

Guest-dependent organic photochromism of 7-bromo-1,4,8-triphenyl-2,3-benzo[3.3.0]octa-2,4,7-trien-6-one in the solid state

Koichi Tanaka^{a*}, Tomoyuki Watanabe^a and Masako Kato^b

^aDepartment of Applied Chemistry, Faculty of Engineering, Ehime University, Matsuyama, Ehime 790-8577, Japan

^bDivision of Material Science, Graduate School of Human Culture, Nara Women's University, Nara, Japan

Inclusion crystals of 7-bromo-1,4,8-triphenyl-2,3-benzo[3.3.0]octa-2,4,7-trien-6-one (**1a**) and its chloro-derivative (**1b**) showed a reversible colour change from yellow to green on exposure to UV-light, and this depends on the guest molecules present. The crystal structures of the inclusion complex were determined by X-ray analysis.

Keywords: organic photochromism, 7-bromo-1,4,8-triphenyl-2,3-benzo[3,3,0]octa-2,4,7-trien-6-one

Organic photochromic compounds have received considerable attention in recent years due to their potential applications in information storage, electronic display systems, optical switching devices, ophthalmic glasses, *etc.*¹ Several types of organic photochromic compounds such as naphthopyrans, spiropyrans, fulgides, anils, hydrazones, stilbenes, and diarylethenes have been discovered and their properties investigated.² Recently, we have found that the host compound **1** forms inclusion complex crystals with various kinds of organic guest molecules and some of these inclusion crystals show a reversible colour change from yellow to green upon photoirradiation in the solid state.³ Interestingly, the photochromism of **1** depends on the structure of the included guest molecules and in some cases the chirality of the inclusion crystals. The X-ray crystal structures of the inclusion crystals are also reported.

Result and discussion

Host compound **1a** formed stable inclusion crystals with a wide range of organic guest compounds in 1:1 or 2:1 ratios. (Table 1) Some of these inclusion crystals showed photochromism turning from yellow to green in the solid state, although **1a** itself does not show any photochromism. For example, upon photoirradiation (>300 nm) yellow crystals of the 2:1 inclusion compound of **1a** with *p*-xylene turned to green crystals immediately. The green crystals reverted into yellow crystals on storage in the dark for 10 h at room temperature or quickly on heating at 60 °C. The UV change of the 2:1 inclusion crystals is shown in Fig. 1. The UV absorption around 500–900 nm gradually decreased and finally disappeared. Similarly, the inclusion crystals with acetone (1:1), 2-butanone (1:1), cyclopentanone (1:1), cyclohexanone (1:1), dioxane (1:1), carbon tetrachloride (1:1), 1,1-dichloroethane (1:1), 1,1,2,2-tetrachloroethane (1:1), benzene (1:1), *o*-xylene (1:1), anisole (2:1), *m*-dimethoxybenzene (2:1), *p*-dimethoxybenzene (2:1) and 2-picoline (1:1) showed similar photochromism in the solid state (Table 1).

The photochromism of the inclusion crystals of **1a** was very sensitive to the structure of the guest compounds. For example, acetone and 2-butanone showed photochromism, while 3-pentanone did not. Similarly, dioxane, 1,2-dichloroethane and 2-picoline show photochromism, but tetrahydropyran,

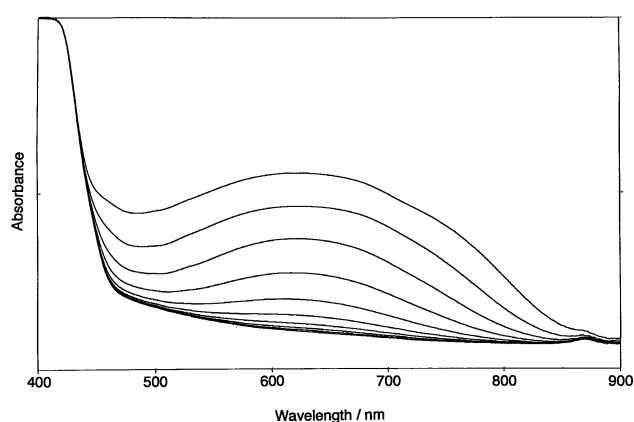


Fig. 1 UV spectral changes of 2:1 inclusion complex of **1a** with *p*-xylene in the solid state. Successive measurements were recorded every 60 min from the top to the bottom.

Table 1 Inclusion complex of **1a** with various guest compounds

Guest	H:G	Photochromism	Bleaching time/h
Acetone	1:1	yes	504
2-butanone	1:1	yes	164
3-pentanone	1:1 ^a	no	
Cyclopentanone	1:1	yes	4
Cyclohexanone	1:1	yes	10
THF	1:1 ^a	no	
Tetrahydropyran	1:1 ^a	no	
Dioxan	1:1	yes	504
CH ₂ Cl ₂	1:1	no	
CHCl ₃	1:1	no	
CCl ₄	1:1	yes	9
CH ₃ CHCl ₂	1:1	yes	10
Cl ₂ CHCHCl ₂	1:1	yes	10
Benzene	1:1	yes	3
<i>o</i> -xylene	1:1	yes	12
<i>p</i> -xylene	2:1	yes	10
<i>o</i> -dichlorobenzene	1:1	no	
<i>p</i> -dichlorobenzene	1:1	no	
Anisole	2:1	yes	12
<i>o</i> -dimethoxybenzene	2:1	no	
<i>m</i> -dimethoxybenzene	2:1	yes	9
<i>p</i> -dimethoxybenzene	2:1	yes	6
Pyridine	1:1 ^a	no	
2-methylpyridine	1:1 ^a	yes	5
3-methylpyridine	2:1	no	
4-methylpyridine	1:1	no	

^aConglomerate

* To receive any correspondence. E-mail: ktanaka@eng.ehime-u.ac.jp

† This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

1,1-dichloroethane and 4-picoline do not. Furthermore, the photochromism of **1a** depends in some cases on the chirality of its inclusion crystals. Previously, we have reported that **1a** forms either a conglomerate or a racemate by inclusion complexation with achiral guest compounds, and this phenomenon depends on the type of guest compounds.^{4b} For example, when (\pm)-**1a** was crystallised from 2-butanone, a 1:1 racemate inclusion complex of (\pm)-**1a** with 2-butanone was obtained and showed photochromism. Interestingly, however, when (\pm)-**1a** was crystallised from 3-pentanone, a 1:1 conglomerate inclusion crystals of (+)- or (-)-**1a** with 3-pentanone was obtained and showed no photochromism. Similarly, the conglomerate inclusion crystals of **1a** with THF, tetrahydropyran and pyridine did not show any photochromism, although the 1:1 conglomerate inclusion crystals with 2-pyridine showed photochromism (Table 1).

It is also interesting that the stability of the photochromism depends on the type of guest molecules. For example, the bleaching times of the green colour of the inclusion crystals of **1a** which developed upon photoirradiation were 3h (benzene), 4h (cyclopentanone), 5h (2-methylpyridine), 6h (*p*-dimethoxybenzene), 9h (*m*-dimethoxybenzene), 10h (cyclohexanone, *p*-xylene and 1,1-dichloroethane), 12h (anisole and *o*-xylene), 164h (2-butanone), and 504h (acetone and dioxane), respectively (Table 1).

On the other hand, host **1b** included limited numbers of guest compounds to form racemate crystals and showed similar photochromism in the solid state. (Table 2) For example, yellow crystals of the 1:1 inclusion complex of **1b** with CCl₄ turned green carbon tetrachloride upon photoirradiation and reverted to yellow crystals on storage in the dark for 10 h at room temperature. The UV spectral change of the 1:1 inclusion complex is shown in Fig. 2. The green form of the 1:1 inclusion crystals of **1b** and *p*-dimethoxybenzene was labile and reverted to the yellow form within 2 h in the dark. (Table 2).

The solid-state IR spectrum of the green crystals of **1** was identical with that of the yellow crystals, and no ESR signal developed upon photoirradiation. The photochromic properties of **1** are probably due to π - π interactions owing to its suitable molecular packing in the inclusion crystals, because photoirradiation of **1** in solution did not show any photochromic properties. In order to elucidate the reason for the photochromism depending on the guest molecules, the X-ray analyses of the inclusion complexes of **1** were studied.

The 1:1 inclusion complex of **1a** and 2-butanone crystallised in a space group $P\bar{1}$, in which a pair of (*R*)- and (*S*)-enantiomer of **1a** are arranged together by π - π stacking between phenyl groups of these enantiomers. (Fig. 3) The distance and dihedral angle between two phenyl rings of C19-C24 and C49-C54 are 3.504(8) Å and 1.0(1)°, respectively. On the other hand, 1:1 inclusion complex of **1a** and 3-pentanone adopts a space group of $P2_12_12_1$ and the cell parameter and the crystal structure resembles to the previously reported 1,2-dichloromethane complex of **1a**.⁵ (Fig. 4) However, no π - π stacking between the phenyl groups was observed in this crystal. The colour change upon photoirradiation of the inclusion crystals of **1a** arises due to the π - π interaction between phenyl groups of the host molecules **1a**, which adopts suitable conformation in the presence of the guest molecules.

Experimental

Preparation of 1. The host compound **1a** and **1b** were prepared by the reported method.⁴

Preparation of inclusion crystals of 1. The host compounds **1a** and **1b** were dissolved by heating in a minimum amount of the neat guest compounds. After keeping for 12 h at room temperature, the inclusion crystals which formed, were collected. The host:guest stoichiometric ratios were determined by TG, NMR and elemental analysis. Data for

Table 2 Inclusion complex of **1b** with various guest compounds

Guest	H:G	Photochromism	Bleaching time/h
CCl ₄	1:1	yes	10
Cyclohexanone	1:1	no	—
Dioxane	1:1	no	—
<i>p</i> -dimethoxybenzene	2:1	yes	2

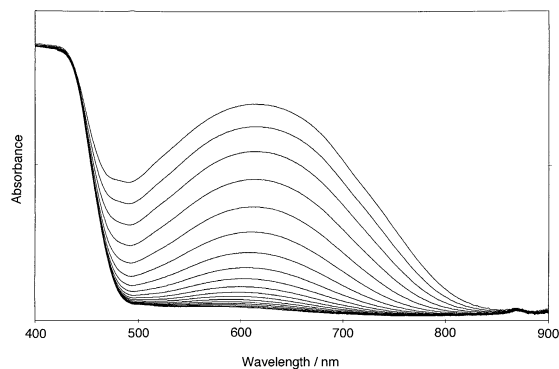


Fig. 2 UV spectral changes of 1:1 inclusion complex of **1b** with CCl₄ in the solid state. Successive measurements were recorded every 30 min from the top to the bottom.

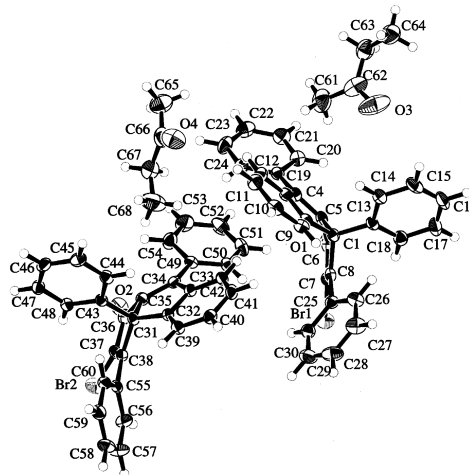


Fig. 3 Ortep drawing of 1:1 inclusion complex of (*R,S*)-**1a** with 2-butanone. The 1:1 inclusion complex of **1a** and 2-butanone crystallised in a space group $P\bar{1}$, in which a pair of (*R*)- and (*S*)-enantiomer of **1a** are arranged together by π - π stacking between phenyl groups of these enantiomers.

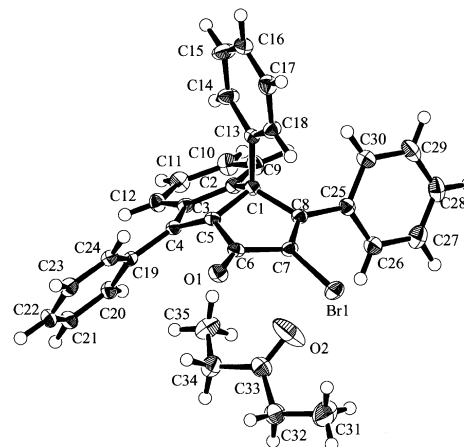


Fig. 4 Ortep drawing of 1:1 inclusion complex of (*S*)-**1a** with 3-pentanone. The 1:1 inclusion complex of **1a** and 3-pentanone adopts a space group of $P2_12_12_1$.

each compound are given in Table 1 and 2. Elemental analyses. **1a**, acetone (1:1): Found: C, 74.50; H, 4.78%. Calcd for $C_{33}H_{25}BrO_2$: C, 74.30; H, 4.72%. **1a**, 2-butanone (1:1): Found: C, 74.59; H, 4.97%. Calcd for $C_{34}H_{27}BrO_2$: C, 74.59; H, 4.97%. **1a**, 3-pentanone (1:1): Found: C, 75.07; H, 5.23%. Calcd for $C_{35}H_{29}BrO_2$: C, 74.87; H, 5.21%. **1a**, cyclopentanone (1:1): Found: C, 75.26; H, 5.01%. Calcd for $C_{35}H_{27}BrO_2$: C, 75.14; H, 4.86%. **1a**, cyclohexanone (1:1): Found: C, 75.50; H, 5.31%. Calcd for $C_{36}H_{29}BrO_2$: C, 75.39; H, 5.10%. **1a**, tetrahydrofuran (1:1): Found: C, 74.55; H, 5.19%. Calcd for $C_{34}H_{27}BrO_2$: C, 74.59; H, 4.97%. **1a**, tetrahydropyran (1:1): Found: C, 75.05; H, 5.24%. Calcd for $C_{35}H_{29}BrO_2$: C, 74.87; H, 5.21%. **1a**, dioxane (1:1): Found: C, 72.81; H, 4.83%. Calcd for $C_{34}H_{27}BrO_3$: C, 72.47; H, 4.83%. **1a**, dichloromethane (1:1): Found: C, 66.66; H, 3.83%. Calcd for $C_{31}H_{21}BrCl_2O$: C, 66.45; H, 3.78%. **1a**, chloroform (1:1): Found: C, 62.77; H, 3.47%. Calcd for $C_{31}H_{20}BrCl_3O$: C, 62.60; H, 3.39%. **1a**, carbontetrachloride (1:1): Found: C, 58.80; H, 3.06%. Calcd for $C_{31}H_{19}BrCl_4O$: C, 59.18; H, 3.04%. **1a**, 1,1-dichloroethane (1:1): Found: C, 67.10; H, 4.09%. Calcd for $C_{32}H_{23}BrCl_2O$: C, 66.92; H, 4.04%. **1a**, 1,1,2,2-tetrachloroethane (1:1): Found: C, 59.69; H, 3.28%. Calcd for $C_{32}H_{21}BrCl_4O$: C, 59.75; H, 3.29%. **1a**, benzene (1:1): Found: C, 78.37; H, 4.80. Calcd for $C_{36}H_{25}BrO$: C, 78.12; H, 4.55%. **1a**, *o*-xylene (1:1): Found: C, 78.73; H, 5.12. Calcd for $C_{38}H_{29}BrO$: C, 78.48; H, 5.13%. **1a**, *p*-xylene (2:1): Found: C, 77.56; H, 4.61. Calcd for $C_{34}H_{24}BrO$: C, 77.27; H, 4.58%. **1a**, *o*-dichlorobenzene (1:1): Found: C, 69.54; H, 3.75. Calcd for $C_{36}H_{23}BrCl_2O$: C, 69.47; H, 3.72%. **1a**, *p*-dichlorobenzene (1:1): Found: C, 69.59; H, 3.80. Calcd for $C_{36}H_{23}BrCl_2O$: C, 69.47; H, 3.72%. **1a**, anisole (2:1): Found: C, 76.11; H, 4.43. Calcd for $C_{67}H_{46}Br_2O_3$: C, 76.00; H, 4.38%. **1a**, *m*-dimethoxybenzene (2:1): Found: C, 75.02; H, 4.53. Calcd for $C_{34}H_{24}BrO_2$: C, 75.00; H, 4.44%. **1a**, *p*-dimethoxybenzene (2:1): Found: C, 75.21; H, 4.49. Calcd for $C_{34}H_{24}BrO_2$: C, 75.00; H, 4.44%. **1a**, pyridine (1:1): Found: C, 75.94; H, 4.56; N, 2.57%. Calcd for $C_{35}H_{24}BrNO$: C, 75.81; H, 4.36; N, 2.53%. **1a**, 2-methylpyridine (1:1): Found: C, 76.31; H, 4.88; N, 2.67%. Calcd for $C_{36}H_{26}BrNO$: C, 76.06; H, 4.61; N, 2.46%. **1a**, 3-methylpyridine (2:1): Found: C, 75.92; H, 4.27; N, 1.31%. Calcd for $C_{66}H_{45}Br_2NO_2$: C, 75.94; H, 4.35; N, 1.34%. **1a**, 4-methylpyridine (1:1): Found: C, 76.32; H, 4.76; N, 2.57%. Calcd for $C_{36}H_{26}BrNO$: C, 76.06; H, 4.61; N, 2.46%. **1b**, carbontetrachloride (1:1): Found: C, 63.39; H, 3.31%. Calcd for $C_{31}H_{19}Cl_4O$: C, 63.67; H, 3.28%. **1b**, cyclohexanone (1:1): Found: C, 82.01; H, 5.63%. Calcd for $C_{36}H_{29}ClO_2$: C, 81.73; H, 5.52%. **1b**, dioxane (1:1): Found: C, 78.95; H, 5.38%. Calcd for $C_{34}H_{27}ClO_3$: C, 78.68; H, 5.24%. **1b**, *p*-dimethoxybenzene (2:1): Found: C, 82.06; H, 5.03. Calcd for $C_{34}H_{24}ClO_2$: C, 81.67; H, 4.84%.

Measurement of the diffuse reflectance UV spectra of the inclusion crystals: The coloured inclusion crystals were developed by photoirradiation with a high-pressure Hg lamp through a Pyrex filter for 10 min under aerobic conditions, and their diffuse reflectance UV spectra monitored by using a Shimadzu MPS-2000 spectrophotometer.

X-ray crystallography: X-ray diffraction data were obtained on a Rigaku/MSFC AFC-8-Mercury diffractometer with graphite monochromated MoK α radiation. The crystal structures were determined by the direct method. The structures were refined with

anisotropic temperature factors for the non-H atoms. The hydrogen atoms were treated with a riding model. Calculations of full matrix least-square refinement converged nicely with normal bond lengths and angles. Crystal data for (*S*)-**1a**-3-pentanone: $C_{35}H_{29}BrO_2$, $M = 561.52$, orthorhombic, $a = 16.6596(7)$, $b = 17.5032(7)$, $c = 9.3885(4)$ Å, $U = 2737.7(2)$ Å³, $T = 173$ K, space group $P2_12_12_1$ (no. 19), $Z = 4$, $D_c = 1.362$ g cm⁻³, (Mo K α) = 1.536 mm⁻¹. 20882 reflections measured, 6156 unique ($R_{int} = 0.054$). The final R indices: $R(F) = 0.023$ based on 5941 reflections ($I > 2\sigma(I)$), $wR(F^2) = 0.056$ based on all data and 343 parameters, GOF = 1.03. Crystal data for **1a**-2-butanone: $C_{34}H_{27}BrO_2$, $M = 547.49$, triclinic, $a = 11.017(3)$, $b = 14.068(4)$, $c = 17.671(5)$ Å, $\alpha = 88.550(9)^\circ$, $\beta = 99.646(8)^\circ$, $\gamma = 104.651(6)^\circ$, $U = 2611(1)$ Å³, $T = 173$ K, space group $P\bar{1}$ (no. 2), $Z = 4$, $D_c = 1.392$ g cm⁻³, (Mo K α) = 1.608 mm⁻¹. 20739 reflections measured, 11419 unique ($R_{int} = 0.044$). The final R indices: $R(F) = 0.062$ based on 9204 reflections ($I > 2\sigma(I)$), $wR(F^2) = 0.154$ based on all data and 667 parameters, GOF = 1.11.

Experimental details, and positional and thermal parameters for all crystals are included in the Supporting Information. All calculations were performed using the teXsan crystallographic software package.⁶

Received 25 March 2003; accepted 29 May 2003

Paper 03/1832

References

- 1 B.V. Gemert, In *Organic Photochromic and Thermochromic Compounds*, Eds. J.C. Crano and R.J. Guglielmetti, Plenum Press, New York, 1999.
- 2 (a) K. Tanaka and F. Toda, *J. Chem. Soc. Perkin Trans 1*, 2000, 873; (b) H. Yoshikawa and S. Nishikiori, *Chem. Lett*, 2000, 142; (c) M. Nanasawa, M. Miwa, M. Hirai and T. Kuwabara, *J. Org. Chem.*, 2000, **65**, 593; (d) L. Dinescu and Z.Y. Wang, *Chem. Commun.*, 1999, 2497; (e) S. Kobatake, M. Yamada, T. Yamada and M. Irie, *J. Am. Chem. Soc.*, 1999, **121**, 2380 and 8450; (f) T. Arai and M. Ikegami, *Chem. Lett.*, 1999, 965; (g) H. Kurata, T. Tanaka and M. Oda, *Chem. Lett.*, 1999, 749; (h) S. Delbaere, B.L-Houze, C. Bochu, Y. Teral, M. Campredon and G. Vermeersch, *J. Chem. Soc., Perkin Trans 2*, 1998, 1153; (i) Y. Eichen, J.-M. Lehn, M. Scherl, D. Haarer, J. Fischer, A. DeCian, A. Corval and P. Trommsdorff, *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 2530; (j) H. Koyama, T. Kawato, H. Kanatomi, H. Hatsushita and K. Yonetani, *J. Chem. Soc., Chem. Commun.*, 1994, 579.
- 3 Preliminary communication: K. Tanaka, T. Watanabe, F. Toda, *Chem. Commun.*, 2000, 1361.
- 4 (a) F. Toda, M. Sasaoka, Y. Todo, K. Iida, T. Hino, Y. Nishiyama, H. Ueda and T. Oshima, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 3314; (b) F. Toda and K. Tanaka, *Tetrahedron: Asym.*, 1990, **1**, 359.
- 5 F. Toda, K. Tanaka and R. Kuroda, *Chem. Commun.*, 1997, 1227.
- 6 Crystal Structure Analysis Package, Molecular Structure Corporation (1985&1999).