

Structure and photochromism of halo-bridged dimeric mercury(II) complexes of 1-alkyl-2-(*p*-nitro-phenylazo)imidazoles

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Mercury(II) complexes, $[Hg(p-NO_2aaiR)(\mu-X)(X)]_2$ (2-4) of $p-NO_2$ -aaiR [1-alkyl-2-(p-nitro-phenylazo)imidazole (1), where R = - CH₃ (1a), -C₂H₅ (1b) and X = Cl (2), Br (3), I (4)] have been studied by spectral data. X-Ray crystallography study in case of $[Hg(p-NO_2aai-CH_3)(\mu-I)(I)]_2$ (4a) has revealed the distorted dinuclear halobridge tetra-atomic puckered rhombohedral geometry. The ligand, $p-NO_2aaiR$ shows trans(E)-cis(Z) isomerisation both in free and coordination state on shocking UV light in the solution phase. The Z-to-E transformation is carried out by thermal treatment while photoisomerization is carried out very slowly on visible light absorption and $\phi_{E\rightarrow Z}$ (quantum yields for *E*-to-*Z* isomerisation) is superior for free ligand than the complex phase. The isomerisation rate follows $[Hg(p-NO_2aaiR)(\mu-I)(I)]_2$ (4) < $[Hg(p-NO_2aaiR)(\mu-Br)(Br)]_2$ (3) < $[Hg(p-NO_2aaiR)(\mu-CI)(CI)]_2$ (2) which is also the sequence of molar mass of the compounds. The energy gap calculation of the optimized structures by DFT (Density Functional Theory) also supports this conjecture.

Keywords: Photochromism, p-nitro-phenylazo-imidazole, Hg(II), X-ray, DFT.

Introduction

The structural change of some aromatic-azo compounds^{1,2} by absorbing light has massive applications in the field of molecular machines³, data storage⁴, bio-conjugates⁵, polymers towards optical stimuli-response⁶, nanomaterials^{7,8} etc. The prospect of azobenzene in this field is inspiring to focus on group of azo molecules, arylazoimidazoles, in particular². Photochromism of 1-alkyl-2-(arylazo)imidazole^{9,10} and some of their complexes are published^{11–14}. For detail investigation on the influence of substituent on the photoisomerisation, a nitro (-NO₂) functionalised azoimidazole, 1-alkyl-2-(p-nitro-phenylazo)imidazole, p-NO₂-aaiR (1) $(R = -CH_3(1a), -C_2H_5(1b))$ and its Hg(II) complexes are synthesized. The spectroscopic techniques are used for the characterisation of ligands and compounds. The single crystal X-ray structure determination is help ful for the establishment of structure of one of the complexes only. Through this work, the isomerisation rates and quantum yields are compared between free ligand and coordination phase in the complex in presence of different halides. Theoretical study has been attempted to describe the light induced structural change.



Scheme 1. Isomerisation of 1-alkyl-2-(*p*-nitro-phenylazo)imidazole, *p*-NO₂aaiR, (1).

Experimental

Materials:

1-Alkyl-2-(*p*-nitro-phenylazo)imidazoles (*p*-NO₂aaiR, **1**) were prepared by the literature procedure¹⁵. Mercury halides were received from Loba Chemicals, Mumbai, India and remaining chemicals were collected from Aldrich.

Physical measurements:

The elemental (C, H, N) analysis carried out by Perkin-Elmer 2400 CHNS/O elemental analyzer. The UV-Vis spectra were recorded from Perkin-Elmer Lambda 25 spectrophotometer. By using KBr pellets Perkin-Elmer RX-1 FTIR collected IR spectra. The Perkin-Elmer LS-55 spectrofluorimeter was used for photo excitation. The NMR spectra were taken from Bruker (AC) 300 MHz FTNMR spectrometer.

Synthesis of compounds

[Hg(p-NO₂aai-CH₃)(μ-I)(I)]₂ (**4a**):

To the solution of methanol (10 ml) 1-methyl-2-(p-NO₂phenylazo)imidazole (46.20 mg, 0.20 mmol) was added along with ethyleneglycol monomethyl ether (EGME) solution (5 ml) of Hgl₂ (90.88 mg, 0.20 mmol) and stirred (8 h) and filtered. The filtrate was allowed to evaporate slowly for a couple of weeks and needle shape; dark red colour crystals appeared (yield, 63%). Identical procedure were followed to preparer other complexes where the yield varied 60-70%. Microanalytical data: Calcd. for C₂₀H₁₈N₁₀O₄Hg₂Cl₄ (2a) C, 23.89; H, 1.80; N, 13.93. Found: C, 23.95; H, 1.75; N, 13.99%. FT-IR (v, cm^{-1}) 1586 (C=N), 1365 (N=N); UV-Vis $(\lambda_{max}, nm (10^{-4}))$ ε, M⁻¹ cm⁻¹) in DMF), 273 (0.59), 351 (0.40), 384 (0.45) 407 (0.41); ¹H NMR (300 MHz, DMSO-*d*⁶) δ, ppm: 8.11 (2H, d, 9.0 Hz, 7,11-H), 8.43 (2H, 9.0 Hz, 8,10-H), 7.39 (1H, bs, 4-H), 7.10 (1H, bs, 5-H), 4.11 (3H, s, 1-CH₃). Calcd. for C₂₂H₂₂N₁₀O₄Hg₂Cl₄ (**2b**) C, 25.57; H, 2.15; N, 13.55. Found: C, 25.52; H, 2.19; N, 13.59%; FT-IR (v, cm⁻¹) 1587 (C=N), 1362 (N=N); UV-Vis (λ_{max} , nm (10⁻⁴ ϵ , M⁻¹ cm⁻¹) in DMF), 273 (0.59), 354 (0.39), 380 (0.46) 403 (0.44); ¹H NMR (300 MHz, DMSO-*d*⁶) δ, ppm: 8.11 (2H, d, 9.2 Hz, 7,11-H), 8.44 (2H, d, 9.1 Hz, 8,10-H), 7.42 (1H, bs, 4-H), 7.09 (1H, bs, 5-H), 4.03 (2H, q, 6.6 Hz, N-CH₂-), 1.39 (3H, t, 5.6 Hz, N-CH₂-*CH₃).

 $\begin{array}{l} \mbox{Calcd. for C_{20}H$}_{18}N_{10}O_4$Hg_2Br_4$ ($ **3a** $) C, 20.30; H, 1.53; N, $$$1.84. Found: C, 20.35; H, 1.50; N, 11.87\%; FT-IR (v, cm^{-1})$$$1583 (C=N), 1366 (N=N); UV-Vis (λ_{max}, nm (10^{-4} ϵ, M^{-1}$ cm^{-1})$ in DMF), 269 (0.55), 358 (0.41), 381 (0.47) 405 (0.47); $$$$} \label{eq:calculation}$

¹H NMR (300 MHz, DMSO-*d*⁶) δ, ppm: 8.10 (2H, d, 9.0 Hz, 7,11-H), 8.42 (2H, 9.0 Hz, 8,10-H), 7.40 (1H, bs, 4-H), 7.09 (1H, bs, 5-H), 4.09 (3H, s, 1-CH₃). Calcd. for C₂₂H₂₂N₁₀O₄Hg₂Br₄ (**3b**) C, 21.81; H, 1.83; N, 11.56. Found: C, 21.87; H, 1.87; N, 11.59%; FT-IR (ν, cm⁻¹) 1583 (C=N), 1367 (N=N); UV-Vis (λ_{max} , nm (10⁻⁴ ε, M⁻¹ cm⁻¹) in DMF), 273 (0.59), 358 (0.43), 380 (0.49) 403 (0.43); ¹H NMR (300 MHz, DMSO-*d*⁶) δ, ppm: 8.11 (2H, d, 9.1 Hz, 7,11-H), 8.43 (2H, d, 9.0 Hz, 8,10-H), 7.39 (1H, bs, 4-H), 7.08 (1H, bs, 5-H), 4.03 (2H, q, 6.6 Hz, N-CH₂-), 1.38 (3H, t, 5.7 Hz, N-CH₂-*CH₃).

Calcd. for $C_{20}H_{18}N_{10}O_4Hg_2I_4$ (**4a**) C, 17.52; H,1.32; N, 10.21. Found: C, 17.47; H, 1.36; N, 10.19%; FT-IR (v, cm⁻¹) 1586 (C=N), 1367 (N=N); UV-Vis (λ_{max} , nm (10⁻⁴ ϵ , M⁻¹ cm⁻¹) in DMF), 271 (0.58), 355 (0.41), 381(0.47) 402 (0.45); ¹H NMR (300 MHz, DMSO-*d*⁶) δ , ppm: 8.09 (2H, d, 9.0 Hz, 7,11-H), 8.41 (2H, 9.0 Hz, 8,10-H), 7.39 (1H, bs, 4-H), 7.08 (1H, bs, 5-H), 4.09 (3H, s, 1-CH₃). Calcd. for C₂₂H₂₂N₁₀O₄Hg₂I₄ (**4b**) C, 18.88; H, 1.58; N, 10.01. Found: C, 18.92; H, 1.63; N, 10.07%; FT-IR (v, cm⁻¹) 1583 (C=N), 1365 (N=N); UV-Vis (λ_{max} , nm (10⁻⁴ ϵ , M⁻¹ cm⁻¹) in DMF), 270 (0.59), 353 (0.40), 383 (0.49) 409 (0.45); ¹H NMR (300 MHz, DMSO-*d*⁶) δ , ppm: 8.09 (2H, d, 9.0 Hz, 7,11-H), 8.42 (2H, d, 9.0 Hz, 8,10-H), 7.40 (1H, bs, 4-H), 7.08 (1H, bs, 5-H), 4.02 (2H, q, 6.5 Hz, N-CH₂-), 1.37 (3H, t, 5.8 Hz, N-CH₂*CH₃).

General X-ray crystallography

Red colour needle shaped crystal of size $(0.112 \times 0.101 \times 0.090 \text{ mm}^3)$ was diffracted and data were collected from a diffractometer of Bruker SMARTAPEX III where graphite-monochromated Mo-K α radiation (λ , 0.71073 Å) was used. Data collection details were recorded in Table 1. The least-squares refinement of all reflections within *hkl* range $-14 \le h \le 14$, $-9 \le k \le 9$, $-19 \le l \le 19$ were used for the calculation of unit cell parameters and crystal-orientation matrices. Lorentz and polarization effects¹⁶ were used for intensity data on applying the condition $l > 2\sigma$ (l). Full matrix least-squares refinements on F^2 were performed via SAINT program using SHELXL-97¹⁷ for all non-hydrogen atoms to measure the anisotropic displacement parameters.

Photometric measurements:

Perkin-Elmer Lambda 25 UV/Vis spectrophotometer used to accumulate absorption spectra at 298 K using Peltier

thermostat. The source light was Xenon lamp in the Perkin-Elmer LS 55 spectrofluorimeter. The concentration of *cis*isomer from irradiated solution was measured from absorption spectra and extrapolated against time of irradiation and the composition was assumed from ¹H NMR integration. The equation, $v = (\Phi I^0/V)(1 - 10^{-Abs}) (I^0$, the photon flux; *V*, the volume of the solution; Abs, the initial absorbance at the irradiation wavelength) was used to calculate quantum yields (Φ) by measuring initial *trans*-to-*cis* (*E-to-Z*) isomerization rates (v). Azobenzene ($\Phi = 0.11$ for π - π^* excitation) was used for the calculation of I^{0} ¹⁸.

The isomerisation rates (*cis*-to-*trans*, *Z*-to-*E*) at constant temperatures (298–313 K) were acquired by measuring the absorption changes intermittently from a *cis*-rich isomer. The Arrhenius equation, $\ln k = \ln A - E_a/RT$ (*k*, the measured rate constant; *R*, the gas constant, and *T*, temperature) was used for the calculation of activation energy (*E_a*) and the frequency factor (A). Using $\Delta G^* = E_a - RT - T\Delta S^*$ and $\Delta S^* = [\ln A - 1 - \ln (k_BT/h)/R (k_B, Boltzmann's constant;$ *h* $, Plank's constant) the activation free energy (<math>\Delta G^*$) and activation entropy (ΔS^*) were calculated.

Computational methods:

To get theoretical insight, DFT was used in GAUSSIAN 09 (G09) program package¹⁹ and was implemented for the compounds $[Hg(p-NO_2aaiCH_3)(\mu-X)(X)]_2$ (X = CI (2a), Br (3a), I (4a)). The basis function B3LYP²⁰ (for C, H, N, O, CI) and LanL2DZ^{21–23} (for Hg, Br and I) were used. The calculation of vibrational frequency had been achieved with the designed complexes; and the optimized molecular geometries at the local minima were ensured that and the only positive Eigen values were taken for grand. The coordinates from single crystal X-ray structure was used in the calculation. The experimental spectra are analysed using time dependent DFT (TD-DFT) calculations. Virtual transitions in DMF medium following the conductor-like polarizable continuum model were assigned to the lowest 25 singlet-singlet transition and TD-DFT calculation results were comparable. GaussSum²⁴ was used for fractional contribution measurements.

Results and discussion

The compounds:

The ligands, p-NO₂aaiR (1), [R = -CH₃ (1a), -C₂H₅ (1b); {p-NO₂aaiR = 1-Alkyl-2-(p-nitro-phenylazo)imidazole}], were

prepared by literature process¹⁵. The complexes [Hg(p- NO_2aaiR)(μ -X)X]₂[X = CI, Br and I] (2-4) were synthesized by the reaction of p-NO₂aaiR (in MeOH) and HgX₂ (in EGME) (Scheme 2). The composition of the compounds were supported by microanalytical data. The intense stretches of the complexes, 2-4 (Supplementary Fig. 1) at 1580–1605 cm⁻¹ for $\nu_{(C=N)},\,1360-1375\,\,\text{cm}^{-1}$ for $\nu_{(N=N),}\,1509-1515\,\,\text{cm}^{-1}$ and 1335–1345 cm^1 for $\nu_{(N\text{-}O)asym}$ and $\nu_{(N\text{-}O)sym}$ respectively (vide Experimental section) are indicator of the presence of functional groups. These stretching are appeared in diminished by 10–20 cm⁻¹ unit relative to free ligand data²⁵. This observation supports that the imidazolyI-N and azo-N atoms are coordinated to $Hq(II)^{26-28}$. DMF solution of the complexes shows intense absorptions at 270-275, 350-380 and 400-410 nm, and a weak band at 500-550 nm (Supplementary Fig. 2). The N(1)-alkyl signal appears at 4.03 ppm. Imidazolyl protons (4,5-H) observe at δ 7.26–7.30 and 7.15–7.20 ppm, respectively (Supplementary Fig. 3). The downfield shift of protons compare to the free ligand values^{29,30} support the chelate ring formation of N(imidazolyl) and N(azo) atoms of ligand to the Hg(II) ion.



 $\begin{array}{l} \label{eq:p-NO_2aai-CH_3(1a), p-NO_2aai-C_2H_5(1b), $[Hg($p$-NO_2aai-CH_3)($\mu$-Cl)(Cl)]_2$ (2a), $[Hg($p$-NO_2aai-C_2H_5)($\mu$-Cl)(Cl)]_2$ (2b) $[Hg($p$-NO_2aai-CH_3)($\mu$-Br)(Br)]_2$ (3a), $[Hg($p$-NO_2aai-C_2H_5)($\mu$-Br)(Br)]_2$ (3b), $[Hg($p$-NO_2aai-CH_3)($\mu$-l)(l)]_2$ (4a), $[Hg($p$-NO_2aai-C_2H_5)($\mu$-l)(l)]_2$ (4b) $ \end{array}$

Scheme 2. Ligands and Hg(II)-halide complexes.

The crystal structure of $[Hg(p-NO_2aai-CH_3)(\mu-I)(I)]_2$ (4a): The structure of $[Hg(p-NO_2aai-CH_3)(\mu-I)(I)]_2$ (4a), crystal system, monoclinic; space group, P21/c; *Z*, 4) is given in Fig. 1 and also the bond lengths and bond angles are given in Table 1. The unit structure consists of dinuclear iodobridged Hg₂I₂ fragment. Mallick et al.: Structure and photochromism of halo-bridged dimeric mercury(II) complexes etc.



Fig. 1. (a) Asymmetric unit of compound [Hg(p-NO₂aai-CH₃)(μ-I)(I)]₂ (4a).

Table 1. Summarized crystallographic data for [Hg(<i>p</i> -NO ₂ aaiMe) (μ-I)(I)] ₂ (4a)				
Compound	[Hg(<i>p</i> -NO ₂ aaiMe)(μ-I)(I)] ₂ (4a)			
Empirical formula	C ₂₀ H ₁₈ I ₄ N ₁₀ O ₄ Hg ₂			
Formula weight	1371.22			
Temperature (K)	273(2)			
Crystal system	Monoclinic			
Space group	P21/c			
a (Å)	7.8271(4)			
b (Å)	18.8750(9)			
<i>c</i> (Å)	22.0966(10)			
β (°)	94.032(2)			
V (Å) ³	3256.4(3)			
Z	4			
μ (MoK $lpha$) (mm ⁻¹)	13.252			
θ range	2.140–27.512			
hkl range	-10 < h < 10; -24 < k < 24; -28 < l < 28			
D _{Calcd.} (mg m ⁻³)	2.797			
Refine parameters	363			
Total reflections	47075			
Unique reflections	7466			
R1 ^a [<i>I</i> > 2σ (<i>I</i>)]	0.0502			
wR ^{2b}	0.1376			
Goodness of fit	1.108			
^a $R = \Sigma F_0 - F_c /\Sigma F_0 $. ^b $wR^2 = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_0)^2 + (0.0778P)^2 + 9.4074P]$; where $P = ((F_0^2 + 2F_c^2)/3$.				

tortion around central metal ion is caused for the generation of small chelate angle (62.89°). The (Hg(1)-N(1), 2.333(8) Å) is shorter than (Hg(1)-N(4), 2.811 Å, that implements the stronger interaction between Hg(II) to N(imidazolyI). The van der Waals radii of Hg(II) (1.55 Å) and N(sp²) (1.53 Å) suggest some sort of Hg----N(azo) interaction. The long Hg(1/2)-N(azo) distance promotes the molecules for activation by light followed by cleavage of the bond and rotation about -N=N- to govern photoisomerisation (vide infra). The N=N distance, 1.260(11) Å, is analogous with published result $(1.262(6) \text{ Å})^{13,14}$. Neighbouring molecules show π -- π interactions with p-NO2 phenyl and imidazolyl groups forming supramolecular aggregation; the weak C-H-- π secondary interactions between CH₂-H (imidazolyl) and aromatic rings p-NO₂ phenyl also play the pivotal to design the self-assembled molecular structure (Fig. 2). This supramolecular aggregation may be inspired the exhibited molecular properties.

-y, -z) support the distorted geometry¹³. The geometrical dis-



Fig. 2. (a) Supramolecular interactions in Hg-compound; (b) Space fill view of supramolecular aggregated Hg-compound via different secondary interactions.

Table 2. Selected bond distances (Å) and angles (°) for

p-NO₂aaiCH₃ is a N,N'-chelating ligand (N and N' refer to N(imidazolyl) and N(azo) donor centres) and a non-bridging I is appended from the axial position. The tetra-atomic puckered rhombohedral geometry of Hg₂I₂ bridge is exhibited by metric parameters: Hg(1)-I (1), 2.6736(10) Å; Hg (1)-I (4), 3.2844(10) Å (*symmetry: -x, -y, -z). The bond angles, I(1)-Hg(1)-I(2), 129.65°, I(1)-Hg-I(4), 92.20° (*symmetry, -x,

[Hg(<i>p</i> -NO ₂ aai-CH ₃)(μ-I)(I)] ₂ (4a)				
Bond distances (Å)		Bond angles (°)		
Hg(1)-I(1)	2.6736(10)	I(1)-Hg(1)-I(4)	95.67(3)	
Hg(1)-I(2)	2.6639(11)	l(1)-Hg(2)-l(4)	92.20 (3)	
Hg(1)-I(4)	3.2844(10)	N(1)-Hg(1)-N(4)	62.89 (3)	
Hg(1)-N(1)	2.333(8)	N(6)-Hg(2)-N(9)	61.72 (3)	
Hg(1)-N(4)	2.811(8)	N(4)-Hg(1)-I(4)	151.71(2)	
Hg(2)-I(1)	3.449 (1)	I(1)-Hg(1)-I(2)	129.65(3)	

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		Table	e-2 (contd.)	
Hg(2)-I(3)	2.6194(9)	Hg(1)-I(4)-Hg(2)	85.37(3)	
Hg(2)-I(4)	2.6597(10)	Hg(1)-I(1)-Hg(2)	81.92(3)	
Hg(2)-N(6)	2.419(8)	I(3)–Hg(2)-I(4)	148.80(3)	
Hg(2)-N(9)	2.819(8)			
N(4)-N(3)	1.260(11)			
N(8)-N(9)	1.232(11)			
*Symmetry: -x, -y, -z; ** Symmetry: 1-x, 2-y, 1-z				

Photochromism:

Light absorption in UV wavelength (λ_{max} , 364 nm) causes *trans*-(*E*-isomer) to *cis*-(*Z*-isomer) isomerisation² (Fig. 3 and Fig. 4). For free ligand methanol solution of ligand is used while the complex is sparingly soluble in MeOH so DMF solution is used. The absorption at UV region is decreased followed by the augmentation at the longer wavelength portion of the spectrum till a stationary state is reached. The *E*-to-*Z* transformation continues and becomes inaccessible at the *Z* molar ratio of ~ 65%. The continual spectral change is associated with isosbestic point (~340 nm).

Repetitive irradiation followed by spectral measurements of both the ligands and the complexes give an idea about little signal of dilapidation at least upto 15 cycles. The *E*-to-*Z* ($\Phi_{E\rightarrow Z}$) photoisomerisation for all the compounds has been quantitatively compared with their calculated rates and quantum yields (Table 3). Data may be correlated with molar mass of the photochrome which suggest that increase in mass of the molecule decreases the rate and quantum yield. Besides, the coordinated halide (CI, Br, I) may have photo bleaching activity³¹ and may grasp sizeable amount of energy from π - π^* excited state; I (iodo) has highest efficiency in this regard.



Fig. 3. Evolution of absorption of *p*-NO₂aaiMe (1a) in MeOH upon irradiation at 364 nm at 3 min interval at 25°C.



Fig. 4. Evolution of absorption of $[Hg(p-NO_2aai-CH_3)(\mu-I)(I)]_2$ (4a) in DMF upon irradiation at 368 nm at 5 min interval at 25°C.

Table 3. Results of photochromism, rate of conversion and quantum yields upon UV light irradiation				
Compds.	λ_{π,π^*} (nm)	Isobestic point (nm)	Rate of $E \rightarrow Z$ conversion×10 ⁸ (s ⁻¹)	$\phi_{E \rightarrow Z}$ conversion
1a	364	343, 493	5.010	0.221±0.002
1b	365	343, 491	4.861	0.209±0.006
2a	364	341, 489	2.127	0.153±0.002
2b	366	339, 490	2.057	0.148±0.003
3a	367	342, 491	2.336	0.168±0.002
3b	366	341, 492	2.238	0.161±0.001
4a	368	340, 496	2.630	0.186±0.002
4b	367	342, 493	2.511	0.181±0.003

The spectral measurements of cis(Z) to trans(E) isomerisation of the compounds (Supplementary Figs. 4 and 5) at 298-313 K show linear relation with 1/T vs $-\ln(k/T)$ (Eyring plots) and the ΔS^* and ΔH^* are calculated (Table 4, Fig. 5) from the data. The E_a s of the complexes are much lower than that of respective free ligand; this accounts the faster *Z*-to-*E* thermal isomerisation of the complex. The ΔS^*



Fig. 5. The Eyring plots of Z-to-E isomerisation: (a) p-NO₂aaiMe (1a) and (b) [Hg(p-NO₂aaiMe)(μ-I)(I)]₂ (4a) at 298–313 K.

of the complexes are much lower than free ligands.

Electronic structure and spectra:

Using optimized molecular structures of [Hg(p-NO₂aaiMe) $(\mu$ -X)(X)]₂ {X = Cl (2a), Br (3a), I (4a)} theoretical calculations are performed. From Gauss Sum calculation the energy values of molecular orbitals and fractional contributions of structural components are obtained. In 2a the HOMO and HOMO-1 are degenerated (E_{HOMO} , -7.05 eV and $E_{\text{HOMO-1}}$, -7.10 eV) in which contribution of CI is 97% (Supplementary Table 1). The LUMO and LUMO+1 are closer in energy and have been constituted from the ligand side (E_{LUMO.} -4.42 eV and E_{LUMO+1}, -3.26 (eV). The HOMO-2 and lower MOs change both from energy and composition. Other unoccupied MOs appear at higher energy. In HOMO and HOMO-1 of 3a Br covers 98%. In 4a the observation is comparable to 2a and 3a i.e. the HOMO, HOMO-1 etc. have chief input (98%) from I. Therefore, theoretical measurements conclude about the major contributions of halogen atoms in major molecular orbitals.

UV light shocking is compulsory for photochromic process which implements that *trans*-isomer (E) is more stable

Table 4. Rate and activation parameters for $Z(c) \rightarrow E(t)$ thermal isomerisation						
Compd.	Temp. (K)	Rate of thermal $c \rightarrow t$ conversion×10 ⁴ (s ⁻¹)	E _a (kJ mol ^{−1})	ΔH^* (kJ mol ⁻¹)	ΔS^* (J mol ⁻¹ K ⁻¹)	ΔG^{*c} (kJ mol ⁻¹)
1a	298	0.795	84.65	82.11	-48.14	96.82
	303	1.194				
	308	2.654				
	313	3.756				
1b	298	0.778	81.47	78.93	-58.61	96.84
	303	1.321				
	308	2.453				
	313	3.642				
2a	298	1.841	35.59	33.06	-205.60	96.40
	303	2.314				
	308	2.745				
	313	3.741				
2b	298	1.851	34.57	32.61	-206.98	95.84
	303	2.455				
	308	2.751				
	313	3.748				
3 a	298	1.875	38.43	35.90	-195.28	95.56
	303	2.641				
	308	3.241				

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Fig. 6. Correlation between HOMO (H) and LUMO (L) in terms of their energy of 2a, 3a and 4a. Results obtained from DFT calculation of optimized geometries.

(a)

than *cis*-isomer (*Z*). The UV radiation absorption involves $\pi \rightarrow \pi^*$ transition. Involvement of MLCT or XLCTs in the transition may associate with energy loss by energy transfer to the coordinated azoimidazole (via Hg-N(azo) bond cleavage) and hence is not sufficient to perform isomerisation.

Energy correlation diagram (Fig. 6) shows the order of MOs of the complexes. The energies of the MOs show very close in **2a** and **3a** while **4a** differs significantly. The difference in energy ($\Delta E = E_{LUMO} - E_{HOMO}$) maintains the ordering [Hg(p-NO₂aaiMe)(μ -I)(I)]₂ (**4a**) (1.96 eV) < [Hg(p-NO₂aaiMe)(μ -Br)(Br)]₂ (**3a**) (2.29 eV) < [Hg(p-NO₂aaiMe)(μ -Cl)(Cl)]₂ (**2a**) (2.63 eV). It is observed a liner relation between ΔE versus rates of isomerisation and quantum yields (Fig. 7). This is an indication of the straight forward relation between photophysical process and activation energy.



(b)

Fig. 7. Correlation between (a) $\Delta E = E_{LUMO} - E_{HOMO}$ vs rates of photoisomerisation and (b) $\Delta E = E_{LUMO} - E_{HOMO}$ vs quantum yield.

Conclusion

Hg(II)-halide complexes of 1-alkyl-2-(*p*-nitro-phenylazo) imidazoles, $[Hg(p-NO_2aaiR)(\mu-X)(X)]_2$ (**2-4**) have been spectroscopically characterized and the structures has been confirmed by X-ray diffraction measurement in one case. UV light assisted photochromic behaviour of ligands and the complexes are checked. The rate and quantum yields of *E*-to-*Z* isomerisation of the complexes are less than that of free ligand data may be due to the higher rotor mass and volume that may be the regulating factors. DFT and TD-DFT calculations also support the experimental data of the rate and quantum yields.

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Supporting Information

Crystallographic data for the structure $[Hg(p-NO_2aai-CH_3)(\mu-I)(I)]_2$ (**4a**) has been deposited to the Cambridge Crystallographic Data Center, CCDC No. 2010214. Related information may be available to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (E-mail: deposit@ccdc.cam. ac.uk or www:htpp://www.ccdc.cam.ac.uk).

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