Tetrahedron Letters 51 (2010) 449–452

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Synthesis, crystal structures and photochromic properties of novel chiral Schiff base macrocycles

Koichi Tanaka [a,*], Ryota Shimoura [a], Mino R. Caira [b,*]

[a] Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and Bioengineering & High-Tech Research Centre, Kansai University, Suita, Osaka 564-8680, Japan
[b] Department of Chemistry, University of Cape Town, Rondebosch 7701, South Africa

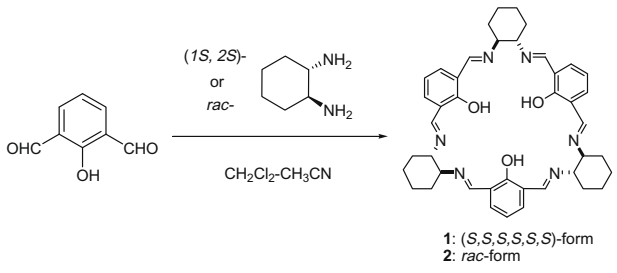
ARTICLE INFO

Article history:
Received 28 September 2009
Revised 13 November 2009
Accepted 16 November 2009
Available online 1 December 2009

ABSTRACT

Enantiomerically pure and racemic forms of calixsalen-type macrocycles **1** and **2** were synthesized and their crystal structures were determined. The enantiomerically pure crystals of (*S,S,S,S,S,S*)-**1** exhibited thermally reversible photochromism from yellow to orange-red upon photoirradiation in the solid state, while *rac*-crystals of **2** with the guest CH_3CN did not show any photocolouration.

Photochromic compounds have received considerable attention in recent years for their potential applications, such as information storage, electronic display systems, optical switching devices, ophthalmic glasses and macro-scale mechanical motion of materials.[1] Several types of organic photochromic compounds, such as naphthopyrans, spiropyrans, fulgides, chromenes and *N*-salicylideneanilines have been discovered, and their photochromic properties have been studied mostly in solution. However, organic compounds showing photochromism in the crystalline state are rare.[2] In the course of our recent study on the chiral recognition of guest molecules in the presence of optically active macrocyclic amines,[3] we have now synthesized new chiral macrocyclic Schiff bases (*S,S,S,S,S,S*)-**1** and *rac*-**2** and encountered their photochromic properties in the solid state. The enantiomerically pure crystals **1** showed a colour change from yellow to orange-red upon photoirradiation in the solid state, while the crystals of *rac*-**2** did not. X-ray crystallographic analyses of both (*S,S,S,S,S,S*)-**1** and *rac*-**2** were carried out in order to gain information on the crystalline photochromism.



Both racemic and optically pure macrocyclic Schiff bases were synthesized through [3+3]condensation of *rac*- or (*S,S*)-1,2-diaminocyclohexane with 2,6-diformylphenol in CH_2Cl_2–CH_3CN solution, respectively.[4] The *rac*-**2** was obtained as an inclusion complex with $1.5CH_3CN$.

Upon photoirradiation of (*S,S,S,S,S,S*)-**1** with >300 nm light, the yellow crystals changed to orange-red crystals immediately (Fig. 1). The orange-red crystals returned to their initial yellow state after storage for 1 h in the dark. In contrast, the *rac*-**2** with the guest CH_3CN did not change its colour upon photoirradiation. Figure 2 shows the changes in the solid-state absorption spectra of (*S,S,S,S,S,S*)-**1**. The colour change of **1** may be caused by enol–keto tautomerism involving intramolecular proton transfer from

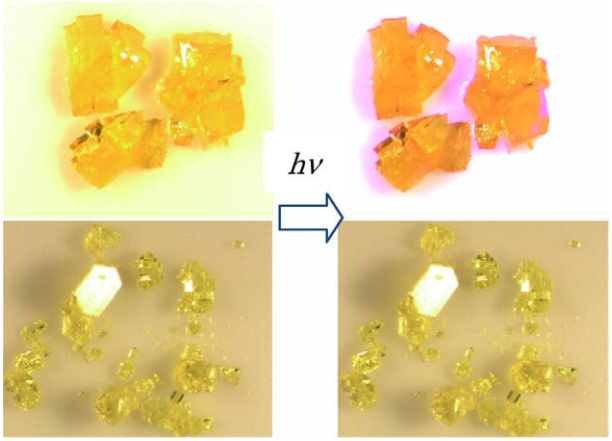


Figure 1. Photographs of (*S,S,S,S,S,S*)-**1** (upper) and *rac*-**2**·1.5MeCN (below) before and after photoirradiation with >300 nm light.

* Corresponding author.
E-mail address: ktanaka@ipcku.kansai-u.ac.jp (K. Tanaka).

0040-4039/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2009.11.062

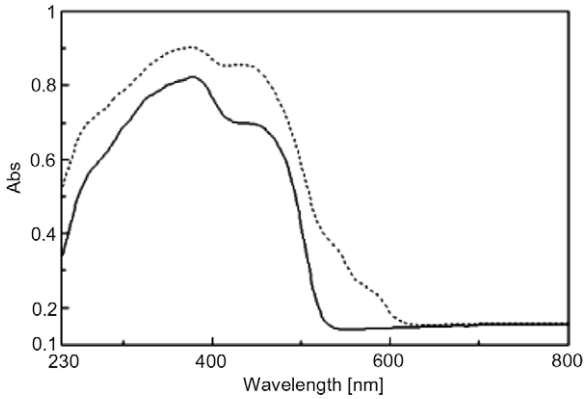


Figure 2. UV–vis spectra of (*S,S,S,S,S,S*)-**1** before (solid lines) and after photoirradiation (dashed lines) in the solid state.

phenolic oxygen to the imino nitrogen atom as reported by Kawato[5] and Ohashi.[6] To clarify whether the opposed photochromic behaviour is due to the chirality differences, or to the presence of guest molecules, we prepared the desolvated *rac*-**2** by removal of the guest molecules on heating the crystals under reduced pressure. However, the desolvated *rac*-**2** was inert for photoirradiation.

In solution, however, both (*S,S,S,S,S,S*)-**1** and *rac*-**2** show photochromism. For example, the colourless solution of (*S,S,S,S,S,S*)-**1** turns yellow with a new absorption at 443 nm upon irradiation in CH_2Cl_2. The solution of *rac*-**2** also gave the same spectra as (*S,S,S,S,S,S*)-**1** (Fig. 3). The solid state absorption spectra in Figure 2 are red-shifted as compared to those of the solution spectra in Figure 3. This may be due to solid state packing effects. The CD spectra of enantiomers of **1** were changed dramatically upon irradiation in CH_2Cl_2 as shown in Figure 4.

Crystal structure analysis of (*S,S,S,S,S,S*)-**1** revealed two homochiral host molecules (A and B) in the asymmetric unit, one of which (A) is shown in Figure 5, as representative.[7] Unequivocal location of all H atoms in the two independent host molecules confirmed the enol tautomeric structure shown in Figure 5, including the presence of a uniform belt of homodromic intramolecular O–H···N hydrogen bonds in both molecules (O···N range 2.577(2)–2.635(2) Å and all O–H···N angles 148°, $n = 6$). The two independent host molecules A and B form a dimer by mutual insertion of one phenyl ring into the partner host cavity, (Fig. 6), the two phenyl rings engaging in π-stacking with a very short centroid–centroid distance of 3.424 Å.

An analogous dimer occurs in the crystal of the related macrocyclic compound whose structure differs from (*S,S,S,S,S,S*)-**1** in that each of the three phenyl rings is substituted by a methyl group at the position *para* to the hydroxyl group and all chiral centres have the *R*-configuration.[8] The presence of the methyl group in the latter

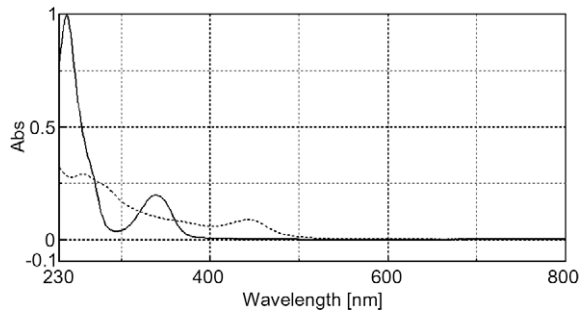


Figure 3. UV–vis spectra of (*S,S,S,S,S,S*)-**1a** before (solid lines) and after photoirradiation (dashed lines) in CH_2Cl_2.

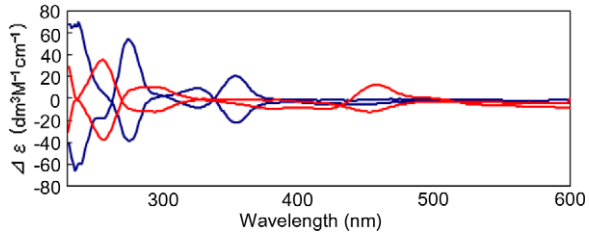


Figure 4. Changes in CD spectra of enantiomers of **1** before (blue lines) and after photoirradiation (red lines).

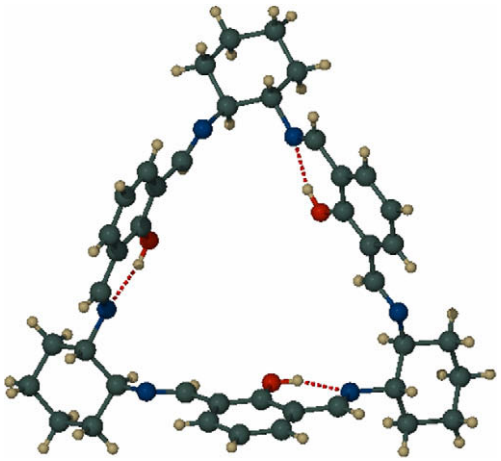


Figure 5. Representative molecule A in the asymmetric unit of compound (*S,S,S,S,S,S*)-**1**.

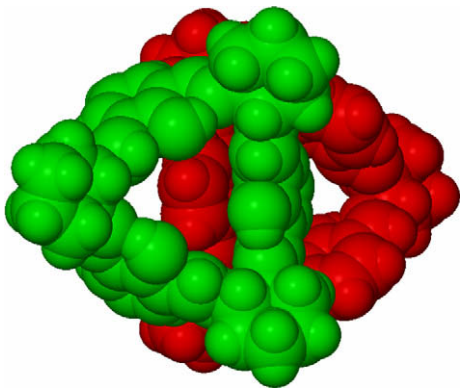


Figure 6. Space-filling representation of the dimer formed between independent host molecules A (green) and B (red) in the crystal of (*S,S,S,S,S,S*)-**1**.

macrocycle results in a less favourable phenyl···phenyl interaction and the centroid–centroid distance is significantly longer (3.581 Å) than that in (*S,S,S,S,S,S*)-**1**. The dimers shown in Figure 6 pack in the space group $P2_1$ with a second intermolecular phenyl···phenyl interaction (centroid–centroid distance 3.628 Å) stabilizing the crystal structure (Fig. 7). A single intermolecular C–H···O interaction with C···O 3.221(3) Å was also identified.

A distinctly different structural arrangement is adopted in the crystal of *rac*-**2**, which is characterized by significant solvent content. Comparison of the host molecule with *S*-configurations at the chiral centres with that in (*S,S,S,S,S,S*)-**1** mentioned-above showed identical enol tautomers with very similar hydrogen bond geometries (O···N range 2.547(4)–2.587(4) Å and O–H···N angle range 147–148°, $n = 3$) and relatively small conformational differ-

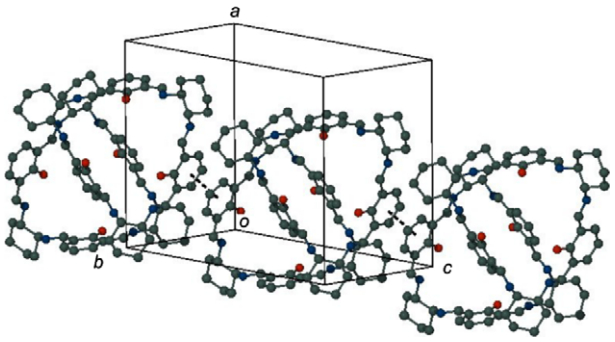


Figure 7. Dimeric host units linked by phenyl···phenyl interactions (dashed lines) along the *c*-axis. H atoms are omitted for clarity.

ences. In contrast to (*S,S,S,S,S,S*)-**1** however, the molecules in *rac*-**2** form dimers which are centrosymmetric and of different geometry. There is no effective insertion of one unit of the dimer into the cavity of the second as occurs in (*S,S,S,S,S,S*)-**1**. Furthermore, the dimer cavity in *rac*-**2** is occupied by disordered acetonitrile molecules. These features are detailed in the stereoviews of Figure 8.

In summary, while the conformations of the host molecules in (*S,S,S,S,S,S*)-**1** and *rac*-**2** are quite similar, their crystal structures are based on very different dimeric motifs and are stabilized by different interactions. The crystal structure of (*S,S,S,S,S,S*)-**1** is characterized by strong π–π interactions, both within a host dimer and between host dimers. In contrast, π–π interactions do not occur in the crystal structure of *rac*-**2** and the geometrically different host dimer motif provides a cavity which is threaded by solvent molecules. Photochromic behaviour arising from the tautomeric change suggested may or may not involve significant molecular movement and could be influenced by all of the structural features highlighted here. As noted in a recent review the photochromic process in Schiff bases is described as a 'delicate subject and a small change of neighbouring environment influences strongly their properties'.[9] If the phototautomerism in this system were to depend on significant conformational changes in the host molecule, it is likely that differences in crystal packing efficiencies could partially account for the differences in the behaviours of (*S,S,S,S,S,S*)-**1** and *rac*-**2**. It can be argued that since the former must necessarily pack in a chiral space group, it has a limited number of packing modes compared with *rac*-**2**, whose accessible space groups should allow greater chance of its achieving close-packing. However, calculation of packing coefficients (PFs) revealed that *rac*-**2** actually has a marginally smaller PF than (*S,S,S,S,S,S*)-**1** (60.3% vs 63.2%). The slightly tighter packing in (*S,S,S,S,S,S*)-**1** is consistent with the close intermolecular interactions described above for this crystal. Calculation of the total void volumes yielded very similar values for (*S,S,S,S,S,S*)-**1** and *rac*-**2** (2.9% and 2.7%, respectively) and the locations of the voids suggested possibilities of molecular conformational change in each case. Thus, analysis based on packing efficiencies and void volumes does not lead to a conclusive argument for the origin of phototautomerism here. Postulation of a convincing mechanism awaits the determination of the X-ray structure of the irradiated form of (*S,S,S,S,S,S*)-**1**, following the two-photon excitation method employed earlier.[6] The conditions for achieving this will be investigated. The syntheses and photochromic studies of a series of compounds of this type are in progress in our laboratory. The role of the chirality and guest solvent molecules will be extensively studied on these novel systems.

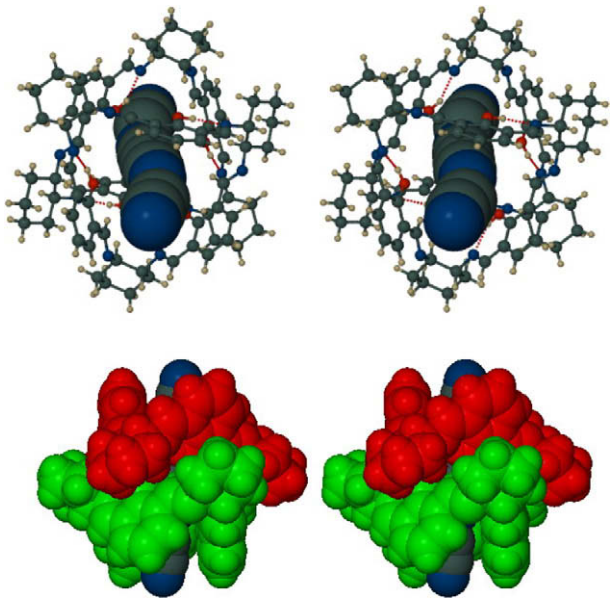


Figure 8. Stereoviews of the centrosymmetric dimeric host unit in *rac*-**2** showing disordered CH_3CN molecules occupying the dimer cavity (top), and a side view of the same unit with all atoms in space-filling representation (bottom).

Acknowledgements

This work was supported by Grant-in-Aids for Scientific Research on Priority Area 'New Frontiers in Photochromism (No. 471)' from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

References and notes

1. (a) Durr, H.; Bouas-Laurent, H. *Photochromism: Molecules and Systems*; Elsevier: Amsterdam, 1990; (b) Crano, J. C.; Guglielmetti, R. J. *Organic Photochromic and Thermochromic Compounds*; Plenum Press: New York, 1999; (c) Irie, M. *Chem. Rev.* **2000**, *100*, 1685; (d) Hadjoudis, E.; Mavridis, I. M. *Chem. Soc. Rev.* **2004**, *33*, 579; (e) Tian, H.; Yang, S. J. *Chem. Soc. Rev.* **2004**, *33*, 85; (f) Kobatake, S.; Takami, S.; Muto, H.; Ishikawa, T.; Irie, M. *Nature* **2007**, *446*, 778.
2. (a) Takami, S.; Kuroki, L.; Irie, M. *J. Am. Chem. Soc.* **2007**, *129*, 7319; (b) Nakai, H.; Mizuno, M.; Nishioka, T.; Koga, N.; Shiomi, K.; Miyano, Y.; Irie, M.; Breedlove, B. K.; Kinoshita, I.; Hayashi, Y.; Ozawa, Y.; Yonezawa, T.; Toriumi, K.; Isobe, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 6473; (c) Tanaka, K.; Tomomori, A.; Scott, J. L. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 294; (d) Taneda, M.; Koyama, K.; Amimoto, H.; Kawato, T. *Org. Biomol. Chem.* **2004**, *2*, 499; (e) Tanaka, K.; Yamamoto, Y.; Caira, M. R. *CrystEngCommun.* **2004**, *6*, 1; (f) Moorthy, J. N.; Mal, P.; Singhal, N.; Venkatakrishnan, P.; Malik, R.; Venugopalan, P. *J. Org. Chem.* **2004**, *69*, 8459; (g) Mal, P.; Lourderaj, U.; Parveen, V. P.; Morrthy, J. N.; Sathyamurthy, N. *J. Org. Chem.* **2003**, *68*, 3446; (h) Tanaka, K.; Yamamoto, Y.; Ohba, S. *Chem. Commun.* **2003**, 1866; (i) Naumov, P.; Sekine, A.; Uekusa, H.; Ohashi, Y. *J. Am. Chem. Soc.* **2002**, *124*, 8540; (j) Godsi, O.; Peskin, U.; Kapon, M.; Natan, E.; Eichen, Y. *Chem. Commun.* **2001**, 2132; (k) Moothy, J. N.; Mal, P.; Natarajan, R.; Venugoplan, P. *Org. Lett.* **2001**, *3*, 1579; (l) Tanaka, K.; Toda, F. *J. Chem. Soc., Perkin Trans. 1* **2000**, 873; (m) Sakar, T. K.; Ghosh, S. K.; Moorthy, J. N.; Fang, J.-M.; Nandy, S. K.; Sathyamurthy, N.; Chakraborthy, D. *Tetrahedron Lett.* **2000**, *41*, 6909.
3. Tanaka, K.; Fukuda, N. *Tetrahedron: Asymmetry* **2009**, *20*, 111.
4. *Synthesis of* (*S,S,S,S,S,S*)-**1**: To a solution of (*S,S*)-(+)-1,2-diaminocyclohexane (0.08 g, 0.67 mmol) in CH_3CN (30 ml) was added a solution of 2,6-diformyl-4-methylphenol (0.1 g, 0.67 mmol) in MeOH (15 ml). The mixture was stirred at room temperature for 24 h. The Schiff base macrocycle separated as a yellow solid (0.093 g), was filtered and recrystallized from CH_2Cl_2–CH_3CN. (*S,S,S,S,S,S*)-**1**: Yellow prisms, mp >300 °C. Yield 61%. $[\alpha]_D$ +180° (*c* 0.1, CH_2Cl_2). IR: 2650 cm^{-1} (OH), 1639 cm^{-1} (C=N). ^1H NMR ($CDCl_3$) δ 14.17 (s, OH), 8.69 (s, HC=N), 8.24 (s, HC=N), 7.80 (d, *J* = 11 Hz, Ar-H), 7.13 (d, *J* = 11 Hz, Ar-H), 6.68 (t, *J* = 11 Hz, Ar-H), 3.36 (m, =N–CH), 1.87–1.46 (m, CH_2–CH_2). ^{13}C NMR ($CDCl_3$) δ 24.30, 33.17, 33.46, 73.22, 75.32, 117.75, 119.04, 123.64, 129.38, 133.59, 155.98, 161.67, 163.52. Synthesis of *rac*-**2**: To a solution of *rac-trans*-1,2-diaminocyclohexane (0.08 g, 0.67 mmol) in CH_3CN (30 ml) was added a solution of 2,6-diformyl-4-methylphenol (0.1 g, 0.67 mmol) in MeOH (15 ml). The mixture was stirred at room temperature for 24 h. The Schiff base macrocycle separated as a yellow solid (0.15 g) was filtered and recrystallized from CH_2Cl_2–CH_3CN. Solvent content was quantified by thermogravimetry. *rac*-**2**·1.5CH_3CN complex: yellow prisms, mp >300 °C. Yield 98%.
5. Amimoto, K.; Kawato, T. *J. Photochem. Photobiol. C.* **2005**, *6*, 207.
6. Harada, J.; Uekusa, H.; Ohashi, Y. *J. Am. Chem. Soc.* **1999**, *121*, 5809.

7. Crystal data for (*S*,*S*,*S*,*S*,*S*,*S*)-**1**: $C_{42}H_{48}N_6O_3$, T = 173(2) K, M_r = 684.86 g mol^{-1}, crystal size: 0.12 × 0.40 × 0.42 mm, monoclinic, space group $P2_1$, a = 14.5731(4), b = 16.9192(4), c = 15.6664(4) Å, β = 97.790(1)°, V = 3827.1(2) Å^3, Z = 4, ρ_{calcd} = 1.189 g cm^{-3}, μ = 0.076 mm^{-1}, $2\theta_{max}$ = 51.36°, 41,597 reflections measured, 14,483 unique, (R_{int} = 0.0410), 925 refined parameters, $R_1[(I) > 2\sigma(I)]$ = 0.0410, $wR_2(F^2)$ = 0.0787, R_1(all data) = 0.0678, wR_2(all data) = 0.0891, $\Delta\rho$ (min/max) = −0.186, 0.128 eÅ^{-3}. Crystal data for *rac*-**2**: $C_{42}H_{48}N_6O_3{\cdot}1.5CH_3CN$, T = 173(2) K, M_r = 746.45 g mol^{-1}, crystal size: 0.18 × 0.20 × 0.32 mm, monoclinic, space group $C2/c$, a = 25.5232(7), b = 14.3181(3), c = 25.4041(7) Å, β = 107.370(1)°, V = 8860.4(4) Å^3, Z = 8, ρ_{calcd} = 1.119 g cm^{-3}, μ = 0.072 mm^{-1}, $2\theta_{max}$ = 52.04°, 47,804 reflections measured, 16,415 unique, (R_{int} = 0.0590), 496 refined parameters, $R_1[(I) > 2\sigma(I)]$ = 0.0853, $wR_2(F^2)$ = 0.2362, R_1(all data) = 0.1612, wR_2(all data) = 0.2891, $\Delta\rho$ (min/max) = −0.328, 1.449 eÅ^{-3}. CCDC−734842, 734843 contain the supplementary crystallographic data for this Letter. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
8. Chu, Z.; Huang, W.; Wang, L.; Gou, S. *Polyhedron* **2008**, *27*, 1079.
9. Fukuda, H.; Amimoto, K.; Koyama, H.; Kawato, T. *Tetrahedron Lett.* **2009**, *50*, 5376.