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Photochromism of (*E*)-4-phenyl-1-(pyridine-2ylmethylene)semicarbazide[†]

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Lirong Lin,* Weizhen Fan, Shui Chen, Jie Ma, Wangxia Hu, Yiji Lin, Hui Zhang and Rongbin Huang

Photochromism of (E)-4-phenyl-1-(pyridine-2-ylmethylene)semicarbazide (1) in solution was shown to result from the *trans-cis* photoisomerization of its C=N double bond and its photochromism in solid state was found to take place, too, but via changes in the molecular geometry and packing upon UV irradiation.



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Photochromism of (*E*)-4-phenyl-1-(pyridine-2ylmethylene)semicarbazide[†]

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A photochromism molecule of (*E*)-4-phenyl-1-(pyridine-2-ylmethylene)semicarbazide (1) was reported. Photochromism of 1 in solution was shown to result from the *trans-cis* photoisomerization of its C=N double bond, by using absorption, ¹H NMR (including 2D NOESY) and directly the crystal structure of 1 obtained from solutions before and after UV irradiation. Photochromism 1 in solid state was found to take place too, but via changes in the molecular geometry and packing upon LW irradiation.

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Introduction

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cis-trans photoisomerization of organic compounds such as olefins plays an important role in chemistry and biochemistry.¹⁻⁵ This phenomenon is utilized for photochromism and a large

- ¹⁵ number of photochromic molecules based on the *cis-trans* isomerization of olefins and azo compounds have been designed and studied.⁶⁻¹⁵ It has been shown that the C=N double bond in a Schiff base exhibits *cis-trans* isomerization. There are, however, a number of photochromic Schiff bases whose photochromism is ²⁰ not by way of the *cis-trans* isomerism of the C=N double bond.
- ²⁰ hot by way of the *cis-trans* isomerism of the C-1V double bond, but undergoes through intramolecular proton transfer from the *o*-OH to the imino nitrogen atom of *N*-salicylideneanilines.¹⁶⁻²² While the chemistry of *cis-trans* photoisomerzation of Schiff base have been elucidated in great detail and several mechanisms were
- ²⁵ postulated for the *cis-trans* isomerization, direct observation of the *cis-trans* crystal structure obtained in solution is still few.²³ Here we report a photochromic Schiff base, (E)-4-phenyl-1-(pyridine-2-ylmethylene)semicarbazide (1, Scheme 1), which exhibits photochromism in both solution and the solid state. The
- ³⁰ photochromism of 1 in solution was revealed by the mechanism of *trans-cis* photoisomerization of its C=N double bond, while in the solid state was ascribed to the changes in the geometry of the molecule and the molecular packing.

Experimental

35 Materials and general experimental procedures.

All the chemicals were obtained from commercial sources and used as received. Solvents of analytical grade (Shanghai Chemicals Group Company, China) were redistilled before use. ESI-MS data were obtained on a Bruker ESQUIRE-3000plus LC-

- ⁴⁰ MS/MS spectrometer and elemental analysis was performed on a CE Instruments EA 1110. Solution absorption spectra were recorded on a Shimadzu UV224012PC absorption spectrophotometer. Solid state absorption spectra were scanned on Varian Cary 5000 UV-VIS-NIR absorption spectrometer by ⁴⁵ using baseline correction with BaSO₄. ¹H NMR was acquired on
- is using baseline correction with BaSO₄. [•]H NMR was acquired or

a Bruker Unity 400 MHz spectrometer using TMS as an internal standard. Melting point was determined on a noncorrected X-4 micromelting point apparatus. Photoirradiation was carried out by using the UV light of 302nm or 365nm of a 4-mW low-pressure ⁵⁰ Hg lamp. XRD patterns were collected on a X'pert PRO powder diffractometer equipped with a Cu *Ka* source ($\lambda = 1.51418$ Å) with the detector operating at 40 kV and 30 mA. The X-ray diffraction data were collected on a Gemini S Ultra CrysAlis CCD diffractometer equipped with a graphite-monochromatic ⁵⁵ MoKa ($\lambda = 0.71073$ Å) radiation using CrysAlis RED Oxford Diffractometer equipped with a graphite-monochromatic MoKa ($\lambda = 0.71073$ Å) radiation using an ω scan mode. The structure was solved by direct methods with SHELXS-97 and refer to the full motion.

⁶⁰ refined by full-matrix least-squares calculations with SHELXL-97 based on F^2 . All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at the calculated positions.

65 Syntheses and characterizations.

Synthesis of (E)-4-phenyl-1-(pyridine-2ylmethylene)semicarbazide (1): 4-phenylsemicarbazide (1.0 mmol, 0.151 g) was added to 20 mL ethanol, to which 0.107 g (1.0 mmol) pyridine-2-carboxaldehyde was added and the mixed 70 solution was stirred at 78 °C for 2 hrs. The mixture was then allowed to cool down to room temperature, after which the solvent was removed, affording crude white residue. The residue was recrystallized from CH2Cl2/CH3OH (95:5, v/v), leading to white precipitate which was then filtered off under low pressure 75 to afford the titled compound. m.p.:179.0-179.4 °C. ESI-MS: M⁺ 241. Anal. cacld. (%) for C₁₃H₁₂N₄O: C, 64.99; H, 5.03; N, 23.32; found (%): C, 65.02; H, 5.01; N, 23.24. IR (KBr): v_{max} (cm⁻¹): 3382s, 3110w, 1700m, 1590m, 1540m, 1471m, 1445m, 1425m, 1369m, 1150w, 756w, 623w, 532w. ¹H NMR (CDCl₃): (δ, ppm) ⁸⁰ 9.13 (s, 1H, NH), 8.67 (d, J = 8.0 Hz, 1H, ArH), 8.27(s, 1H, NH), 7.93 (s, 1H, CH), 7.90 (d, J = 8.0 Hz, 1H, ArH), 7.83 (t, J = 8.0 Hz, 8.0 Hz, 1H, ArH), 7.61 (d, J = 8.0 Hz, 2H, ArH), 7.38 - 7.36

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(m, 2H, ArH), 7.35 - 7.30 (m, 1H, ArH), 7.13 (t, *J* = 8.0 Hz 1H, ArH).

Syntheses of **2**, **3**, **4** and **5** were carried out in a procedure similar to that for **1**.

- $_{5}$ 2: m.p.:185.1-186.6 °C. ESI-MS: M⁺ 241. Anal. cacld. (%) for C₁₃H₁₂N₄O: C, 64.99; H, 5.03; N, 24.12; found (%): C, 65.09; H, 5.11; N, 23.50. IR (KBr): ν_{max} (cm⁻¹): 3196m, 3080m, 2947m, 2872m, 1679s, 1596s, 1532s, 1445s, 1367m, 1336m, 1283m, 1153m, 881w, 751w, 724w, 696w, 532m. ¹H NMR (DMSO- d_{6}):
- ¹⁰ (δ , ppm) 10.92 (s, 1H, NH), 9.03 8.96 (m, 2H, ArH), 8.56 (dd, J = 4.8, 1.6 Hz, 1H, ArH), 8.31 (dt, J = 8.0, 1.9 Hz, 1H, NH), 7.98 (s, 1H, CH), 7.66 (dd, J = 8.6, 1.0 Hz, 2H, ArH), 7.45 (dd, J = 8.0, 4.7 Hz, 1H, ArH), 7.30 (dd, J = 10.7, 5.2 Hz, 2H, ArH), 7.03 (t, J = 7.4 Hz, 1H, ArH).
- ¹⁵ 3: m.p.:198.4-198.9 °C. ESI-MS: M⁺ 241. Anal. cacld. (%) for C₁₃H₁₂N₄O: C, 64.99; H, 5.03; N, 24.12; found (%): C, 65.13; H, 5.16; N, 23.95. IR (KBr): ν_{max} (cm⁻¹): 3186s, 3062s, 2945s, 1718s, 1679s, 1598s, 1546s, 1500s, 1447m, 1360m, 1280s, 1242m, 922m, 810s, 764s, 717s, 539m, 516m. ¹H NMR (DMSO-*d₆*): (*δ*, 20 ppm) 11.06 (s, 1H, NH), 9.02 (s, 1H, NH), 8.62 8.60 (m, 2H, ArH), 7.92 (s, 1H, CH), 7.83 7.82 (m, 2H, ArH), 7.66 7.63(m, 2H, ArH), 7.31 7.28 (m, 2H, ArH), 7.06 (t, *J* = 8.0 Hz, 1H,
- ArH). **4**: m.p.:204.2-205.5 °C. ESI-MS: M⁺ 165. Anal. cacld. (%) for ²⁵ C₇H₈N₄O: C, 51.21; H, 4.91; N, 34.13; found (%): C, 51.35; H, 4.94; N, 34.56. IR (KBr): v_{max} (cm⁻¹): 3428s, 3237s, 3090s, 2927s, 1707s, 1630s, 1581s, 1418s, 1353s, 1167s, 945m, 830s, 639s, 585d, 454s. ¹H NMR (DMSO-*d*₆): (δ , ppm) 1088 (s, 1H, NH), 8.70 (d, *J* = 6.4 Hz, 1H, NH), 8.04 (d, *J* = 6.4 Hz, 2H, ArH), 7.87 ³⁰ (s, 1H, CH), 6.81 (s, 2H, NH).

5: m.p.:178.0-178.4 °C. ESI-MS: M⁺ 240. Anal. cacld. (%) for $C_{14}H_{13}N_3O$: C, 70.55; H, 5.69; N, 18.21; found (%): C, 70.28; H, 5.48; N, 18.56; IR (KBr): v_{max} (cm⁻¹): 3371s, 3098s, 2953m, 1685s, 1595s, 1546s, 1500s, 1447m, 1335m, 1230s, 1144s, 945s, ³⁵ 749s, 688s, 607w, 536s, 504s. ¹H NMR (DMSO- d_6): (δ , ppm)

10.75 (s, 1H, NH), 8.89 (s, 1H, NH), 7.95 (s, 1H, CH), 7.85 - 7.83 (m, 2H, ArH), 7.66 (d, J = 7.6Hz, 2H, ArH), 7.45 - 7.37 (m, 3H, ArH), 7.31 (t, J = 8.0 Hz, 2H, ArH), 7.03 (t, J = 6.4 Hz, 1H, ArH).



Scheme 1. Molecular structures of semicarbazides

Results and discussion

Figure 1 shows typical time profiles of the absorption spectra of 1 ⁵⁰ in dichloromethane and hexane upon UV irradiation at 302 nm

(or 365nm). The absorption maximum of **1** appears at 300 nm in CH_2Cl_2 and at 304 nm in hexane. Upon UV irradiation a new band is developed at 320–430 nm in CH_2Cl_2 and 300–350 nm in hexane at the expense of the respective original band at 300 nm ⁵⁵ and 304 nm, with an isosbestic point at 313 nm. This is a spectral indication of the occurrence of the photoisomerization in solution. The photoisomerization reaction of **1** in solution under 302 nm light irradiation was found to obey the first-order reaction kinetics in CH_2Cl_2 and hexane, respectively (Fig. 2). The ⁶⁰ photoisomerization process was hence shown to proceed by a unimolecular reaction pathway without any side reaction.²³ When the UV irradiation ceased, the system did not return to its initial state with visible irradiation, but the system could be recovered to its initial state after the solution of **1** (1.0×10^{-5} mol L⁻¹) staying in ⁶⁵ the dark for about 150h at room temperature.



Fig.1 Traces of the absorption spectra of 1 $(1.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1})$ in ⁸⁰ dichloromethane and hexane upon irradiation



⁹⁵ Fig. 2. Plots of $\ln[(A\infty - A0)/(A\infty - At)]$ with time for the photocoloration reaction of 1 under 302 nm light irradiation, where $A_0, A\infty, At$ are the observed absoption data corresponding to 360 nm wavelength in CH₂Cl₂(or 323 nm in hexane) at the time zero, infinite time, and time t of the reaction, respectively.

Semicarbazides of **2-4** (Scheme 1) also exhibit photoisomerization in dichloromethane (CH₂Cl₂) upon irradiation (Supplementary Figs. S1-S4). In a hydrogen bonding solvent such as ethanol, acetone or tetrahydrofuran, photoisomerization of **1-4** ¹⁰⁵ does not occur. With **5** (Scheme 1) photoisomerization does not occur in both hydrogen bonding and non-hydrogen bonding solvents such as dichloromethane, ethanol, tetrahydrofuran and acetonitrile (Supplementary Fig. S5). It was hence shown that the photoisomerization of **1-4** is related to the pyridine nitrogen atom.

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Furthermore, the position of the pyridine nitrogen atom with respect to the C=N double bond is important too and the *ortho*-nitrogen position leads to the most photoreactive consequence. In order to exclude the possibility of chlorinated solvent induced

s photocoloration, the dichloromethane solution of 1 was titrated with acetic acid. It was found that upon protonation of the pyridine nitrogen atom, the absorption spectrum did not shift much (Supplementary Fig. S6) and irradiation of the pyridine-protonated 1 in dichloromethane did not show more
 photocoloration compared to that of the pure 1 (Supplementary Fig. S7). It is important to indicate that 1-4 can also exhibit photoisomerization in polar acetonitrile or apolar hexane. All these observation confirmed that the photocoloration of 1-4 is due

to the nitrogen atom of pyridine moiety but not the solvent photochemistry. Colorless plate crystals of **1** were obtained by slow evaporation of its dichloromethane solution. Sincle crystal X-ray analysis

of its dichloromethane solution. Single crystal X-ray analysis indicates its space group of *P*2₁2₁2₁. Ten successful repeated experiments to grow the crystal lead to the same crystal structure. ²⁰ The crystal structure reveals that the C=N double bond takes *E*-

conformation (Fig. 3). The dihedral angle between two ring planes of pyridine and benzene in this *E*-1 crystal is 11.01° (0.16). An N(1)-H(1)···N(3) intramolecular hydrogen bonding is shown.
1 forms a left-handed helix running along the crystallographic *a* 25 axis via the strong intermolecular hydrogen bonding N(2)-H(7)···N(4), that is supported by the observed CD signal of the solid powder (Supplementary Fig. S8), in well agreement of our previous report on the chiral property of 1.²⁵ Crystal of 1 grown in acetone^{‡2} was found to be of *P*bcn space group (Supplementary 30 Fig. S9) and the solid powder of this crystal is a racemic conglomerate from which CD signal was not detected, suggesting its achiral character.



Fig. 3. Crystal structure of *trans*-**1** (*E*-**1**), thermal ellipsoid plot of *E*-**1** at the 50% probability level. $^{\pm 1}$

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Table 1. ¹H NMR Chemical shifts of 1 before and after with UV irradiation for 20mins in CDCl₃ solution

δ	$\delta_{H(7)}$	$\delta_{H\left(1\right)}$	$\delta_{H\!(8)}$	$\delta_{H\left(13\right)}$	$\delta_{H\left(10\right)}$
before	9.13	8.27	7.93	8.67	7.90
After	9.35	8.23	7.94	8.66	7.91

¹H NMR data of **1** before and after UV irradiation in CDCl₃ ⁵⁰ were found differing very much (Table 1 and Supplementary Fig. S10). The chemical shifts of protons H(7) and H(1) change dramatically differently upon UV irradiation, the signal of the amido -NH(7) and -NH(1) protons undergo respectively downfield shift by 0.22 ppm and upfield shift by 0.04 ppm. This ⁵⁵ observation suggests that the strong N(4)–H(7)···N(2)

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intermolecular hydrogen bond was deteriated upon UV irradiation so that the NMR signal of the -NH(7) proton is shifted to downfield. This conclusion is supported by the observation that signal of aniline -NH(1) is shifted to upfield from 8.27 to 60 8.23 ppm, whereas those of H(13) and H(10) next to N4 of pyridine moiety do not shift much, from 8.67 to 8.66 and 7.90 to 7.91 ppm, respectively, and those of protons far away from the C=N double bond are hardly affected. In a hydrogen bonding solvent such as ethanol, acetone or tetrahydrofuran, no 65 photoisomerization of **1** was observed because hydrogen bonding of **1** with solvent molecule likely prevents the isomerization.

To further identify the isomers, 2D-NOESY spectra were taken (Fig. 4). Before UV irradiation, NOESY of **1** in CDCl₃ shows H8-H7 and H8-H13 cross-peaks of the protons on adjacent C/N 70 atoms with spatial distances shorter than 0.5 nm. After UV irradiation, NOESY changed evidently, H13-H7 cross-peak is observed while that of H8-H13 disappears. Changes in the NOESY of **1** after UV irradiation indicate that the positions of H8 or the conformation of the C=N double bond is changed upon UV 75 irradiation.



95 Fig. 4. NOESY spectra of 1 before and after UV irradition in CDCl₃. [1] = 1.0 mM.

Direct evidence for this photoisomerization is the change of the crystal structure of 1 that grows from the dichloromethane 100 solution of 1 after UV irradiation, now with a Z-conformation of the C=N double bond. The light-yellowish plate crystal of the Zisomer of 1 was found to be of the monoclinic space group $P2_1/c_1$, in which an N(1)-H(1)...N(3) intramolecular hydrogen bond was identified (Fig. 5). Importantly, in the cis-isomer crystal, the ¹⁰⁵ Platon program²⁶ leads to the discovery of the N(4)···H(7)–N(2) and O(1)…H(2)-C(2) intramolecular hydrogen bonds with D-H···A angles are 134.2° and 122.1° respectively. Hydrogen-bond directionality at the donor H atom with D-H…A angles in the range 120-140° are seen to have substantially reduced 110 stabilisation energies so that formation of N(4)···H(7)–N(2) and O(1)···H(2)–C(2) hydrogen bondings stabilize the *cis*-isomer.²⁷ Therefore, the UV irradiation switches the strong N(4)-H(7)...N(2) intermolecular hydrogen bond in the E-isomer into

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the N(4)···H(7)–N(2) and O(1)···H(2)–C(2) intramolecular hydrogen bond that accounts for the change in the conformation of **1** around the C=N double bond. Formation of the intramolecular hydrogen bonds establishes the channel for E/Z⁵ isomerization in the solution phase. The solid state UV-vis. absorption spectrum, fluorescence spectrum, and IR spectrum of *Z*-1 were measured using the isolated *Z*-1 isomer as can be seen in supplementary Figs. S11-S13.



Fig. 5. Crystal structure of *cis*-1 (*Z*-1), thermal ellipsoid plot of *Z*-1 at the 50% probability level. The asymmetric unit has two independent molecules and only one of these is shown. ^{‡3}

Among 1-4 that exhibit photoisomerization in solution phase, only 1 was observed to exhibit photocoloration in solid state. It is noted from Fig. 6 that 1 shows a photochromic transformation from white to kelly green upon UV irradiation in the solid state, ²⁵ and color can be reversed by heating to 160 °C. ¹H NMR spectrum confirms that the heated powder is the same as the white powder before UV irradiation. Fig. 7 shows the variation of the absorption spectrum of 1 in the solid state upon UV irradiation, which shows that a new broad band at 370-480 nm is ³⁰ developed upon irradiation. The absorption maximum in the solid state shifts substantially to the longer wavelength in comparison with that in solution Phase (Fig. 1). This spectral shift is ascribed to the difference in the conformations of the molecule in the crystal and in the solution phase.²⁸



Fig. 6. Photochromism of **1** in the solid state



Fig. 7. Traces of the absorption spectrum of **1** in the solid state ⁵⁰ upon UV irradiation recorded in five-minute time interval. The inset displays the plots of $\ln[(A\infty - A_0)/(A\infty - At)]$ with time (the observed absoption data corresponding at 445nm wavelength).

The kelly green compound obtained after the photoirradiation ⁵⁵ of **1** is stable for at least several months at room temperature in the open air. It undergoes complete reversible transformation to a white powder upon heating at 160°C in the air. A nice straight line was also found by plotting of $\ln[(A\infty - A0)/(A\infty - At)]$ with time for the photocoloration reaction of **1** under 302 nm light ⁶⁰ irradiation (Fig. 7). Again the photocoloration of **1** in the solid state indictes a unimolecular reaction pathway too.

The photocoloration process in solid state is also supported by the FT-IR spectra of **1** before and after UV irradiation (Fig. 8). Two new and sharp bands develop at 3361 and 3341 cm⁻¹ while ⁶⁵ the peaks at 1471 and 1425 cm⁻¹ almost disappear after **1** is irradiated under UV light. These observations indicate that the N-H stretching and bending vibrations and the C-N stretching



Fig. 8. FT-IR spectra of 1 before (I) and after (II) UV irradiation

vibration in the molecule change after the sample was irradiated with UV light. The 3361 and 3341 cm⁻¹ new bands are attributed to the formation of NH conformers of different hydrogen bonding ⁸⁵ when **1** is UV-irradiated. Disappearance of the 1471 and 1425 cm⁻¹ bands results from the coupling of the N-H bending and the C-N stretching that occurs upon UV irradiation. It was also observed that the solid state fluorescence of **1** excited at 360 nm was enhanced by irradiation under UV light (Fig. 9). The shape ⁹⁰ of the fluorescence spectra did not change by by UV irradiation and only the intensity of fluorescence was enhanced. The



Fig. 9. Fluorescence specta of **1** upon UV irradiation in the solid state.

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enhanced fluorescence could be correlated to the variations in the molecular packing.²⁹ This indicates that the solid state photochromism is not due to *trans-* to *cis-* transformation. We

- ⁵ tried to photoirradiate the crystal of 1 with different wavelength, but the crystal structure of 1 does not change upon UV irradiation, even with 500nm or 750nm of 4W laser irradiation. The fact that the XRD patterns of 1 before and after UV irradiation are more or less the same (Fig.11) further proves that the solid state
- ¹⁰ photocoloration of 1 does not result from the change in the crystal structure. The *trans*- to *cis*-crystal transformation of 1 is difficult to take place in the crystalline phase. The photocoloration of the solid state may probably be ascribed to the changes in the geometry of the molecule and the molecular packing.

15 Conclusions

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E/Z-photoisomerization of pyridine substituted semicarbazide Schiff bases in solution was directly evidenced by the C=N double bond photoisomerization. (*E*)-4-Phenyl-1-(pyridine-2ylmethylene)semicarbazide (1) exhibits photochromism in both

²⁰ solution phase and the solid state. The photochromism of **1** in solution was revealed to operate under the mechanism of C=N *trans-cis* photoisomerization. The solid state photochromism of **1** was shown to result from changes in the geometry of the molecule and the molecular packing. The results are useful for ²⁵ the design and synthesis of other similar Schiff bases showing

photochromism.



⁴⁰ Fig. 11. X-ray powder diffraction patterns of **1** before and after UV irradiation

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Notes and references

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† Supplementary data associated with this article can be found in the online version, at DOI: 10.1039/b000000x/. CCDC-739528 (E-1),
 55 CCDC-758818 (Z-1), and CCDC-824334 (E-1 crystalized in acetone)

View Online can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

- [±]1 *X-ray Structure* for *E*-1: *trans*-C₁₃H₁₂N₄O, *M* = 240.27, orthorhombic space group *P*2₁2₁2₁, a = 5.187(3) Å, b = 9.245(5) Å, c = 25.359(1) Å, a = 90°, β = 90°, γ = 90°, V = 1216.2(1) Å³, Z = 4, ρ_{cald} = 1.31 gcm⁻³, μ = 0.088 mm⁻¹, F(000) = 504, T = 153(2)K, 5181 reflections measured, 1419 unique (R_{int} = 0.049), 809 (I > 2σ(I)) which were used in all calculations with final R=0.034. (CCDC 739528)
- ⁶⁵ ‡2 *X-ray Structure* csrystalized in acetone for *E*-form: *trans*-2 (C₁₃H₁₂N₄O)·C₃H₆O, *M* = 523.59, orthorhombic space group *P*bcn, a = 17.669(3) Å, b = 8.668(1) Å, c = 18.288(2) Å, α = 90°, β = 109.72°, γ = 90°, V = 2835.9(1) Å³, Z = 4, ρ_{cald} = 1.26 gcm⁻³, μ = 0.086 mm⁻¹, F(000) = 1135.7, T = 153(2)K, 12064 reflections measured, 2597 unique (R_{int} =
- 70 0.038), 3375 (I > 2σ (I)) which were used in all calculations with final R=0.076. (CCDC 824334) 3 X-ray Structure for Z-1: cis-C₁₃H₁₂N₄O, M = 240.27, monoclinc space
- group P1 21/C1, a = 22.602(7) Å, b = 5.69(2) Å, c = 20.209(7) Å, α = 90°, β = 109.72°, γ = 90°, V = 2394.5(6) Å³, Z = 8, ρ_{cald} = 1.33 gcm⁻³, μ =
- $_{75}$ 0.089 mm⁻¹, F(000) = 1007.7, T = 153(2)K, 12309 reflections measured, 4676 unique (R_{int} = 0.039), 3375 (I > 2\sigma(I)) which were used in all calculations with final R=0.071. (CCDC 758818)
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