

Origin and switch of different colors: Thermo-isomerism and crystal structure of (1E,2E)-bis[1-(4-nitrophenyl)ethylidene] hydrazine

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Abstract. A new symmetric branched 4-nitrophenyl hydrazine compound has been prepared in one-step procedure by direct condensation of aromatic ketone with hydrazine in MeOH. The synthesized compound, red isomer, was characterized by IR, ¹H and ¹³C NMR spectroscopy, Elemental analyses, Mass spectrometry and X-ray crystallography. Refluxing in MeOH solution led to thermo-isomerism offering a white isomer product that was characterized by X-ray crystallography. The red isomer crystallizes in the orthorhombic system having space group *Pbcn*, with *a* = 12.7612(4), *b* = 11.5197(3), *c* = 20.1586(7) Å, *V* = 2963.42(16) Å³, *Z* = 8 while the white isomer crystallizes in the triclinic system having space group *P*[−]1, with *a* = 7.8007(4), 8.5966(7), 12.224 (1) Å, *α* = 71.133(7), *β* = 81.281(5), *γ* = 74.895(5)°, *V* = 746.86(9) Å³, *Z* = 2. Molecules of both compounds are twisted at N2–N3 bond with the C7–N2–N3–C9 torsion angle of 155.23(12) and −113.36(18)°, respectively. The crystal structures of both compounds are stabilized by weak intramolecular C—H...N contacts and intermolecular C—H...O hydrogen bonding interactions. In addition, *π*–*π* stacking interactions are observed between the same aromatic rings of molecules.

Keywords. Hydrazine derivative; crystal structure; thermo-isomerism; color switching.

1. Introduction

π-conjugated fluorescent compounds with C=N–N=C moiety can be useful models for fluorescent electronic and bio-materials.^{1–17} A list of known *π*-conjugated compounds is given in Supplementary Information (figure S1). The concept of a fluorescent material is fundamentally based on intramolecular charge transfer that occurs in its simplest form in *π*-conjugated hydrazone systems. Hydrazones have been intensively investigated mostly because of their potential applications^{1–17} as antimicrobial agents and as fluorescent chemosensors

for metal ions. The title compound was synthesized to study antibacterial activity and fluorescence properties in order to get more detail on the structure-activity relationship by comparison with other closely related compounds.

In search of new bioactive *π*-conjugated fluorescent compounds to study the difference between fluorescent and normal bioactive agents, we have considered the simple case of compound (1). Cooperation between terminal substituents of phenyl groups played a key role in the *trans-cis* isomerism even though fluorescent compounds are used in these systems. It would then be anticipated that the two thermo isomers could be reorganized and brought selectively in close proximity such as those in nature.

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2. Experimental

2.1 Materials and measurements

All solvents and other chemicals, obtained from usual commercial sources, were of analytical grade and used without further purification. The proton NMR spectra were obtained with a Bruker AC 300 spectrometer. Elemental analyses were performed by Microanalysis Central Service (CNRS). Molecular weights were determined on a JEOL JMS DX-300 Mass Spectrometer.

2.2 X-ray structure determination of (1a) and (1b)

Suitable single crystal of hydrazine derivative C₁₆H₁₄N₄O₄ was obtained by recrystallization from methanol. The crystal was mounted on a glass fiber. For compounds **1a** and **1b** (see below), all measurements were made in the ω -scan technique on a CCD Sapphire 3 Xcalibur diffractometer with graphite monochromatized MoK α radiation at low temperature [130(2) K]. Absorption corrections were not applied. H atoms were geometrically located in calculated positions and treated as riding on their parent atoms, with C–H = 0.95 and 0.98 Å, and with U_{iso}(H) = 1.2U_{eq}(C) for aromatic H atoms and U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms.

Crystal data collection: CrysAlis CCD.¹⁸ Cell refinement: CrysAlis RED.¹⁸ Data reduction: CrysAlis RED.¹⁸ Program(s) used to solve structure: SIR97.¹⁹ Program(s) used to refine structure: SHELXL97.²⁰ Molecular graphics: ORTEP-3 for Windows.²¹ Software used to prepare material for publication: WinGX.²²

2.3 (1E,2E)-bis[1-(4-nitrophenyl)ethylidene]hydrazine

1-(4-nitrophenyl)ethanone (5.5 g, 31.24 mmol) was dissolved in ethanol (50 mL) and 0.5 equivalent of hydrazine (0.5 g, 15.63 mmol) was added. The mixture was under continuous stirring at room temperature for 3

days using two drops of catalyst (acetic acid). The formed product was filtered and washed with ethanol. The final purification was achieved by recrystallization in hot methanol solution giving two types of crystals: **1a** (red isomer-1) and **1b** (white Isomer-2) which were separated manually and characterized by X-ray crystallography.

2.3a 1a (Red Isomer-1): Yield 82.13%. R_f = 0.7 (silica/CH₂Cl₂). IR: ν (C=N, imine) = 1623 cm⁻¹. ¹H NMR (300 MHz, DMSO) δ ppm: 8.29 (d, 4H, aromatic, C₃-H, C₅-H); 8.15 (d, 4H, aromatic, C₂-H, C₆-H); 2.30 (s, 6H, imine, CH₃). ¹³C NMR (75 MHz, DMSO) δ ppm: 156.5 (2C, aromatic, C₁); 148.6 (2C, aromatic, C₄), 143.9 (2C, imine, C=N); 128.3 (4C, aromatic, C₂, C₆); 124.1 (4C, aromatic, C₃, C₅); 15.5 (2C, aliphatic, CH₃-C=N). m/z (M⁺): 327.15.

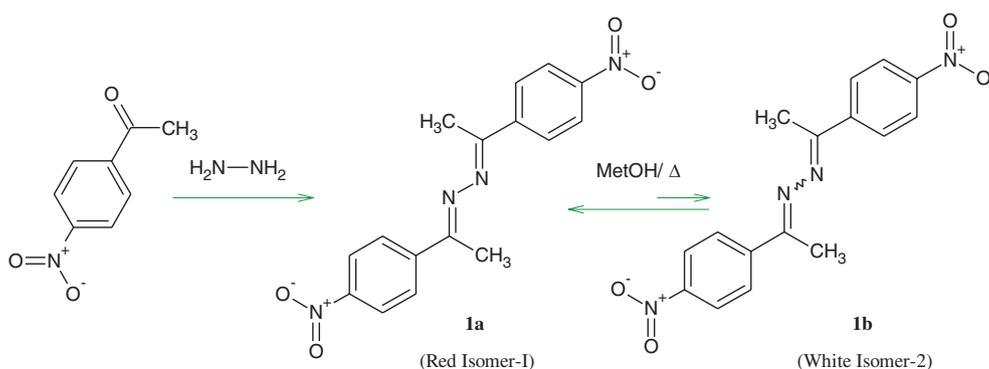
2.3b 1b (White Isomer-2): Yield 10%. R_f = 0.7 (silica/CH₂Cl₂). IR: ν (C=N, imine) = 1623 cm⁻¹. ¹H NMR (300 MHz, DMSO) δ ppm: 8.29 (d, 4H, aromatic, C₃-H, C₅-H); 8.15 (d, 4H, aromatic, C₂-H, C₆-H); 2.30 (s, 6H, imine, CH₃). ¹³C NMR (75 MHz, DMSO) δ ppm: 156.5 (2C, aromatic, C₁); 148.6 (2C, aromatic, C₄), 143.9 (2C, imine, C=N); 128.3 (4C, aromatic, C₂, C₆); 124.1 (4C, aromatic, C₃, C₅); 15.5 (2C, aliphatic, CH₃-C=N). m/z (M⁺): 327.15.

3. Results and Discussion

3.1 Chemistry

Our strategy was to develop a simple and acceptable procedure, in one step, to prepare the desired colored compound (**1**). The result of our investigation is given below (scheme 1).

The title compound was also synthesized by mixing a solution (1:2 molar ratio) of hydrazine hydrate (0.20 mL, 4 mmol) and 4-nitroacetophenone (1.42 g, 8 mmol) in ethanol (50 mL). The resulting solution was



Scheme 1. Synthesis of (1E,2E)-bis[1-(4-nitrophenyl)ethylidene]hydrazine compound.

refluxed for 4 h yielding a mixture of a red crystalline solid (**1a**) and a white crystalline solid (**1b**). The resultant mixture was filtered off and washed with methanol. Red and white block-shaped single crystals of the title compound suitable for X-ray structure determination were obtained by recrystallization from MeOH by slow evaporation of the solvent at room temperature over three days.

3.2 Crystal structures of **1a** (red isomer-1) and **1b** (white isomer-2)

The details of the crystal and experimental data for compounds **1a** and **1b** are listed in table 1. Selected

bond distances and bond angles are given in Supplementary Information, table S1. The data presented in table S1 show that the bond lengths of the selected atoms fall in their respective single or double bond range. The molecular structures of the compounds **1a** and **1b** are shown in figures 1 and 2, respectively. Packing and hydrogen bonding interactions are illustrated in Supplementary Information, figures S2–S5. The packing diagram of the compound **1a** (red isomer) makes a wave like structure when viewed along a-axis as shown in figure S2. The same molecule when viewed along c-axis, then it forms a sandwich like structure as given in figure S3. The packing diagram of the compound **1b** (white isomer) makes a zig-zag-like structure

Table 1. Crystal data and refinement parameters of **1a** (red isomer) and **1b** (white isomer).

	1a (red isomer) CCDC No. 984384	1b (white isomer) CCDC No. 984383
Chemical formula	C ₁₆ H ₁₄ N ₄ O ₄	C ₁₆ H ₁₄ N ₄ O ₄
<i>M_r</i>	326.31	326.31
Crystal system, space group	Orthorhombic, <i>pbcn</i>	Triclinic, <i>P</i> ⁻¹
Temperature (K)	130	140
<i>a</i> , <i>b</i> , <i>c</i> (Å)	12.7612 (4), 11.5197 (3), 20.1586 (7)	7.8007 (4), 8.5966 (7), 12.224 (1)
α , β , γ (°)	90, 90, 90	71.133 (7), 81.281 (5), 74.895 (5)
<i>V</i> (Å ³)	2963.42 (16)	746.86 (9)
<i>Z</i>	8	2
<i>F</i> (000)	1360	340
<i>D_x</i> (Mg m ⁻³)	1.463	1.451
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
No. of reflections for cell measurement	14528	3242
θ range (°) for cell measurement	3.1–27.5	3.1–27.5
μ (mm ⁻¹)	0.11	0.11
Crystal shape	Prism	Prism
Colour	Red	Colourless
Crystal size (mm)	0.25 × 0.19 × 0.10	0.22 × 0.17 × 0.15
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	21937, 3228, 2452	5541, 3249, 2393
<i>R</i> _{int}	0.037	0.024
θ values (°)	$\theta_{\max} = 27.0$, $\theta_{\min} = 3.1$	$\theta_{\max} = 27.0$, $\theta_{\min} = 3.1$
($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.639	0.639
Range of <i>h</i> , <i>k</i> , <i>l</i>	<i>h</i> = -15 → 16, <i>k</i> = -14 → 14, <i>l</i> = -20 → 25	<i>h</i> = -9 → 9, <i>k</i> = -10 → 10, <i>l</i> = -15 → 14
Refinement on	<i>F</i> ²	<i>F</i> ²
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.037, 0.108, 1.03	0.045, 0.120, 1.04
No. of reflections	3228	3249
No. of parameters	219	219
No. of restraints	0	0
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0579P)^2 + 0.3184P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2 + 0.078P]$ where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ) _{max}	<0.0001	<0.0001
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.22, -0.21	0.21, -0.25
CCDC	984384	984383

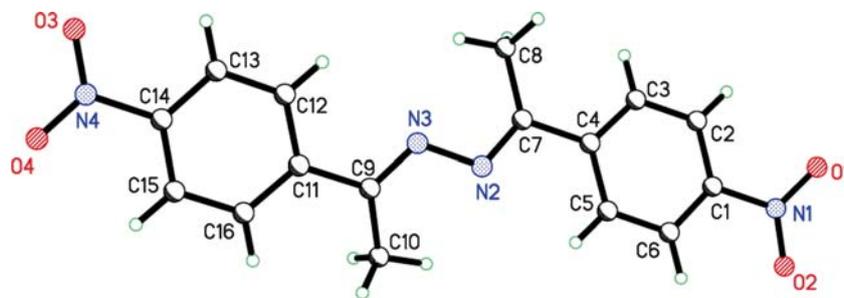


Figure 1. ORTEP view of compound **1a** (red isomer) with the atomic numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

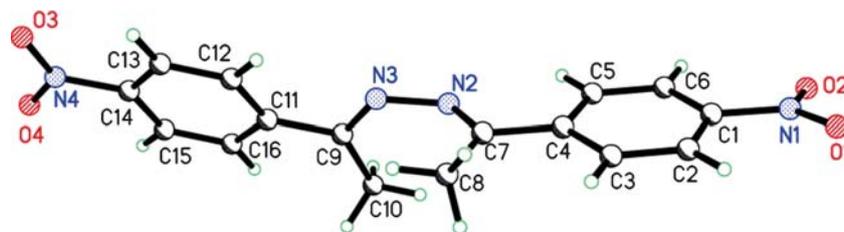


Figure 2. ORTEP view of compound **1b** (white isomer) with the atomic numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

as shown in figure S4 when viewed along *b*-axis and a wall-like structure along *c*-axis (figure S5). Hydrogen bond parameters for compounds **1a** and **1b** are given in table S2. It can be seen from table S2, that there are three types of H-bondings in compound **1a** (red isomer): C8—H8A...N3 = 2.7495(18) Å; C10—H10A...N2 = 2.7403(18) Å; C13—H13...O1 = 3.3255(17) Å while in compound **1b** (white isomer) there are five types: C2—H2...O3 = 3.451(2) Å; C5—H5...O4 = 3.180(2) Å; C8—H8A...N3 = 2.798(3) Å; C10—H10A...N2 = 2.791(2) Å; C12—H12...O2 = 3.324(2) Å.

The single crystal X-ray analysis reveals that the title hydrazine derivatives **1a** (red isomer) and **1b** (white isomer) crystallize respectively as orthorhombic crystal system with space group *Pbcn* and triclinic crystal system with space group *P*⁻¹ (See Supplementary Information). The structure of compound **1a** has been reported by Glaser *et al.*²³ at room temperature (295 K). But we have determined the crystal structure of **1a** at low temperature (130 (2) K) and confirm here its thermo-isomerism for the first time. Molecules of both compounds (**1a** and **1b**) are twisted at N2—N3 bond with the C7—N2—N3—C9 torsion angle of 155.23 (12)° and −113.36 (18)°, respectively. The dihedral angles between the two aromatic rings are 16.51(6)° for **1a** and 62.11(8)° for **1b**. All bond lengths and bond angles in **1a** and **1b** are normal and agree well with that

previously reported for similar structure²³ and with each other. In the crystal structure of both isomers (**1a** and **1b**), molecular conformations are stabilized by weak intramolecular C—H...N contacts. Intermolecular O—O interactions (2.914 Å) of the nitro groups stabilize the crystal structure (figure 3). Furthermore, π – π stacking interactions [centroid-centroid distances = 3.5717(7) and 3.5599(7) Å for **1a**, and 3.8656(10) and 3.6255(10) Å for **1b**] exist between the same aromatic rings of molecules.

3.3 Thermo-isomerism of red isomer (**1a**) to white isomer (**1b**)

The *cisoid-transoid* isomerism chemical equilibrium is highly aromatically driven to the formation of two stabilized isomers. *Cisoid-transoid* isomerism is important in several areas of biochemistry and physics applications; rare *trans* diazine isomers can lead to *cis* mutation because of their altered base-pairing properties. In the present case, the *trans* form is greatly favored due to aromatic stabilization and minimum steric repulsion. The system in *transoid* form is fully conjugated. The *trans-cis* interconversion rate (85/15) under reflux of MeOH is not completed definitively. It was determined accidentally by comparison of the amount of **1b** as a co-product of **1a** and using crystallographic analyses.

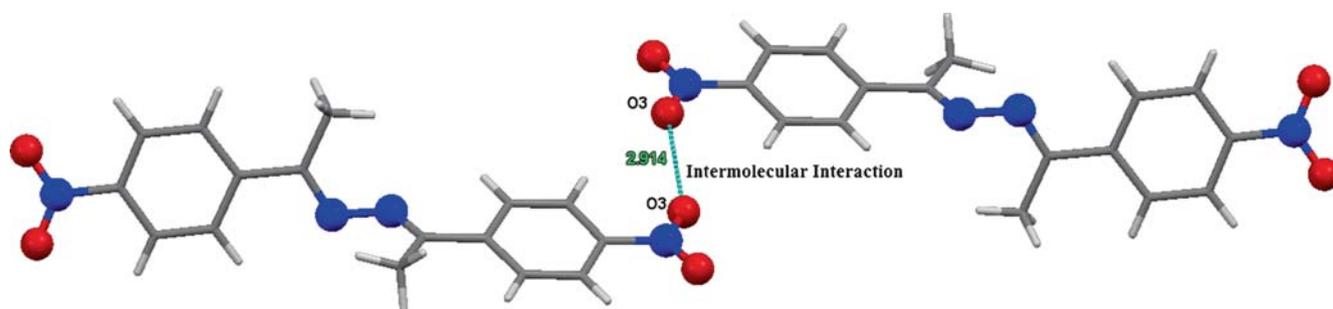
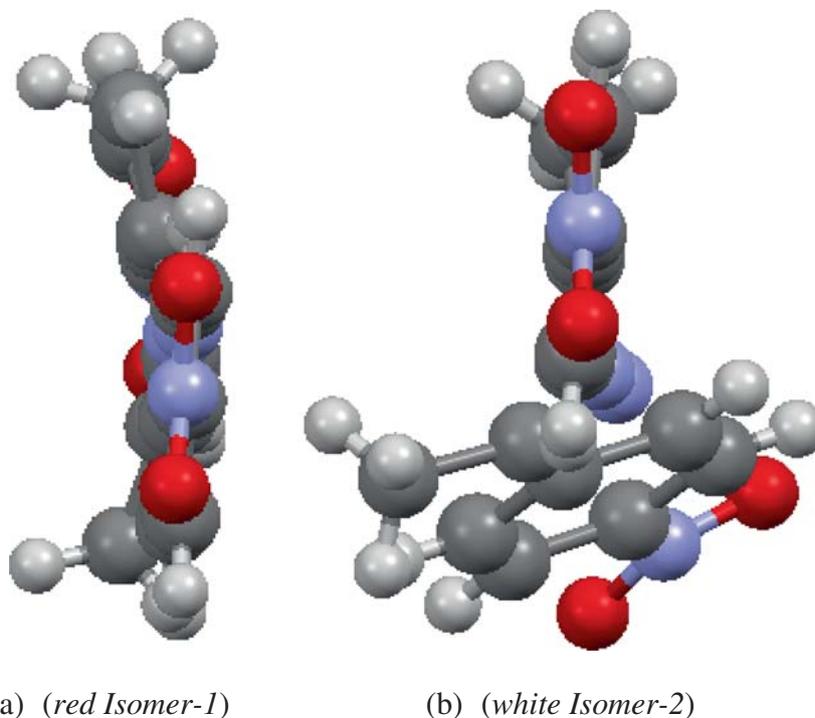


Figure 3. View of intermolecular interaction in **1b** (white isomer).



(a) (*red Isomer-1*)

(b) (*white Isomer-2*)

Figure 4. Origin of switch of colors: from planar (red) to non-planar (white) structure.

The geometry of **1a** is semi-flexible because of the presence of N-N semi- π -conjugated bond of C=N-N=C as central moiety, the molecule is planar and the favored geometry is that which presents less hindered/steric obstruction (figure 4). This compound can act as a colored (red isomer **1a**) or colorless dye (white isomer **1b**) when heating in alcohols.

4. Conclusions

Hydrazone undergoes *trans-cis* isomerism when heated in an appropriate solvent. The reverse *trans-cis* thermo-isomerism can be driven also by light or occurs thermally in the dark. Thermochromatic properties of hydrazones make it an ideal component of numerous molecular devices and functional materials. Despite the abundance of application-driven research, hydrazone,

azobenzene photochemistry and the isomerization mechanisms remain topics of investigation. Understanding the differences in thermo and photochemistry, which originates from substitution, is imperative in exploiting hydrazone and azobenzene in desired applications.

Supplementary Information

Supplementary information is available at www.ias.ac.in/chemsci.

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