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The Crystal and Molecular Structures of 2,2,4,6-Tetraphenyldihydro-1,3,5-triazine Acetone Solvate and 2-Propanol Solvate

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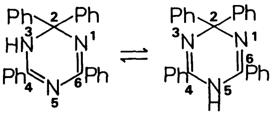
The crystal and molecular structures of 2,2,4,6-tetraphenyldihydro-1,3,5-triazine acetone solvate (**1**) which turns red on exposure to UV light, and 2-propanol solvate (**2**) which shows no photocoloration, have been determined by the X-ray method. The crystals of both inclusion compounds are monoclinic. For **1** the space group is $P2_1/n$; Z=4, with a=16.385(2), b=11.987(2), c=12.939(2) Å, and β=92.24(2)°. For **2** the space group is $C2/c$; Z=8, with a=21.967(3), b=13.418(1), c=19.576(4) Å, and β=118.73(1)°. The final R values were 0.082 and 0.083 for **1** and **2** respectively. In both crystals, the dihydrotriazine ring exists in 2,3-dihydro form, which is one of the two possible tautomeric forms. In **1** each acetone molecule interacts with only one molecule of tetraphenyldihydrotriazine by N(3)-H(3)···O hydrogen bond, while in **2** tetraphenyldihydrotriazine and 2-propanol molecules are alternately connected by N(3)-H(3)···O and N(5)···H-O hydrogen bonds to construct a ribbon-like structure. It was suggested that the N(3)-H(3)···O-H···N(5) hydrogen bonds which exist in **2** but not in **1** inhibit photocoloration of **2**.

2,2,4,6-Tetraphenyldihydro-1,3,5-triazine (hereafter abbreviated as triazine) was synthesized by Lottermoser in 1896 and reported to exhibit photochromism in the solid state,[1] but the structure of the colored species has been undetermined. It has been reported that triazine exists in an equilibrium mixture of 2,3-dihydro (a) and 2,5-dihydro (b) forms, which are prototropic tautomers, in solutions and in the solid state.[2] During the course of the investigation on the photocoloration of triazine we found that triazine forms crystalline inclusion compounds with various solvent molecules having one hetero atom with molar ratio of 1:1 on the recrystallization. These inclusion compounds could be classified into two types in terms of their photochemical behavior. The inclusion compounds composed of acetone, chloroform, tetrahydrofuran or 2-methyltetrahydrofuran turned red or reddish violet on exposure to UV light and the color faded gradually in the dark, while the ones composed of ethanol, 2-propanol or propylamine showed no photocoloration. The crystal and molecular structure of 2,2,4,6-tetraphenyldihydro-1,3,5-triazine ethanol solvate (**3**) has been determined and it was assumed that two types of hydrogen bonds might inhibit the photocoloration of the crystals.[3] In order to confirm the assumption and to reveal the structural differences between photo-active and photo-inactive inclusion compounds, the molecular and crystal structures of the title compounds were determined.



(a) (b)

Experimental

Triazine was synthesized by the method of Lottermoser.[1] Colorless plate-like crystals of **1** and **2** were obtained by recrystallization of triazine from acetone or 2-propanol, respectively. In both cases a crystal was sealed in a glass capillary and set up on a RIGAKU AFC-4 diffractometer. Cell parameters were refined by least squares on the basis of 16 and 18 independent 2θ values for **1** and **2** respectively. Crystal data and some experimental conditions are listed in Table 1. Intensities were measured with graphitemonochromated Mo $K\alpha$ or Cu $K\alpha$ radiation, using the ω–2θ scan technique. Background counts were accumulated for 5 s before and after each scan. Three standard reflections were monitored for every 50 reflections and no significant variations in intensities were observed. Reflections of $|F_o|>3\sigma(|F_o|)$ were considered as observed and used for structure determination. Corrections for the Lorentz and polarization factors were made, but no correction for absorption was applied.

The structure of **1** was solved by the direct method with the program MULTAN 78[4] and refined by the full-matrix least squares with the program SHELX 76.[5] All the hydrogen atoms were found on the difference map. The atoms of acetone molecule were disordered between three sets of positions and were treated as rigid molecules with the usual geometry. The occupancy factor for each set was fixed to 0.33333, considering from the temperature factors. The final refinement was made with the anisotropic temperature factors for non-hydrogen atoms of triazine molecule and the isotropic ones for hydrogen atoms and the atoms of acetone molecule. The quantity minimized was $\sum w(|F_o|-|F_c|)^2$ and $w=[\sigma^2(|F_o|)+0.0021|F_o|^2]^{-1}$. The final R and R_w values became 0.082 and 0.092 for 3488 observed reflections. No peaks higher than 0.35 e Å^{-3} were found on the final difference map.

The procedure of the structure determination for **2** was similar to that for **1**. Some of hydrogen atoms were found on the difference map. The others were calculated geometrically and refined with C-H distances constrained to 1.00 Å. The atoms of 2-propanol molecule were disordered between three sets of positions but were refined with no constraint. The occupancy factors were fixed to 0.5 for one set and 0.25 for the other two sets. The final refinement was made with the anisotropic temperature factors for non-hydrogen atoms of triazine molecule and the isotropic ones for hydrogen

Table 1. Crystal Data and Experimental Conditions of **1** and **2**

	1	**2**
Formula	$C_{27}H_{21}N_3\cdot C_3H_6O$	$C_{27}H_{21}N_3\cdot C_3H_8O$
F.W.	445.55	447.56
Crystal size/mm	0.7×0.5×0.3	0.5×0.3×0.2
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$
a/Å	16.385(2)	21.967(3)
b/Å	11.987(2)	13.418(1)
c/Å	12.939(2)	19.576(4)
β/°	92.24(2)	118.73(1)
V/Å^3	2539.5(6)	5059.5(14)
Z	4	8
D_x/g cm^{-3}	1.17	1.17
λ/Å	0.71069 (Mo$K\alpha$)	1.54184 (Cu$K\alpha$)
μ/cm^{-1}	0.39 (Mo$K\alpha$)	4.87 (Cu$K\alpha$)
F (000)	944.0	1904.0
T/K	293	293
$2\theta_{\max}$/°	50.0	125.0
Scanning rate/° min^{-1}	4 (2θ)	8 (2θ)
Scan width/°	1.0+0.35tanθ	0.8+0.15tanθ

Table 2. Final Atomic Coordinates Multiplied by 10^4 and Equivalent Thermal Parameters, B_{eq}(Å^2), for Non-Hydrogen Atoms of Acetone Solvate (**1**). All the Occupancy Factors for the Three Acetone Molecules, O(31)–C(34), O(31′)–C(34′), and O(31″)–C(34″), Are Fixed to be 0.33333

$$B_{eq}=\frac{4}{3}\sum_i\sum_j B_{ij}\boldsymbol{a}_i\boldsymbol{a}_j$$

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
N(1)	2068(1)	840(2)	10286(2)	3.5	C(22)	1315(3)	4649(3)	9324(3)	5.6
C(2)	2581(2)	1782(2)	10611(2)	3.3	C(23)	2032(3)	4321(3)	8923(3)	5.7
N(3)	3414(2)	1643(2)	10239(2)	3.8	C(24)	2463(2)	3418(3)	9338(3)	4.7
C(4)	3564(2)	992(2)	9437(2)	3.2	C(25)	2652(2)	1835(3)	11803(2)	3.6
N(5)	3014(1)	351(2)	8996(2)	3.7	C(26)	2388(2)	977(3)	12397(3)	4.8
C(6)	2291(2)	261(2)	9520(2)	3.1	C(27)	2509(3)	1013(4)	13471(3)	6.1
C(7)	1741(2)	−654(2)	9135(2)	3.3	C(28)	2885(3)	1912(4)	13932(3)	6.6
C(8)	2008(2)	−1484(3)	8500(2)	3.9	C(29)	3144(3)	2785(4)	13339(3)	6.3
C(9)	1485(2)	−2333(3)	8148(3)	4.8	C(30)	3022(2)	2741(3)	12280(3)	5.1
C(10)	695(3)	−2344(3)	8426(3)	5.4	O(31)	4654(5)	3622(7)	1107(6)	7.9
C(11)	414(3)	−1524(3)	9075(3)	6.1	C(32)	5230(8)	3890(11)	1671(9)	13.7
C(12)	938(2)	−685(3)	9430(3)	4.8	C(33)	5808(8)	4818(12)	1378(12)	11.2
C(13)	4404(2)	988(3)	9038(2)	3.7	C(34)	5504(10)	3182(14)	2596(11)	13.6
C(14)	4949(2)	1836(4)	9241(3)	5.5	O(31′)	4727(7)	3072(10)	1573(12)	18.2
C(15)	5732(3)	1783(5)	8859(4)	7.0	C(32′)	5311(6)	3661(8)	1792(9)	7.0
C(16)	5956(3)	896(4)	8270(3)	6.4	C(33′)	5286(10)	4916(8)	1631(14)	12.2
C(17)	5417(2)	68(4)	8058(3)	5.8	C(34′)	6058(8)	3210(13)	2387(14)	13.0
C(18)	4649(2)	111(3)	8440(3)	4.7	O(31″)	4836(4)	3010(6)	1382(5)	5.5
C(19)	2167(2)	2836(2)	10165(2)	3.4	C(32″)	5413(7)	3329(13)	1920(7)	11.6
C(20)	1447(2)	3193(3)	10576(3)	4.3	C(33″)	6081(8)	4056(16)	1496(11)	14.6
C(21)	1019(2)	4084(3)	10163(3)	5.5	C(34″)	5521(8)	2998(12)	3049(6)	9.4

atoms and the atoms of 2-propanol. The weighting scheme was $w=[\sigma^2(|F_o|)+0.0313|F_o|^2]^{-1}$. The final R and R_w values became 0.083 and 0.110 for 2997 observed reflections. No peaks higher than 0.31 e Å^{-3} were found on the final difference map. The atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[6] The final atomic coordinates and equivalent isotropic temperature factors for non-hydrogen atoms are given in Tables 2 and 3. The lists of the anisotropic temperature factors for non-hydrogen atoms, atomic coordinates and temperature factors for hydrogen atoms, and the observed and calculated structure factors are kept in the office of the Chemical Society of Japan (Document No. 8814). The computation was carried out on HITAC M-280 computer at the Computer Center of the University of Tokyo.

Results and Discussion

The structure of triazine with the atom-numbering in **1** is shown in Fig. 1. For **2** the same numbering

Table 3. Final Atomic Coordinates Multiplied by 10^4 and Equivalent Thermal Parameters, B_{eq}(Å^2), for Non-Hydrogen Atoms of 2-Propanol Solvate (**2**). All the Occupancy Factors for the Three 2-Propanol Molecules, O(31)-C(34), O(31′)-C(34′), and O(31″)-C(34″), Are Fixed To Be 0.5, 0.25, and 0.25 Respectively

$$B_{eq} = \frac{4}{3} \sum_i \sum_j B_{ij} \boldsymbol{a}_i \boldsymbol{a}_j$$

Atom	*x*	*y*	*z*	B_{eq}	Atom	*x*	*y*	*z*	B_{eq}
N(1)	8552(1)	1388(2)	1762(1)	4.5	C(22)	9723(3)	2639(4)	4477(2)	8.0
C(2)	8360(1)	2299(2)	2011(2)	4.1	C(23)	9026(3)	2777(4)	4176(2)	7.7
N(3)	7617(1)	2258(2)	1819(1)	4.1	C(24)	8576(2)	2681(3)	3387(2)	5.9
C(4)	7331(1)	1383(2)	1806(1)	3.5	C(25)	8432(1)	3183(3)	1553(2)	4.3
N(5)	7624(1)	528(2)	1811(1)	5.4	C(26)	8274(2)	3029(3)	778(2)	5.9
C(6)	8205(1)	596(2)	1707(2)	3.8	C(27)	8308(2)	3829(4)	347(2)	6.6
C(7)	8412(2)	−347(3)	1473(2)	4.4	C(28)	8484(2)	4753(4)	649(2)	7.5
C(8)	7970(2)	1160(3)	1227(2)	5.4	C(29)	8622(3)	4926(4)	1406(3)	8.6
C(9)	8132(3)	−2038(3)	976(2)	6.6	C(30)	8595(3)	4131(3)	1847(2)	7.1
C(10)	8757(3)	−2096(4)	974(3)	7.9	O(31)	7051(2)	4186(3)	1874(2)	5.7
C(11)	9202(3)	−1302(4)	1218(3)	8.0	C(32)	6657(5)	4813(8)	1202(6)	9.5
C(12)	9038(2)	−424(3)	1464(3)	6.4	C(33)	5940(4)	4931(7)	1138(5)	8.6
C(13)	6630(1)	1350(2)	1744(1)	4.0	C(34)	6641(5)	4432(7)	520(6)	9.4
C(14)	6411(2)	2088(3)	2073(2)	5.0	O(31′)	7014(4)	4159(6)	1907(5)	5.9
C(15)	5754(2)	2014(3)	2019(3)	6.4	C(32′)	6533(5)	4736(8)	1245(6)	4.8
C(16)	5332(2)	1226(4)	1640(2)	6.5	C(33′)	5850(6)	4671(11)	1245(7)	6.1
C(17)	5541(2)	506(4)	1299(3)	6.1	C(34′)	6498(5)	4049(9)	496(6)	5.0
C(18)	6192(2)	555(3)	1357(2)	5.0	O(31″)	7172(3)	4255(5)	1884(3)	3.7
C(19)	8827(1)	2429(3)	2889(2)	4.4	C(32″)	6627(5)	4762(9)	1224(6)	4.7
C(20)	9539(2)	2302(4)	3200(2)	8.0	C(33″)	7009(8)	5531(12)	1048(10)	7.8
C(21)	9977(3)	2384(6)	3985(3)	9.6	C(34″)	6191(10)	4047(16)	599(11)	9.9

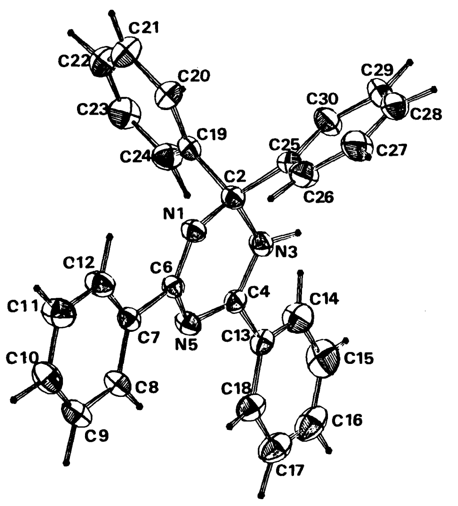


Fig. 1. ORTEP[7)] plot of tetraphenyldihydrotriazine molecule in **1** with the atom-numbering. The anisotropic ellipsoids for non-H atoms enclose 30% probability.

Table 4. Selected Bond Distances (Å) and Angles (deg)

	1	**2**	**3**[3)]
N(1)-C(2)	1.460(4)	1.453(4)	1.465(3)
C(2)-N(3)	1.474(4)	1.488(4)	1.481(3)
N(3)-C(4)	1.329(4)	1.327(4)	1.336(3)
C(4)-N(5)	1.299(4)	1.314(4)	1.312(3)
N(5)-C(6)	1.393(4)	1.387(4)	1.396(3)
N(1)-C(6)	1.274(4)	1.282(4)	1.278(3)
C(2)-C(19)	1.535(4)	1.530(5)	1.537(4)
C(2)-C(25)	1.544(4)	1.540(5)	1.527(4)
C(4)-C(13)	1.489(4)	1.486(4)	1.490(4)
C(6)-C(7)	1.493(4)	1.489(5)	1.490(4)
N(1)-C(2)-N(3)	110.4(2)	110.1(2)	109.2(2)
C(2)-N(3)-C(4)	121.6(3)	119.4(3)	119.5(2)
N(3)-C(4)-N(5)	123.0(3)	123.1(3)	122.0(2)
C(4)-N(5)-C(6)	114.9(2)	115.0(3)	114.6(2)
N(5)-C(6)-N(1)	127.7(3)	126.4(3)	127.2(2)
C(6)-N(1)-C(2)	117.8(2)	117.9(3)	116.2(2)

scheme is used. The crystal structures of **1** and **2** are shown in Fig. 2. Selected bond distances and angles of **1** and **2** are listed in Table 4, and the torsion angles, the dihedral angles and the hydrogen bond distances of **1** and **2** are listed in Table 5, together with the corresponding ones of **3**.[3)] The molecular structures of **1** and **2** are closely similar to that of **3**. During the refinements the difference maps showed that N(3), not N(5), is bound to a hydrogen atom, that is, the dihydrotriazine exists in 2,3-dihydro form, in both **1** and **2**, as was reported in **3**. The triazine structure is also confirmed by the bond distances: N(3)-C(4) is longer than N(5)-C(4). The dihydrotriazine ring in **1** and **2** was found to exist in the boat conformation with the apexes of C(2) and N(5), as was observed in **3**, but the dihedral angles between the least-squares plane of N(1), C(6), C(4), and N(3) and the plane through N(1), C(2), and N(3) or that through C(4), N(5), and C(6) varied with the kind of included solvent. In **1** these dihedral angles are smaller than

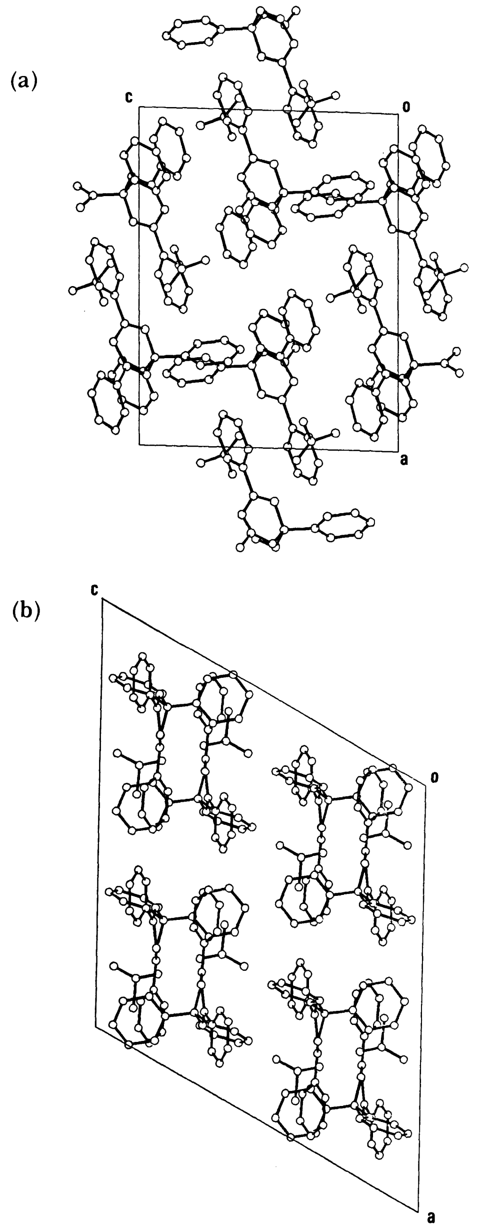


Fig. 2. Crystal structure viewed along the b axis. (a) **1** and (b) **2**. For the solvent molecules the atoms with prime or double prime are omitted.

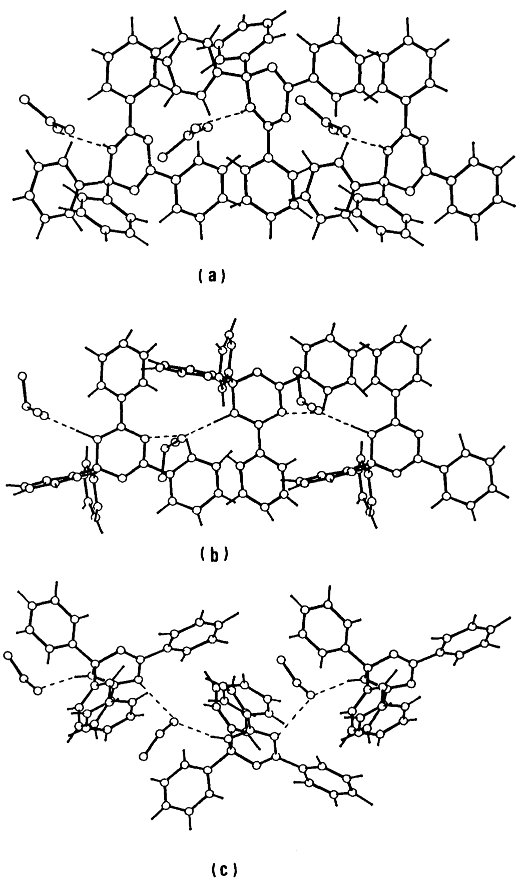


Fig. 3. Hydrogen bonding scheme drawn schematically for (a) **1**, (b) **2**, and (c) **3**. The hydrogen bonds are indicated by broken lines. For the solvent molecules the atoms with prime or double prime are omitted.

those in **2** or **3**, which means that the dihydrotriazine ring in **1** is more planar. The corresponding bond distances and angles of the three inclusion compounds are almost consistent within experimental error, except that the angle C(2)–N(3)–C(4) of **1** (121.6°) is slightly larger than that of **2** (119.4°) or of **3** (119.5°). In the three inclusion compounds the torsion angles N(5)–C(6)–C(7)–C(8) and N(3)–C(4)–C(13)–C(14) are relatively small, indicating that the two phenyl rings at 4- and 6-positions are nearly coplanar with the dihydrotriazine ring. On the other hand, the two phenyl rings at 2-position are perpendicular to the dihydrotriazine ring. The two perpendicular phenyl rings serve to prevent the close packing of triazine molecules and in both crystals of **1** and **2** each acetone or 2-propanol molecule is placed in a cavity which is formed by phenyl rings of neighboring triazines, respectively. In both crystals solvent molecules are disordered, probably since there is enough space around them. Oxygen atoms in both solvent molecules are located near N(3) of triazine and involved in hydrogen bonds. However, the hydrogen bonding scheme is significantly different between **1** and **2**. As is shown in Fig. 3(b), the triazine and solvent molecules in **2** are alternately connected to form an infinite helix around the two-fold screw axis by the two types of hydrogen bond: N(3)–H(3)···O and N(5)···H–O. This hydrogen bonding scheme was also seen in **3** (Fig. 3(c)) and the pitch of the helix, that is, the value of b of **2** (13.418 Å) is similar to that of **3** (13.527 Å). On the other hand, in the case of **1**, although the crystal packing is similar to that of **2** or **3**, each acetone molecule interacts with one triazine molecule by the hydrogen bond of N(3)–H(3)···O and each hydrogen bonding pair is isolated (Fig. 3(a)). The distances N(5)···O and N(3)···O of **2** are similar to those of **3**, but the distance N(3)···O of **1** is longer as is shown in

Table 5. Comparison of the Torsion Angles, the Dihedral Angles[a] (deg) and the Hydrogen Bond Distances (Å)

	1	**2**	**3**[3]
N(5)-C(6)-C(7)-C(8)	14.6(4)	12.6(5)	20.3(4)
N(3)-C(4)-C(13)-C(14)	−19.8(5)	−32.5(5)	−20.1(4)
[1]	83.4(1)	79.0(2)	96.4(1)
[2]	56.0(1)	69.5(2)	73.9(1)
[3]	18.6(3)	24.2(3)	28.9(2)
[4]	8.2(3)	10.0(4)	11.5(3)
N(3)-O(31)	3.29(1)[b]	2.90(1)	2.86(1)
N(3)-O(31′)	3.20(2)	2.92(1)	3.01(3)
N(3)-O(31″)	3.17(1)	2.88(1)	
O(31)-N(5)		2.94(1)	2.90(1)
O(31′)-N(5)		2.92(1)	2.78(2)
O(31″)-N(5)		2.90(1)	

a) [1]: the angle between the least-squares plane of N(1), C(6), N(3), and C(4) (plane A) and that of C(19), C(20), C(21), C(22), C(23), and C(24), [2]: the angle between the plane A and the least-squares plane of C(25), C(26), C(27), C(28), C(29), and C(30), [3]: the angle between the plane A and the plane of N(1), C(2), and N(3), [4]: the angle between the plane A and the plane of C(4), N(5), and C(6). b) The distances of O(31)···H(3), O(31′)···H(3), and O(31″)···H(3) are 2.51(3), 2.35(4), and 2.31(3)Å, respectively.

Table 5. In **2** and **3** the solvent molecules seem to interact more strongly with triazine through the two types of hydrogen bonds than in **1**. Except for the hydrogen bonds, there are no unusually short contacts in **1** and **2** as well as **3**.

On the basis of the crystal structures of the three inclusion compounds **1**, **2**, and **3** and the molecular structures of triazine in them, the difference in the photochemical behavior between the two types of inclusion compounds is probably ascribable to the difference in the hydrogen bonding scheme. Although the structure of the colored species is still open to the question, it is strongly suggested that the N(3)-H(3)···O-H···N(5) hydrogen bonds, by which triazine and solvent molecules are alternately connected in **2** and **3**, inhibit the photocoloration. If the colored species is formed on irradiation, because of the instability of the electronic state, it would easily change back to the stable initial state due to the chain like hydrogen bonds. On the other hand, the crystal of **1** exhibits the photocoloration because each N(3)-H(3)···O hydrogen bond is isolated.

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