



## Original article

# Red and yellow color aspects of compound 3-dicyclopropylmethylene-5-dicyanomethylene-4-diphenylmethylenetetrahydrofuran-2-one: Chromism effect



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## ABSTRACT

The title compound exists as yellow (**1Y**) and red (**1R**) crystals, but both gave red solutions. The intermolecular interactions between the CN parts of the crystals in **1Y** are very weak. By the mechanical crushing as well as in solution **1Y** again becomes red due to the absence of intermolecular interactions. We explain this color behavior by crystallochromism and solvation chromism.

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## 1. Introduction

Previously [1] we shed light on the color change behavior of the title compound by tribochromism (color change due to mechanical friction). Now we introduce the crystallochromism (color change due to the change of crystal habit) and solvation chromism. Our recent quantum chemical study revealed that crystallochromism and solvation chromism would also be the major factors due to which the title compound, 3-dicyclopropylmethylene-5-dicyanomethylene-4-diphenylmethylenetetrahydrofuran-2-one, gave yellow (**1Y**) and red (**1R**) crystals (Figs. 1 and S1, and Table S1 in Supporting information), while both give red solutions. Previously, we showed that in **1Y** the diphenylmethylene groups are folded, *i.e.*, one phenyl lies above a cyclopropyl group and the other above a cyano group, while in **1R** the diphenylmethylene groups have a twisted orientation (one phenyl lies above a cyclopropyl group and the other below a cyano group) [1]. Moreover, we showed that the important calculated red and blue shifts correspond to the cases where the Al–N bonds are affected in the same direction, *i.e.*, lengthening or shortening at the same time.

The lengthening of Al–N bonds causes a red shift while shortening results in a blue shift [2].

## 2. Computational details

The ground state geometries were optimized at DFT/B3LYP/6-31G\*\* [3] level of theory with Gaussian09 package [4]. The frequency calculations were carried out at the same level of theory. The absorption spectra were computed by using TD-DFT/B3LYP/6-31G\*\* level of theory.

## 3. Results and discussions

Significant differences in bond length (C7–C12), bond angles (C6–C5–C11 and C35–C38–C40) and dihedral angles have been observed between **1R** and **1Y**, see Table S1 (details can be found in Supporting information, labeling Fig. S2). In general, C5–C6, C8–C35 and C7–C12 bond lengths being lengthened in **1R**, *i.e.*, 0.016, 0.013 and 0.036 Å, respectively, while O1–C9, C35–C38 and C12–C13 are being lengthened in **1Y**, *i.e.*, 0.013, 0.021, and 0.023 Å, respectively. The following bond angles being increases in **1R**; C6–C5–C11, C35–C38–C40 and C35–C38–C43, *i.e.*, 2.66, 2.39 and 1.81 Å, respectively, while C7–C12–C13 (1.79 Å) in **1Y**. The noteworthy difference has been observed in the dihedral angles, *e.g.* in **1Y** C1–C6–C5–C11, C8–C35–C36–C46, C7–C12–C13–C14 are 5°, 113°, 20° more twisted

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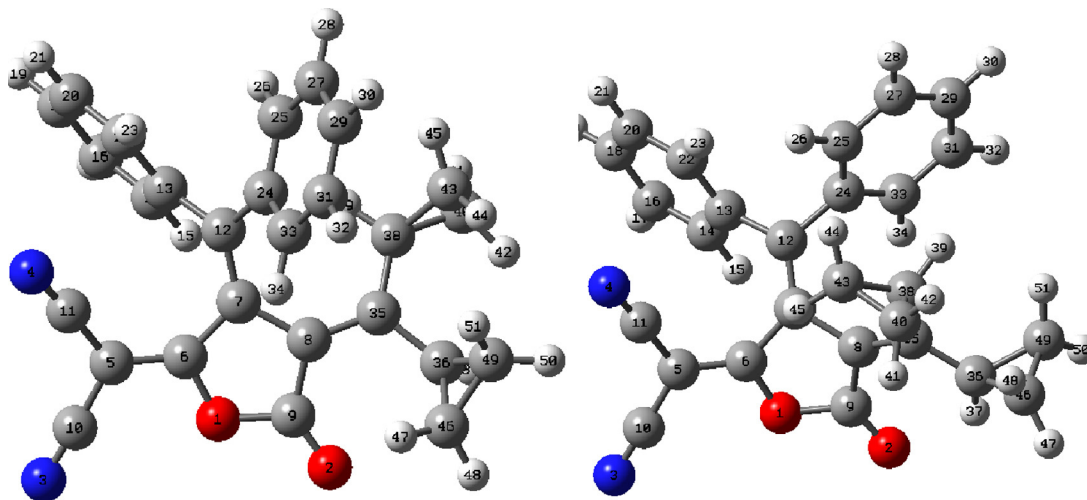


Fig. 1. Optimized structures of **1R** (left) and **1Y** (right) at B3LYP/6-31G\*\* level of theory.

than the **1R**, respectively. The C1–C6–C5–C10 and C8–C35–C38–C43 of **1R** are being  $3^\circ$ ,  $101^\circ$  more twisted than **1R**. In **1R**, C7–C8–C35–C36 and C7–C12–C24–C25 are  $173^\circ$  and  $146^\circ$  while in **1Y**  $-168^\circ$  and  $-118^\circ$ . In **1R**, C8–C35–C38–C40, C8–C35–C36–C49 and C7–C12–C24–C33 are  $-152^\circ$ ,  $-111^\circ$  and  $-38^\circ$  while in **1Y**  $106^\circ$ ,  $138^\circ$  and  $66^\circ$ , respectively. In our previous study [2], we pointed out that the important calculated red and blue shifts correspond to the cases where the Al–N bonds are affected in the same direction, i.e., lengthening or shortening at the same time. The lengthening of Al–N bonds cause red shift while shortening result blue shift. In **1R**, prominent lengthening has been observed 0.036 Å. Moreover, we noticed that the bond angles generally increases in the **1R**. Similarly dihedral angle is also playing its role by twisting. As a whole it is expected that lengthening of bond lengths and superior the bond angles in **1R** than that of **1Y** are also the causes that **1R** is red one. The yellow compound has the dipole moment 9.47 D while red one 11.66 D. Beck [5] and coworkers described that di[1,1-bis(dicyanomethylene)-indan-2-ylidene] can exist in yellow and in red

crystal variations. They explained that in yellow crystals, molecules have a folded structure, while red molecules have a twisted structure. The delocalization of the highest occupied molecular orbital (HOMO) in **1R** is higher than the **1Y**. The charge distribution on HOMO and lowest unoccupied molecular orbital (LUMO) on the right phenyl ring is higher in **1R** than **1Y** (Fig. 2). The **1Y** absorb light in the region 363 nm with the transition H to L, while **1R** absorbs at 345 (H-3 to L) and 528 nm (H to L) (Fig. S3 in Supporting information). It showed that **1R** is absorbing light also at longer wavelengths. The main vibration in **1R** has been observed at  $1592\text{ cm}^{-1}$  for mode 429, while **1Y** at  $1635\text{ cm}^{-1}$  for mode 219 (Fig. S4 in Supporting information). It is suspected that the red of **1R** might be due to the large bond distances, superior bond angles, more charge distribution on frontier molecular orbitals and absorption in longer wavelength compared to **1Y**.

In the next phase, we tried to explain why, in solution, both are red or in other words, yellow turns to red solution. We optimized **1Y** in toluene and found no significant difference in the geometrical

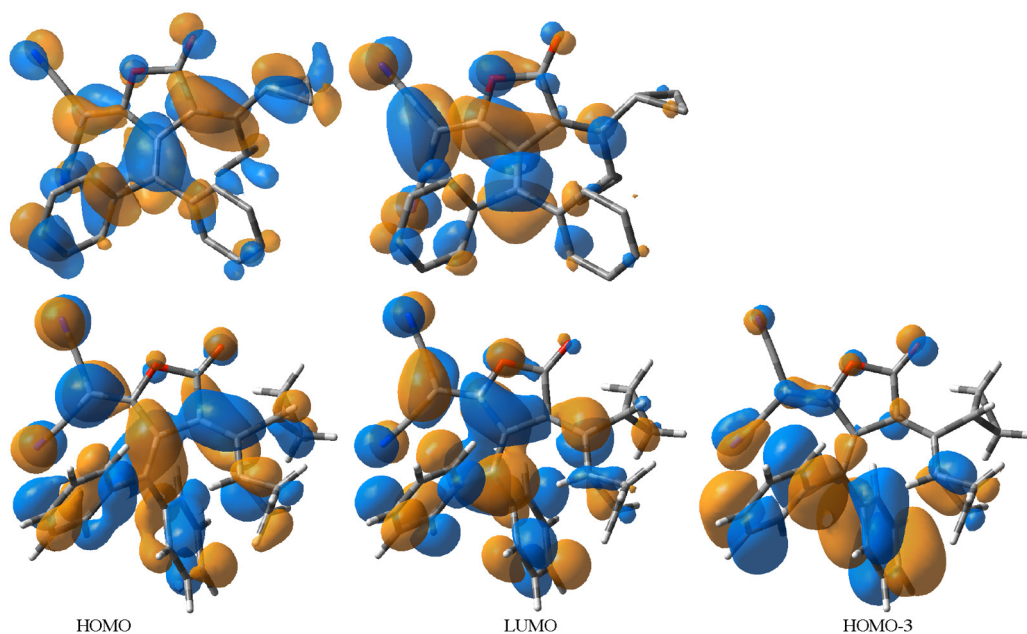


Fig. 2. Frontier molecular orbitals of **1Y** (top) and **1R** (bottom).

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