are gummy masses [19] at room temperature. We have not been able to isolate single crystals of the molecules by conventional techniques. Sometimes addition of H<sup>+</sup> to the solution of the molecules having basic centres may lead to aggregation via protonation and crystalline molecules may appear [20]. This general technique has been employed in crystal engineering [20–23]. We have been successful to collect a single crystal of 1-ethyl-2-(naphthyl- $\alpha$ -azo)imidazolium hexafluorophosphate [ $\alpha$ -NaiEtH<sup>+</sup>][PF<sub>6</sub><sup>−</sup>] by adding HPF<sub>6</sub> (few drops) to an aqueous methanol solution of  $\alpha$ -NaiEt and then slow evaporation in air.

### 3.2. X-ray structure of [ $\alpha$ -NaiEtH<sup>+</sup>][PF<sub>6</sub><sup>−</sup>]

A view of [ $\alpha$ -NaiEtH<sup>+</sup>][PF<sub>6</sub><sup>−</sup>] with the atom numbering scheme is shown in Fig. 1, and selected bond parameters are listed in Table 2. In [ $\alpha$ -NaiEtH<sup>+</sup>][PF<sub>6</sub><sup>−</sup>], the naphthyl fragment is essentially planar with no atom deviating  $\leq 0.03$  Å, and the azo group is virtually coplanar with its neighbouring imidazolic ring with no atom deviating  $\leq 0.06$  Å. However, the dihedral angle between the two least-squares planes of 20.4(1)° means the azo-imidazole and naphthyl

Table 1  
Summarised crystallographic data for [ $\alpha$ -NaiEtH<sup>+</sup>][PF<sub>6</sub><sup>−</sup>]

Empirical formula	C <sub>15</sub> H <sub>15</sub> N <sub>4</sub> PF <sub>6</sub>
Formula weight	396.27
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
$a$ (Å)	8.6901(8)
$b$ (Å)	9.8720(10)
$c$ (Å)	10.4017(10)
$\alpha$ (°)	95.606(2)
$\beta$ (°)	103.769(2)
$\gamma$ (°)	92.727(2)
$\mu$ (cm <sup>−1</sup> )	2.28
$Z$	2
$T$ (K)	293(2)
$\rho_{\text{calc}}$ (gm cm <sup>−3</sup> )	1.526
Index range	$-11 \leq h \leq 11,$ $-13 \leq k \leq 13,$ $-13 \leq l \leq 12$
Reflection collected	9305
Unique data	4125
Refined parameters	271
$R^a$ ( $I > 2\sigma(I)$ )	0.0547
$wR_2^b$	0.1499
GOF <sup>c</sup>	0.94

<sup>a</sup>  $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ .

<sup>b</sup>  $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2}$ ,  $w = 1/[\sigma^2(F_o)^2 + (0.0671P)^2]$ ,  $P = [(F_o^2 + 2F_c^2)/3]$ .

<sup>c</sup> GOF (goodness-of-fit) is defined as  $[w(F_o - F_c)/(n_o - n_v)]^{1/2}$ , where  $n_o$  and  $n_v$  denote the numbers of data and variables, respectively.

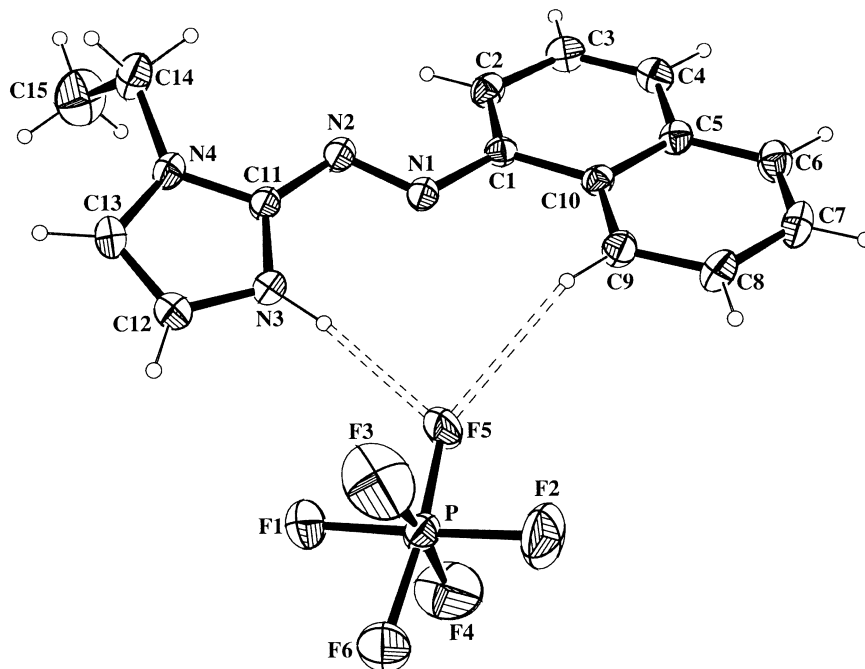


Fig. 1. Single crystal X-ray structure of  $[\alpha\text{-NaiEtH}^+][\text{PF}_6^-]$  showing atom numbering scheme.

moieties are not coplanar. Moreover, the imidazole twists around the N(1)–N(2) bond, meaning the two faces of azo-imidazole ring are not equivalent. The loss of planarity is doubtless as a consequence of the 1-Et group in the imidazole ring. The N=N bond length is 1.267(3) Å and is longer than reported data (1.250(1) Å) [12]. The crystal structure determination of 1-methyl-2-(phenylazo)imidazolium perchlorate [13] shows a N=N distance 1.252(2) Å. The elongation of the N–N bond length in  $[\alpha\text{-NaiEtH}^+][\text{PF}_6^-]$  may be due to a better +I effect and steric crowding provided by the naphthyl group compared to the phenyl group of the earlier compound. The bonding strength between azo-N(2) and

imidazole–C(11) [C(11)–N(2), 1.386(3) Å] is higher than that of azo-N(1) and naphthyl-C(1) [1.404(3) Å]. This suggests that the intramolecular interaction between azo- and imidazole wave functions is stronger than that of naphthyl orbitals.

### 3.2.1. Supramolecular structure of $[\alpha\text{-NaiEtH}^+][\text{PF}_6^-]$

In the structure, the hexafluorophosphate and  $\alpha\text{-NaiEtH}^+$  ions are linked by N–H···F and C–H···F hydrogen bonds (Table 2). The imidazolic N(3) and naphthyl C(9) atoms act as donors to the F(5) (or disordered F(3A) atom). The structure determination

Table 2

Selected bond lengths (Å) and bond angles (°) with e.s.d. in brackets for  $[\alpha\text{-NaiEtH}^+][\text{PF}_6^-]$

Bond lengths				
N(1)–N(2)	1.267(3)	P–F(3A)	1.645(6)	
N(2)–C(11)	1.386(3)	P–F(4)	1.564(6)	
N(1)–C(1)	1.404(3)	P–F(4A)	1.529(6)	
C(11)–N(4)	1.335(3)	P–F(5)	1.522(5)	
C(11)–N(3)	1.327(3)	P–F(5A)	1.545(6)	
P–F(1)	1.570(2)	P–F(6)	1.604(4)	
P–F(2)	1.571(2)	P–F(6A)	1.496(6)	
P–F(3)	1.522(5)			
Bond angles				
N(1)–N(2)–C(11)	110.5(2)	N(2)–C(11)–N(4)	123.0(2)	
N(2)–C(11)–N(3)	128.7(2)	N(2)–N(1)–C(1)	115.7(2)	
Donor (D)–H···Acceptor (A)				
	D–H (Å)	H···A (Å)	D–H···A (Å)	D–H···A (°)
Hydrogen bonds				
N(3)–H···F(5)	0.860(3)	2.082(1)	2.936(6)	171.8(2)
N(3)–H···F(3A)	0.860(3)	2.157(8)	2.903(4)	144.8(3)
C(9)–H···F(5)	0.929(9)	2.532(7)	3.397(9)	154.7(9)

reveals that the interactions between the C–H bond and the P–F bond gives rise to C–H $\cdots$ F hydrogen bonds which are short, and presumably therefore strong, for their type [35,36], and therefore the C–H bond is polarized to C<sup>d-</sup>–H<sup>d+</sup> and P–F bond has strongly polarised to P<sup>d+</sup>–F<sup>d-</sup>, i.e. the C–H $\cdots$ F hydrogen bond is charge assisted. It was envisaged that this charge-assisted interaction might result in the higher acidity of the C(9)–H bond facilitating the C–H bond activation (vide infra). Moreover, the C5 $\rightarrow$ C10 (cg3) ring of naphthyl moiety of the molecule at (1–x, 3–y, 1–z) experiences C–H $\cdots$ p interaction with the C(15)–H of the N(4)–C(14)H<sub>2</sub>–C(15)H<sub>3</sub> group at (x, y, z) belonging to a neighbouring imidazole ring, which leads to a stacked dimer (Fig. 2). For the C–H $\cdots$ p interaction, the distance between the centroid of the ring and the nearest carbon atom, C(15), is 4.090 Å (H(15c) $\cdots$ centroid, 3.149 Å; C(15)–H(15c) $\cdots$ centroid, 167.08°). The dimers, in turn, experience the offset face-to-face p $\cdots$ p interactions between aryl and imidazolic rings. The aryl ring, C(1) $\rightarrow$ C(5)–C(10) (cg2), in the naphthyl portion at (x, y, z) forms p $\cdots$ p stacking interactions with the corresponding ring and C(5) $\rightarrow$ C(10) ring of the neighbouring molecule at (–x, 2–y, 1–z). The dihedral angles between the rings are 0.0 and 1.93°, respectively. The

interplanar spacings are 3.488, 3.470 Å; the distance between the centroids are 3.749, 3.893 Å, so that the centroids are offset by 0.361 and 0.423 Å, respectively. These dimensions are almost ideal for strong p $\cdots$ p stacking interactions [37]. Similarly, the N(3)–C(11)–N(4)–C(12)–C(13) (cg1) imidazole ring forms a p $\cdots$ p stacking interaction with cg2 ring of the neighbouring unit at (1–x, 2–y, 1–z) and P–F(3) $\cdots$ cg1 p interactions. The distances between cg1 members and F(3) of a PF<sub>6</sub>-unit vary from 2.895 to 3.930 Å. Thus, every C–H $\cdots$ p stacked dimer is linked with another dimer via P–F $\cdots$ p interactions (F3 $\cdots$ Cg1, 3.298 Å; <P–F3 $\cdots$ Cg1 118.3°) which results in a supramolecular 1D chain. These parallel chains running along the **b**-direction lie in the *bc*-plane (Fig. 2).

### 3.3. Mercury(II) complexes

The ligands are unsymmetric bidentate N,N'-donor type. The active function of the ligand is the azoimine group, –N=N–C=N–. The imine-N (–C=N–) is an exocyclic group (abbreviated as N). The ligands react smoothly with HgCl<sub>2</sub> in MeOH at room temperature and crimson-red products have been obtained in good yields. The composition of the complexes, Hg( $\alpha/\beta$ -

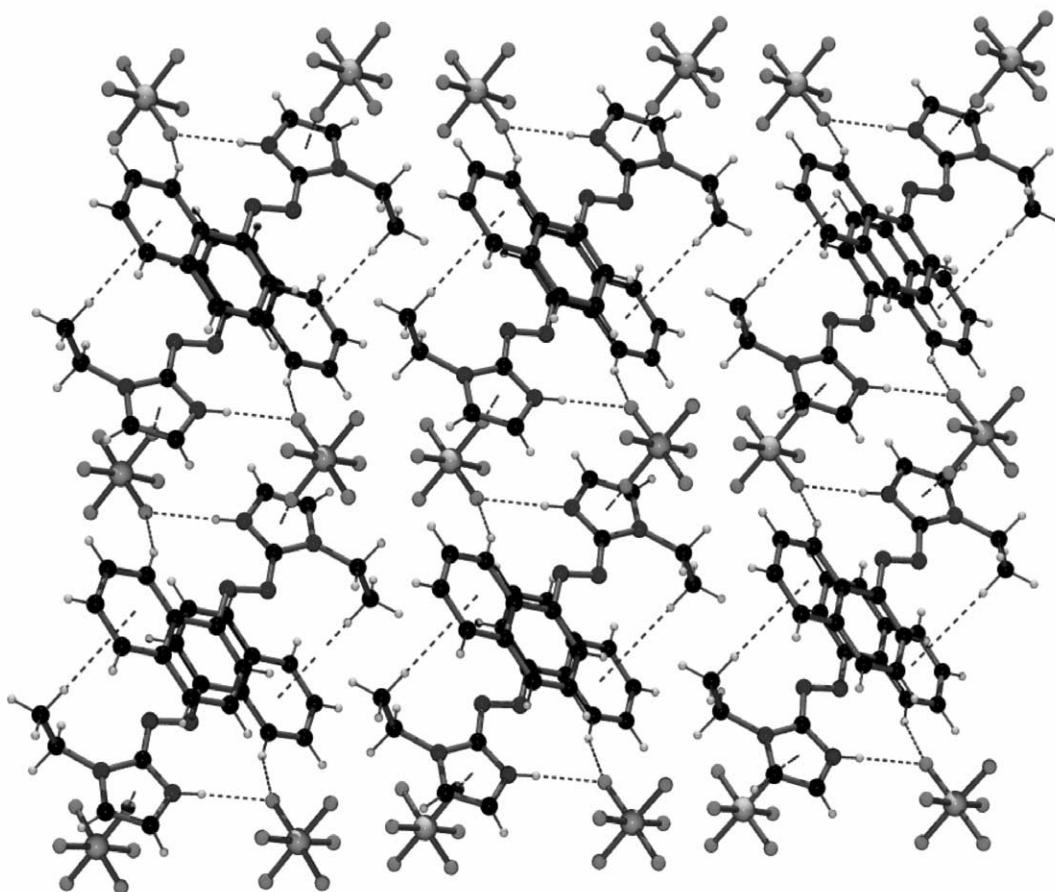
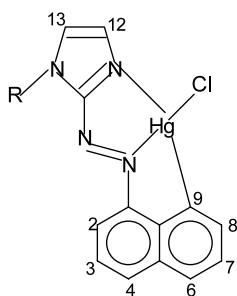


Fig. 2. Packing view of [α-NaiEtH<sup>+</sup>][PF<sub>6</sub><sup>-</sup>] in *bc*-plane showing weak interactions for constructing supramolecular structure.

NaiR)Cl<sub>2</sub> (**4/5**) is supported by elemental analysis. They are non-conducting in MeCN.

The reaction of Hg(OAc)<sup>+</sup> with  $\alpha$ -NaiR (**2**) (1:1 molar ratio) in refluxing dry MeOH followed by the addition of LiCl has synthesised brown-red organomercury derivatives and the compounds are abbreviated, Hg( $\alpha$ -NaiR-H)Cl (**6**). The reaction of  $\beta$ -NaiR (**3**) under identical conditions has isolated only coordination compounds Hg( $\beta$ -NaiR)Cl<sub>2</sub> (**5**). The complexes are characterised by elemental analyses, IR, UV-VIS and <sup>1</sup>H NMR data (vide supra).

The IR spectra of the complexes show a sharp intense band at 1400–1410 cm<sup>-1</sup> that corresponds to the N=N stretching mode and is red shifted by 15–20 cm<sup>-1</sup> compared to free ligand values (1415–1430 cm<sup>-1</sup>) [11]. This is an indication of azo-N coordination to Hg(II). The exocyclic C=N appears at 1620–1625 cm<sup>-1</sup> and other ring stretching corresponding to imidazole and naphthyl ring appear at 1500, 1320, 1200, 1140, 1070, 1000, 900, 650–850 cm<sup>-1</sup>.



The medium intense band around 350 cm<sup>-1</sup> is assignable to  $\nu$ (Hg-Cl) [11]. The solution electronic spectra of the complexes were recorded in DMSO. They exhibit transitions at 460, 420, 400, 340 nm and are red shifted compared to the free ligand transitions at 390, 375 and 260 nm. The transitions  $\leq 400$  nm are associated with intraligand charge transfer ( $n \rightarrow \pi^*$ ,  $\pi \rightarrow \pi^*$ ) transitions. The complexes are structurally characterised by high resolution <sup>1</sup>H NMR spectra on the basis of spin-spin interaction and on comparing with the free ligand values [18,19]. The spectra of NaiR (**2/3**) and Hg(NaiR)Cl<sub>2</sub> (**4/5**) were drawn in CDCl<sub>3</sub> solution (Table 3). All protons in naphthylazoimidazole suffer downfield shifting in Hg(NaiR)Cl<sub>2</sub> compared to the free ligand values. Imidazole protons are shifted by 0.1–0.2 ppm to higher  $\delta$  in coordination compounds, and appear as doublets at 7.3–7.4 and 7.0–7.2 ppm compared to free ligand values 6.9–7.2 and 6.8–7.0 ppm for 12- and 13-H, respectively. In Hg( $\alpha$ -NaiR)Cl<sub>2</sub> (**4**) 2-H appears at ca. 8.92 ppm and it is the highest  $\delta$ . It may be due to the electron withdrawing effect of the azo group adjacent to this C-H group. Other naphthyl protons 3-H–8-H appear as a multiplet at 7.60–7.80 ppm and 9-H appears at ca. 8.07 ppm. Hg( $\beta$ -NaiR)Cl<sub>2</sub> shows a broad signal at the most downfield position at ca. 8.35 ppm which is

assigned to 1-H; the 3-H appears at ca. 8.15 ppm. Other protons 4-H–9-H appear as a multiplet at 7.70–8.00 ppm.

The most striking difference is observed between the spectra of **4** and **6** in the aromatic region (7.00–9.00 ppm). Because of the sparing solubility of **6** in CDCl<sub>3</sub> the <sup>1</sup>H-NMR spectra were recorded in DMSO-*d*<sub>6</sub>. In general, the protons of the complexes (**6**) exhibit resonances at a lower frequency region by 0.05–0.2 ppm compared with the chemical shift data of coordination complexes, **4**. The integration of the spectra of **6** show one proton less than that of **4**. This supports the substitution of one of the naphthyl C-H group by Hg<sup>2+</sup>. A doublet at the highest  $\delta$  (ca. 8.85 ppm) has been assigned to 2-H. A second doublet appears at ca. 7.95 ppm and corresponds to 8-H. The HgCl<sub>2</sub> moiety in the coordination complexes Hg(NaiR)Cl<sub>2</sub> is a stronger electron-withdrawing agent compared to the HgCl moiety in the cyclomercurated product, Hg( $\alpha$ -NaiR-H)Cl (**6**). Thus, the former (**4**) exhibits proton resonances at higher frequency than that of the organomercury compound (**6**).

The <sup>13</sup>C NMR spectra of  $\alpha$ -NaiR (**2**), Hg( $\alpha$ -NaiR)Cl<sub>2</sub> (**4**) and Hg( $\alpha$ -NaiR-H)Cl (**6**) are recorded in CDCl<sub>3</sub> for **2**, **4** and DMSO-*d*<sub>6</sub> for **6**. The spectral data are collected in Table 4. The spectra are complicated due to a large number of C-centres. The assignment has been done on comparing the spectra of free ligands and complexes, and following the intensity of the lines. The DEFT study has also distinguished the primary, secondary, tertiary and quaternary C-centres. There are four quaternary C-centres (C-1, C-5, C-10, C-11), nine secondary C-centres (C-2, C-3, C-4, C-6, C-7, C-8, C-9, C-12, C-13) per naphthylazoimidazole unit, except the 1-R group. The resonances generally appear within the range of 120–180 ppm. The 1-R group resonances usually appear at low  $\delta$  value, 50 to 95 ppm. Data in Table 4 reveal that resonances are shifted to higher  $\delta$  value on going from free ligand to Hg-compounds and the general trend of chemical shift data is  $\alpha$ -NaiR (**2**) < Hg( $\alpha$ -NaiR-H)Cl (**6**) < Hg( $\alpha$ -NaiR)Cl<sub>2</sub> (**4**). The substituent, 1-R has little influence on the naphthyl group C-centre resonances. Some of the <sup>13</sup>C NMR resonances in Table 4 are either of same or very closely spaced values which reflect their resemblances in chemical and electronic environment. A remarkable difference is observed in the  $\delta$  value of C-9 in the cyclomercurated product, **6**, which shows ca. 20 ppm shifting to higher value compared to the coordination compound, **4**. This is in support to the formation of the C(9)-Hg bond.

1-Alkyl-2-(naphthyl-( $\alpha$ / $\beta$ )-azo)imidazoles ( $\alpha$ -NaiR, **2**) are eligible cyclometallating reagents. Treatment of Pd(OAc)<sub>2</sub> in benzene with  $\alpha$ -NaiR has synthesised cyclopalladated compounds and the C(9)-H bond participated in the metallation process. The cyclopalladated compound has been characterised by single crystal

Table 3

<sup>1</sup>H NMR spectral data of Hg(NaiR)Cl<sub>2</sub><sup>a</sup> and Hg(α-NaiR–H)Cl<sup>b</sup>

Compound	12-H <sup>c</sup>	13-H <sup>c</sup>	1-H	2-H	3-H	4-H <sup>e</sup>	6-H <sup>e</sup>	7-H <sup>e</sup>	8-H	9-H	–CH <sub>3</sub>	–CH <sub>2</sub> –
Hg(α-NaiMe)Cl <sub>2</sub> ( <b>4a</b> )	7.3 (7.2)	7.17 (7.2)		8.94 <sup>c</sup> (6.9)	7.86 <sup>e</sup>	7.92	7.65	7.65	7.65 <sup>e</sup>	8.07 <sup>c</sup> (8.0)	4.16	
Hg(α-NaiEt)Cl <sub>2</sub> ( <b>4b</b> )	7.31 (6.9)	7.22 (6.9)		8.92 <sup>c</sup> (6.9)	7.83 <sup>e</sup>	7.70	7.60	7.60	7.60 <sup>e</sup>	8.10 <sup>c</sup> (8.0)	1.60	4.57
Hg(α-NaiCH <sub>2</sub> Ph)Cl <sub>2</sub> ( <b>4c</b> )	7.29 (6.9)	7.20 (6.9)		8.90 <sup>c</sup> (6.9)	7.86 <sup>e</sup>	7.95	7.73	7.73	7.73 <sup>e</sup>	8.05 <sup>c</sup> (8.0)		5.67
Hg(β-NaiMe)Cl <sub>2</sub> ( <b>5a</b> )	7.28 (6.9)	7.15 (6.9)	8.29 <sup>d</sup>		8.15 <sup>e</sup>	7.97	7.70	7.70	7.70 <sup>e</sup>	7.90 <sup>e</sup>	4.13	
Hg(β-NaiEt)Cl <sub>2</sub> ( <b>5b</b> )	7.32 (6.1)	7.16 (6.1)	8.37 <sup>d</sup>		8.00 <sup>e</sup>	7.92	7.75	7.75	7.75 <sup>e</sup>	7.93 <sup>e</sup>	1.60	4.51
Hg(β-NaiCH <sub>2</sub> Ph)Cl <sub>2</sub> ( <b>5c</b> )	7.38 (6.9)	7.26 (6.9)	8.35 <sup>d</sup>		8.25 <sup>e</sup>	8.03	7.72	7.72	7.72 <sup>e</sup>	7.90 <sup>e</sup>		5.62
Hg(α-NaiMe–H)Cl ( <b>6a</b> )	7.21 (6.9)	7.03 (6.9)		8.85 (8.0)	7.82 <sup>f</sup> (8.0)	7.85	7.70	7.78	7.90 <sup>c</sup> (8.0)		4.00	
Hg(α-NaiEt–H)Cl ( <b>6b</b> )	7.23 (6.9)	7.09 (6.9)		8.82 (8.0)	7.87 <sup>f</sup> (8.0)	7.84	7.72	7.81	7.94 <sup>c</sup> (8.0)		1.53	4.44
Hg(α-NaiCH <sub>2</sub> Ph–H)Cl ( <b>6c</b> )	7.19 (7.2)	7.10 (7.2)		8.91 (8.0)	7.90 <sup>f</sup> (8.0)	7.88	7.75	7.85	8.00 <sup>c</sup> (8.0)			5.60

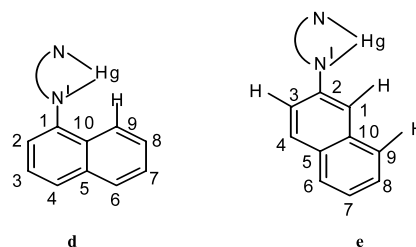
<sup>a</sup> Solvent CDCl<sub>3</sub>.<sup>b</sup> Solvent DMSO-*d*<sub>6</sub>.<sup>c</sup> Doublet.<sup>d</sup> Singlet.<sup>e</sup> Multiplet.<sup>f</sup> Triplet.

X-ray diffraction study [24]. Both Hg(OAc)<sub>2</sub> and Pd(OAc)<sub>2</sub> are two typical C–H activating agents [24–27,38]. Schiff bases and 2-(aryloxy)pyridines have been undergone organomercuriation reactions [25,26] and the electrophile Hg(OAc)<sup>+</sup> selects the highest charge density C-centre in the ring. The reaction is regioselective and the stability of the product depends on steric crowding [25–29]. We have not been able to isolate a single crystal of Hg(α-NaiR–H)Cl. On comparing the C–H activation property of Pd(OAc)<sub>2</sub> and Hg(OAc)<sub>2</sub> as well as the electrophilic sensitivity of the C(9)–H group we may conclude that the complexes **6** are cyclomercurated compounds.

### 3.4. Charge density calculation and organomercuriation reaction

The PM3 method has been employed to calculate the net atomic charges from the optimised geometry of the molecules α-NaiMe, α-NaiEt and β-NaiMe, β-NaiEt. It is clear that the conformation observed in the crystal structure is close to the minimum energy conformation of the isolated molecule. The charge densities along with other physical parameters are listed in Table 5. The charge density calculation shows that the pendant ethyl carbon atom, C15, (–0.126256 e) carries a large residual negative charge, and is responsible for the observed strong charge assisted C<sup>d–</sup>–H<sup>d+</sup>...p<sup>d–</sup> bond. It is observed that the charge densities of α-NaiR and β-NaiR differ significantly on the C-centres of the naphthyl ring compared to the imidazole ring. A striking feature is observed at the C9 centre; the electron density is found to be higher at α-NaiR than that of β-NaiR. This supports the higher acidity of the C9–H bond in α-NaiR compared to β-NaiR. The Hg(N,N') fragment in the structure **d** shows closer proximity to the C9–H bond than that of structure **e**. Although the C(1)–H and C(3)–H in structure **e** are closer to the Hg(N,N')

fragment they do not form a recognisable chelate ring while structure **d** can form a five-member metallacycle via activation of the C9–H bond. This is supported by the formation of cyclopalladated complexes [24] of α-NaiR, Pd(α-NaiR–H)Cl from the coordination complexes, Pd(α-NaiR)Cl<sub>2</sub>. The β-NaiR only forms the coordination complex Pd(β-NaiR)Cl<sub>2</sub>. This argument may be extended to mercury(II) complexes of 1-alkyl-2-(naphthyl-α-azo)imidazoles



These ligands form coordination complexes of the composition Hg(α/β-NaiR)Cl<sub>2</sub>. The α-NaiR can form cyclomercurated compounds when it is reacted with Hg(OAc)<sub>2</sub> in dry MeOH. Hg(OAc)<sup>+</sup> acts as an electrophile and is an agent for the C–H bond activation which upon treatment with LiCl gives Hg(α-NaiR–H)Cl (**6**).

Although the imidazolic C(12) and C(13) are of higher electron density than that of naphthyl-C centres in the molecule, the former are not activated by Hg(OAc)<sup>+</sup>. It is because of the very high charge density at the N(3) centre and the affinity of Hg(II) to imidazole-N; the N(3)→Hg(II)(OAc)<sup>+</sup> coordinated bond is formed first. The moiety then participates in chelation with N(1) to form a Hg(N,N')(OAc)<sup>+</sup> fragment which in turn participates in the C(9)–H activation process to give the cyclomercurated product.

The approximate composition of the frontier orbitals of [α-NaiEtH<sup>+</sup>][PF<sub>6</sub><sup>–</sup>] were estimated by Extended Huckel calculation using crystallographic parameters of the molecule. The HOMO and LUMO of the

Table 4  
 $^{13}\text{C}$  NMR spectral data of  $\alpha$ -NaiR (**2**)<sup>a</sup>, Hg( $\alpha$ -NaiR)Cl<sub>2</sub> (**4**)<sup>a</sup> and Hg( $\alpha$ -NaiR–H)Cl (**6**)<sup>b</sup>

Compound	$\delta$ (ppm)														
	C-1 <sup>d</sup>	C-2 <sup>c</sup>	C-3 <sup>c</sup>	C-4 <sup>c</sup>	C-5 <sup>d</sup>	C-6 <sup>c</sup>	C-7 <sup>c</sup>	C-8 <sup>c</sup>	C-9 <sup>c</sup>	C-10 <sup>d</sup>	C-11 <sup>d</sup>	C-12 <sup>c</sup>	C-13 <sup>c</sup>	1-C(H <sub>3</sub> ) <sup>e</sup>	1-C(H <sub>2</sub> ) <sup>f</sup>
<b>2a</b>	147.7	129.7	129.7	129.7	140.1	129.7	129.7	129.7	135.9	138.3	154.8	122.1	119.1	45.0	
<b>2b</b>	146.8	128.9	128.9	128.9	141.9	128.9	128.9	128.9	137.9	140.1	159.9	123.8	111.8		68.1 <sup>g</sup>
<b>2c</b>	149.8	137.9	137.9	137.9	144.9	137.9	137.9	137.9	143.7	140.1	161.7	130.1	115.6		79.0 <sup>h</sup>
<b>4a</b>	155.2	139.6	139.6	139.6	160.3	139.6	139.6	139.6	144.9	159.8	159.8	139.6	130.3	64.6	
<b>4b</b>	149.8	139.9	139.9	139.9	162.2	139.9	139.9	139.9	145.3	161.8	167.9	139.9	130.5		85.1 <sup>g</sup>
<b>4c</b>	154.8	144.6	144.6	144.6	165.1	144.6	144.6	144.6	149.8	162.2	169.3	144.6	133.2		91.8 <sup>h</sup>
<b>6a</b>	159.5	150.1	144.8	130.5	167.9	135.1	136.8	143.3	165.1	178.1	174.0	129.9	120.1	60.3	
<b>6b</b>	160.1	149.8	144.9	130.5	163.9	135.1	140.1	143.6	167.9	165.9	177.2	135.3	123.4		80.0 <sup>g</sup>
<b>6c</b>	164.9	152.8	147.8	135.3	165.8	138.2	142.0	147.9	172.1	169.9	178.1	137.9	127.8		88.3 <sup>h</sup>

<sup>a</sup> In CDCl<sub>3</sub>.

<sup>b</sup> In DMSO-*d*<sub>6</sub>.

<sup>c</sup> Tertiary (3<sup>o</sup>).

<sup>d</sup> Quaternary (4<sup>o</sup>).

<sup>e</sup> Primary (1<sup>o</sup>).

<sup>f</sup> Secondary (2<sup>o</sup>).

<sup>g</sup>  $\delta$ (C of CH<sub>3</sub>): **2b**, 45.3; **4b**, 60.1; **6b**, 52.3 ppm.

<sup>h</sup>  $\delta$ (C of Ph): **2c**, 130–145; **4c**, 140–155; **6c**, 140–150 ppm.



Table 5

Some physical parameters and calculated charge densities of carbon and nitrogen atoms of  $\alpha$ -NaiMe,  $\alpha$ -NaiEt,  $\beta$ -NaiMe and  $\beta$ -NaiEt by semi-empirical PM3 single point process

Compounds	$\alpha$ -NaiMe	$\alpha$ -NaiEt	$\beta$ -NaiMe	$\beta$ -NaiEt
Total energy (kcal/M)	-57416.99	-60866.18	-57396.97	-60870.37
Binding energy (kcal/M)	-3349.28	-3649.28	-3329.26	-3634.63
Heat of formation (kcal/M)	120.40	144.34	140.43	110.15
Dipole moment ( <i>D</i> )	3.804	3.965	3.957	3.974
Atom number	Charge density			
C-1	-0.06494	-0.06255	-0.014830	-0.05396
C-2	-0.05675	-0.05867	-0.09861	-0.07496
C-3	-0.12005	-0.11947	-0.10098	-0.07192
C-4	-0.06433	-0.06564	-0.09013	-0.09633
C-6	-0.09401	-0.09382	-0.09318	-0.09357
C-7	-0.09698	-0.09712	-0.10266	-0.09156
C-8	-0.08980	-0.09258	-0.10266	-0.10199
C-9	-0.11133	-0.10481	-0.08111	-0.08020
C-11	-0.24510	-0.24232	-0.25189	-0.23406
C-12	-0.14128	-0.14483	-0.15157	-0.14685
C-13	-0.30549	-0.29835	-0.34420	-0.29496
C-14	-0.12632	-0.10748	-0.12863	-0.09502
C-15		-0.12626		-0.12994
N-1	-0.06700	-0.06889	-0.02451	-0.06821
N-2	0.07590	0.075305	0.03961	-0.07496
N-3	-0.05940	-0.05970	-0.08705	-0.05598
N-4	0.32405	0.314258	0.42315	0.30087
HOMO (eV)	-8.69842	-8.68983	-8.79703	-8.86213
LUMO (eV)	-1.21277	-1.09827	-0.96599	-1.00514

compound are depicted in Fig. 3; the HOMO is mainly (87%) composed of naphthyl orbitals and the LUMO is pure imidazole orbitals. Thus, the spectral transition in the UV–VIS region is an intra-molecular charge transfer transitions.

#### 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 168539 for [ $\alpha$ -

MO=51 (85a) E= -1.7051

MO=50 (86a) E= -1.3711

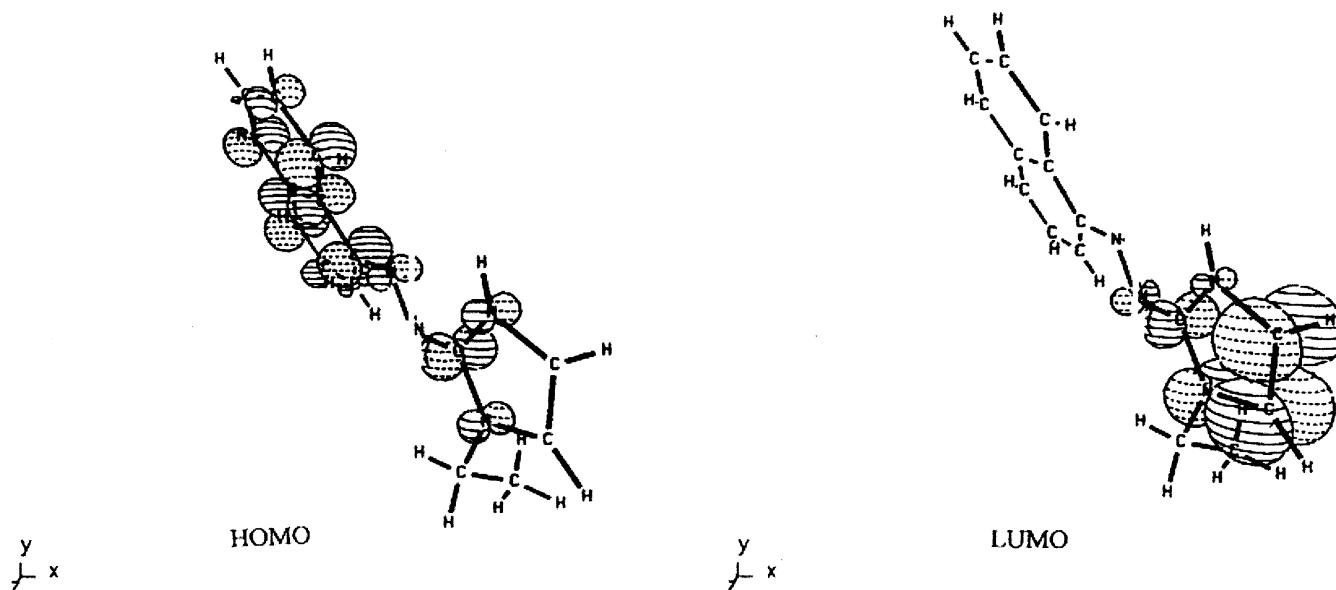


Fig. 3. HOMO and LUMO of [ $\alpha$ -NaiEtH<sup>+</sup>][PF<sub>6</sub><sup>-</sup>].

NaiEtH<sup>+</sup>][PF<sub>6</sub><sup>-</sup>]. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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