Crystal Structure and Photochemical Behavior of 2,2,4,6-Tetraphenyldihydro-1,3,5-triazine and Its Inclusion Compounds

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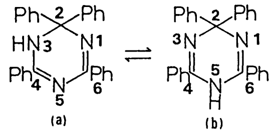
Crystal structures of 2,2,4,6-tetraphenyldihydro-1,3,5-triazine (**1**), which shows photocoloration, and its photostable propylamine solvate (**2**) have been determined. The molecular structure of the dihydrotriazine in **1** and **2** showed that it exists in 2,3-dihydro form in the crystals, but the bond distance of N(3)-C(4) was shorter than a normal C-N single bond, indicating that lone-pair electrons on N(3) interact with the π system of C(4)=N(5)-C(6)=N(1). Comparison of crystal structures of **1**, **2**, and other inclusion compounds previously determined revealed that the difference in the photochemical behavior of the crystals is attributable to different hydrogen bonding schemes. Photolysis of **1** in the solid state, which was carried out in connection with the structural investigation of the photocolored species, gave 2,4,6-triphenyl-1,3,5-triazine as a main product.

2,2,4,6-Tetraphenyldihydro-1,3,5-triazine (abbreviated as TPDT) was reported to exhibit photochromism in the solid state by Lottermoser in 1896,[1] but the structure of the colored species is still undetermined. The photochromism is not observed in solutions around room temperature. In 1985 one of the authors revealed that TPDT exists in an equilibrium mixture



of 2,3-dihydro (a) and 2,5-dihydro (b) forms and the preferred tautomeric form is 2,3-dihydro (a) form both in solutions and in the solid state.[2] Recently we found that TPDT forms 1 : 1 inclusion compounds with various solvent molecules on recrystallization and the inclusion compounds can be classified into two types in terms of their photochemical coloration, that is, photolabile and photostable crystals. In the previous papers[3,4] the crystal structures of photostable ethanol solvate (**3**), 2-propanol solvate (**4**), and photolabile acetone solvate (**5**) were determined and the hydrogen bond between the hydroxyl hydrogen in the solvent molecules and ring nitrogen in TPDT was shown to inhibit the photocoloration. These facts suggested that hydrogen-donating solvents in the inclusion compounds of TPDT inhibit the photocoloration and hydrogen-accepting solvents do not affect the photocoloration. In order to confirm this assumption we have determined the crystal structures of TPDT with no inclusion solvent (**1**), which was recrystallized from toluene-hexane, and its propylamine solvate (**2**) including a different kind of hydrogen-donating solvent from **3** and **4**. Although the red color obtained after irradiation of colorless crystals of **1** gradually faded apparently in the dark, after repeated irradiations and fading processes, TPDT was found to undergo photochemical reactions.

Experimental

Apparatus. Absorption spectra were obtained on a Shimadzu UV-240 spectrophotometer. IR spectra were recorded on a JASCO A-302 IR spectrometer and difference IR spectra were obtained by using a JASCO DP-A330 IR data processor. FT-IR spectra for the reflection method were obtained by a JASCO FT-IR 7000 spectrophotometer. The PA spectrum was measured by Professor Sugitani, University of Tsukuba. The light source was a 500 W xenon lamp (WACOM XD501S), and the light beam was modulated at a frequency of 18 Hz by a chopper. A Nicon P250 spectrometer was used. The output of the microphone was amplified by means of a lock-in amplifier (NF LI-574) and the data were treated with a HP 9816 computer. The correction was carried out by using a PA spectrum of carbon black.

Photolysis of TPDT in the Solid State. The photolysis of **1** or **3** in the solid state was carried out in a KBr pellet [2%(w/w)]. A 100 W high-pressure mercury lamp (Ushio UI-100) was used for the irradiation at room temperature. The progress of the reaction was monitored by difference IR spectra.

General Procedure of Photolysis for Isolation of the Photoproducts in Solutions. All the reactions were performed on solutions (150 cm^3) irradiated by a 400 W high-pressure mercury lamp from outside of a vessel at room temperature under nitrogen. The reactions were monitored by TLC to

Table 1. Crystal Data and Some Experimental Conditions

	1	2
Formula	$C_{27}H_{21}N_3$	$C_{27}H_{21}N_3\cdot C_3H_9N$
F. W.	387.4	446.5
Crystal size /mm	0.5×0.3×0.15	0.3×0.25×0.25
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/a$
a/Å	12.849(2)	17.164(3)
b/Å	12.783(1)	14.343(2)
c/Å	12.621(1)	10.623(3)
β/°	95.28(1)	98.26(2)
V/Å^3	2064.2(4)	2588.1(9)
Z	4	4
D_x/g cm^{-3}	1.246	1.146
μ/cm^{-1}	4.98	4.58
F(000)	816	952
T/K	293	293
$2\theta_{max}$/°	125.0	125.0
scan speed/° min^{-1}	8(2θ)	8(2θ)
scan width/°	1.0+0.15 tan θ	0.8+0.15 tan θ

control the irradiation time. After irradiation was stopped, the solvent was removed under reduced pressure and the resulted residue was chromatographed on a silica gel column with benzene-ethanol as eluent.

Crystal Structure Determination. Colorless plate-like crystals of **1** and **2** were obtained by recrystallization of TPDT from toluene-hexane and propylamine-hexane, respectively. A crystal of **2**, which easily lost the solvent molecule, was sealed in a glass capillary. Cell parameters were refined by least-squares on the basis of 21 and 20 independent 2θ values for **1** and **2**, respectively. Crystal data and some experimental conditions are listed in Table 1. Intensities were measured on a Rigaku AFC-4 diffractometer with graphite-monochromated Cu $K\alpha$ radiation up to $2\theta=125°$, using the ω-2θ scan technique. Background counts were accumulated for 5s before and after each scan. Three standard reflections were monitored for every 50 reflections and no significant variations in intensities were observed. 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[5] and refined by the full-matrix least squares with the program SHELX 76.[6] All the hydrogen atoms were found on the difference map. The final refinement was made with the anisotropic temperature factors for non-hydrogen atoms and the isotropic ones for hydrogen atoms. The quantity minimized was $\sum w(|F_o|-|F_c|)^2$ and $w=[\sigma^2(|F_o|)+0.00654\,|F_o|^2]^{-1}$. The final R and R_w values became 0.063 and 0.080 for 2731 observed reflections. No peaks higher than 0.2 e Å^{-3} were found on the final difference map.

The procedure of the structure determination for **2** was similar to that for **1**. The intense reflections with a low 2θ angle (110, 120, and 111) were removed since their F_o values seemed to suffer from extinction. Some of hydrogen atoms were found on the difference map. The others were calculated geometrically and included in further refinements. The atoms of propylamine molecule were disordered between three sets of positions and were refined under the constrained conditions with the usual geometry (C-N 1.47, C-C 1.54 Å, N-C-C 110, C-C-C 109°). The occupancy factors were fixed to 0.33333 for each set, considering from the temperature factors of the disordered atoms. The final refinement was made with the anisotropic temperature factors for non-hydrogen atoms of TPDT molecule and the isotropic ones for hydrogen atoms and the atoms of propylamine. The weighting scheme was $w=[\sigma^2(|F_o|)+0.0097\,|F_o|^2]^{-1}$. The final R and R_w values became 0.095 and 0.117 for 2957 observed reflections. Considerably high R values may be due to the disordered structure of the solvent molecule. No peaks higher than 0.25 e Å^{-3} were found on the final difference map. The atomic scattering factors were taken from the International Tables for X-ray Crystallography.[7] The computation was carried out on HITAC M-680 computer at the Computer Center of the University of Tokyo.

Results and Discussion

Absorption and Photoacoustic (PA) Spectra of the Colored Species of 1. The crystals of **1** and its inclusion compounds showed no absorption longer than 430 nm in the dark. After irradiation for a few minutes, the color of **1**, **5**, and chloroform solvate turned red. The absorption spectrum of **1** obtained by an opal-glass transmission method after irradiation is shown in Fig. 1(a). The absorption spectrum of the crystals of **5** obtained by irradiation in a KBr pellet is shown in Fig. 1(b). Irradiation of the chloroform solvate gave a spectrum similar to that of **5**. The absorption maxima around 510 and 730 nm for the colored species from **1** are considered to be shifted to slightly longer and shorter wavelengths, respectively, by inclusion of solvent molecules.

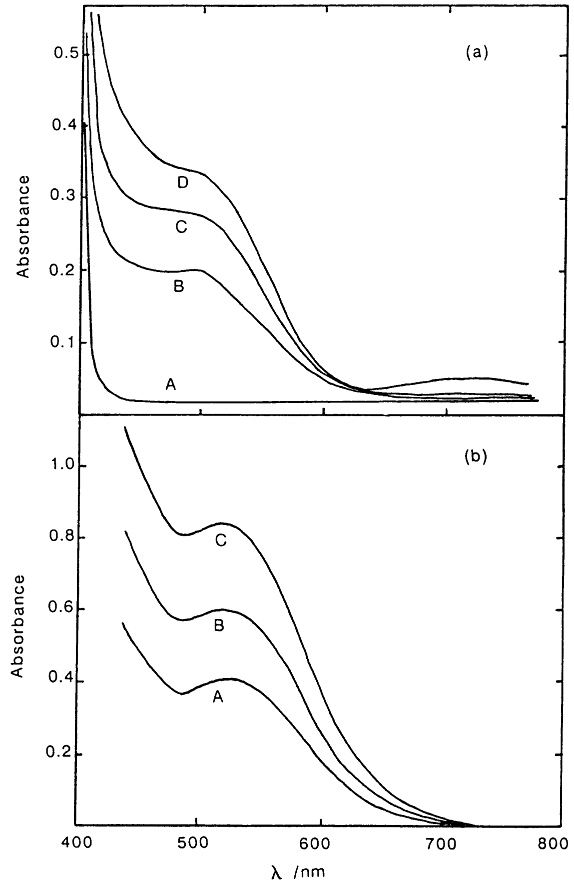


Fig. 1. Variation of absorption spectrum after repeated irradiations. (a) crystal of **1** measured by an opal-glass transmission method (A: before irradiation, B: 1 min, C: 3 min, D: 20 min) (b) acetone solvate (**5**) in a KBr pellet (A: 1 min, B: 4 min, C: 20 min).

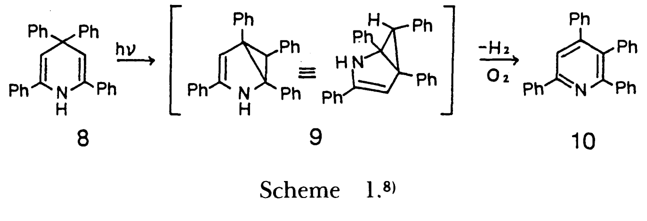
The PA spectrum of **1** after 20 min irradiation showed a broad band around 510 nm and a weaker band around 690 nm. The PA spectrum was similar to the absorption spectrum of **1** obtained after 20 min irradiation shown in Fig. 1(a).

Photochemical Reactions of TPDT. Any recognizable differences between IR spectra of colorless and colored crystals of **1** were not obtained under short-time irradiation. After 2 h irradiation, although the red color still remained, a difference IR spectrum showed a number of new bands indicating occurrence of photochemical reactions. In order to identify the photoproducts, preparative photolysis of **1** was carried out in solutions of benzene or chloroform. On the photolysis of **1** (150 mg) in benzene, the irradiation was stopped after 5 h even **1** still remained, because much longer irradiation afforded dark oily products. In the reaction mixture six products were detected by TLC besides unreacted **1**. Chromatographically two products, 2,4,6-triphenyl-1,3,5-triazine **6** (3 mg) and 2,4,5-triphenylimidazole **7** (5 mg) were isolated and 69 mg of **1** was recovered. Irradiation of **1** in chloroform gave a similar result. After **1** was almost consumed **6** and **7** were isolated in very low yields with a larger amount of dark oily products.

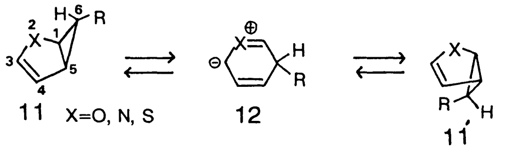
The bands appeared at 1520, 1370, 759, and 690 cm^{-1} in the difference IR spectrum between before and after irradiation of **1** were compared with both of the IR spectrum of the photoproducts **6** and **7**. The bands coinciding with that of **6** indicated the formation of **6** under the solid state photolysis. Although bands assignable to **7** were not found in the difference IR spectrum, after the extraction of the irradiated pellet with benzene **7** was detected by TLC.

In order to obtain the relationship between photocoloration and photoreaction products in the solid state, photolysis of **3** was also carried out. Neither photocoloration nor recognizable differences between IR spectra before and after irradiation (5 h) were found. By extraction of the irradiated pellet with benzene, however, **7** was detected by TLC. The facts indicated that the two types of hydrogen bonds[3] in **3** inhibit both of photocoloration and photoformation of **6**. In connection with the photolysis in the solid state an ethanol solution of **1** (56 mg) was irradiated until **1** was almost consumed. Only one product **7** was detected by TLC and 8 mg of **7** was isolated.

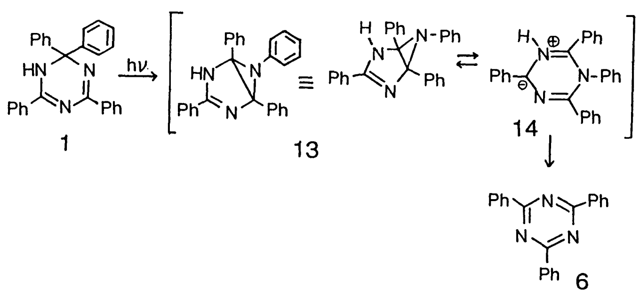
Previously one of the authors reported that irradiation of 2,4,4,6-tetraphenyl-1,4-dihydropyridine (**8**) exhibits photocoloration in deaerated solutions or in the solid state and after a long-time irradiation in solutions 2,3,4,6-tetraphenylpyridine (**10**) was produced. As is shown in Scheme 1 a di-π-methane rearrangement to give 1,3,5,6-tetraphenyl-2-azabicyclo[3.1.0]hex-3-ene (**9**) has been suggested as the unisolable intermediate.[8]



Scheme 1.[8]

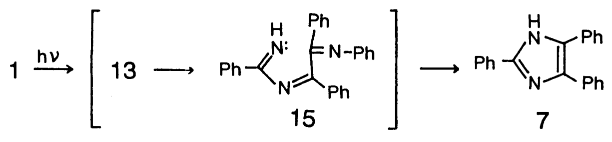


Scheme 2.[10]



Scheme 3.

TPDT has aza-di-π-methane moiety in the molecule, and on the photolysis of **1** occurrence of an aza-di-π-methane rearrangement to give a bicyclic intermediate, 1,3,5,6-tetraphenyl-2,4,6-triazabicyclo[3.1.0]hex-3-ene (**13**), similar to **9** is assumed. Presently carbonyl ylides and azomethine ylides which are the ring-opening products of oxetane and aziridine, respectively, are attracting considerable interest.[9] Furthermore the 1,5-electrocyclic ring-opening reactions of the bicyclic heterocycles such as homofuran, homopyrrole, and homothiophene are shown to lead to ylide intermediates **12**[10] as is shown in Scheme 2. Photochromic reactions involving these types of ylides or zwitter ions as the colored species have been also reported.[11] As is shown in Scheme 3 as one of the possible candidates of the photocolored species an azomethine ylide type intermediate **14** is postulated, which is formed from **13** by cleavage of the central bond C^1-C^5 in aziridine, as required for the electrocyclic process. IR spectrum of TPDT exhibits two C=N stretching bands at 1610 and 1680 cm^{-1} assignable to 2,3-dihydro- and 2,5-dihydro forms of the dihydrotriazine ring respectively.[2] As the bicyclic intermediate **13** containing an imidazoline ring is produced successfully, appearance of another C=N stretching band around 1650 cm^{-1} is postulated.[12] The difference FT-IR spectrum obtained by the reflection method between before and after irradiation of fine crystals of **1** exhibited a weak band at 1655 cm^{-1}, as it was expected, besides the two characteristic C=N stretching bands in TPDT. This observation supports partially the reaction course shown in Scheme 3. Furthermore, broad bands appeared in the FT-IR spectrum on the range of 2400—3300 cm^{-1} obtained after irradiation suggested involvement of **14** in the photocoloration. It is reasonable to consider that the back reaction from **13** to **1** is not possible and the photochemical color change of **1** is not reversible. Conversion of the colored intermediate **14** into **6** stabilized by its resonance energy is postulated (Scheme 3). The formation of trace amount of **7** can be explained by cleavage of one of the peripheral aziridine bonds C^1-N^6 or C^5-N^6 in **13** followed by intramolecular nucleophilic addition of the nitrogen lone pair to the heterodiene system as is shown in Scheme 4.



Scheme 4.

Table 2. Final Atomic Coordinates (×10^4) and Equivalent Thermal Parameters$^{a)}$ for Non-Hydrogen Atoms of **1**

Atom	x	y	z	B_{eq}/Å^2
N(1)	1802(2)	1547(2)	11724(2)	4.5
C(2)	1819(2)	2418(2)	10969(2)	4.1
N(3)	2620(2)	2212(2)	10238(2)	4.3
C(4)	3532(2)	1779(2)	10627(2)	3.5
N(5)	3629(2)	1319(2)	11559(2)	4.1
C(6)	2695(2)	1121(2)	11994(2)	3.7
C(7)	2746(2)	285(2)	12817(2)	4.1
C(8)	3697(3)	−15(3)	13338(2)	5.4
C(9)	3728(4)	−810(3)	14087(3)	6.8
C(10)	2827(4)	−1321(3)	14294(3)	7.3
C(11)	1895(4)	−1043(3)	13774(3)	6.4
C(12)	1840(3)	−231(2)	13044(2)	5.1
C(13)	4411(2)	1772(2)	9954(2)	3.5
C(14)	4368(2)	2284(3)	8977(2)	4.8
C(15)	5191(3)	2240(3)	8357(3)	5.5
C(16)	6068(2)	1682(3)	8688(3)	4.8
C(17)	6132(2)	1174(2)	9650(3)	4.9
C(18)	5313(2)	1220(2)	10280(2)	4.4
C(19)	782(2)	2482(2)	10275(2)	4.3
C(20)	569(2)	3355(3)	9647(3)	5.2
C(21)	−326(3)	3390(3)	8937(3)	6.4
C(22)	−1004(3)	2559(3)	8864(3)	6.2
C(23)	−804(3)	1702(3)	9488(3)	6.4
C(24)	86(2)	1652(3)	10193(3)	5.3
C(25)	2042(2)	3429(2)	11604(2)	4.2
C(26)	2793(3)	4139(3)	11376(3)	5.6
C(27)	2966(3)	5039(3)	11953(3)	6.7
C(28)	2379(3)	5242(3)	12801(3)	7.1
C(29)	1616(3)	4544(3)	13040(3)	6.4
C(30)	1446(3)	3649(3)	12447(3)	5.3

a) $B_{eq}=\frac{4}{3}\sum_i\sum_j B_{ij}a_ia_j$.

On the photolysis of **3**, in which TPDT molecule connected with solvent molecules alternatively to form a helix structure by two types of hydrogen bonds at N(3)-H and N(5),[3] even if the aza-di-π-methane rearrangement should give the bicyclic intermediate **13** successfully, the following ring-opening process to give **14** should be prohibited by the helical structure. Only small amount of **13** probably transforms into **7** in the same fashion shown in Scheme 4.

Molecular and Crystal Structures. The final atomic coordinates and equivalent isotropic temperature factors for non-hydrogen atoms in **1** and **2** are given in Tables 2 and 3 respectively.** Selected bond distan-

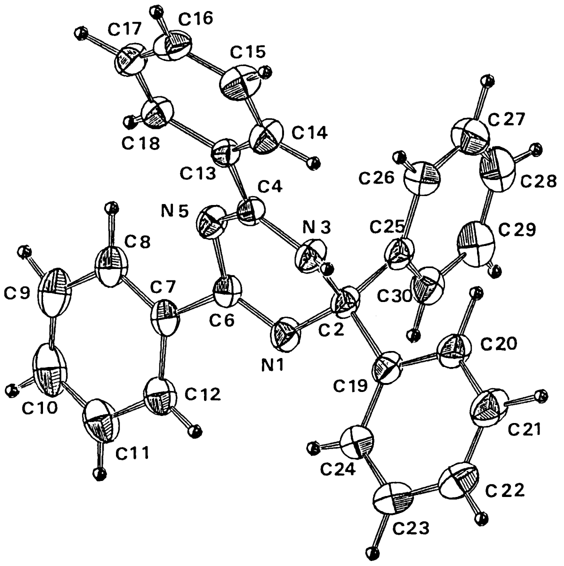


Fig. 2. ORTEP[13] plot of TPDT molecule in **1** with the atom-numbering. The anisotropic ellipsoids for non-hydrogen atoms enclose 30% probability.

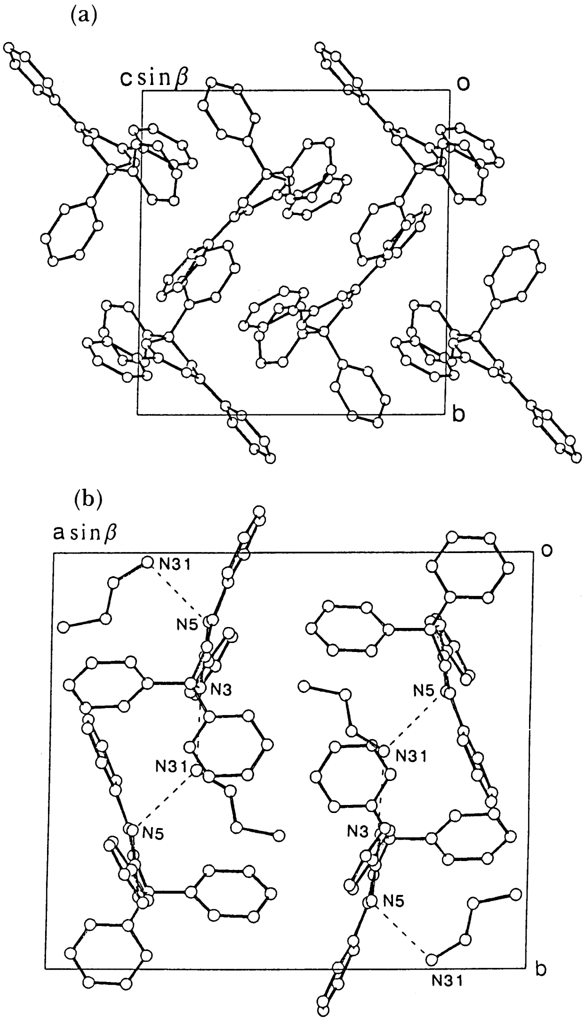


Fig. 3. Crystal structures of **1** and **2**. (a) Viewed along the a axis of **1**. (b) Viewed along the c axis of **2**. The atoms of the solvent molecules with prime or double prime are suppressed for clarity.

** 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. 8899).

Table 3. Final Atomic Coordinates (×10⁴) and Equivalent Thermal Parameters[a] for Non-Hydrogen Atoms of Propylamine Solvate (**5**)[b]

Atom	x	y	z	B[c] or $B_{\mathrm{eq}}/\text{Å}^2$	Atom	x	y	z	B[c] or $B_{\mathrm{eq}}/\text{Å}^2$
N(1)	1780(2)	2737(2)	12616(3)	4.1	C(22)	4632(3)	1829(4)	13291(5)	6.4
C(2)	2107(2)	1861(3)	12216(3)	4.0	C(23)	4172(3)	2355(4)	13956(5)	6.8
N(3)	1906(2)	1755(2)	10820(3)	4.1	C(24)	3351(3)	2374(3)	13600(4)	5.3
C(4)	1819(2)	2506(3)	10090(3)	4.0	C(25)	1706(3)	1068(3)	12840(3)	4.6
N(5)	1752(2)	3349(2)	10518(3)	4.5	C(26)	2102(3)	331(4)	13456(6)	8.1
C(6)	1676(2)	3390(3)	11798(3)	3.7	C(27)	1693(5)	−362(5)	14001(9)	11.5
C(7)	1376(2)	4308(3)	12192(4)	4.2	C(28)	904(5)	−326(6)	13942(7)	9.7
C(8)	1067(3)	4960(3)	11308(4)	5.7	C(29)	512(4)	385(5)	13360(6)	8.3
C(9)	763(4)	5785(4)	11665(6)	7.8	C(30)	910(3)	1087(4)	12811(4)	5.9
C(10)	777(4)	5991(4)	12922(6)	7.9	N(31)	8047(6)	222(7)	−167(9)	5.1(2)
C(11)	1076(3)	5359(4)	13814(5)	7.1	C(32)	8749(10)	708(14)	524(16)	10.9(6)
C(12)	1387(3)	4528(3)	13468(4)	5.4	C(33)	8893(10)	1580(14)	−254(25)	15.9(9)
C(13)	1749(3)	2385(3)	8674(4)	4.8	C(34)	9772(9)	1786(12)	−204(16)	8.4(4)
C(14)	2105(4)	1665(4)	8130(5)	7.8	N(31′)	8096(7)	375(9)	−498(12)	7.0(3)
C(15)	2001(5)	1608(6)	6777(5)	10.9	C(32′)	8722(12)	583(13)	593(17)	14.4(8)
C(16)	1604(4)	2280(6)	6043(5)	9.3	C(33′)	9038(8)	1576(9)	424(13)	6.4(3)
C(17)	1274(4)	2978(5)	6589(4)	8.3	C(34′)	9415(18)	1573(19)	−816(21)	16.0(9)
C(18)	1341(3)	3066(4)	7898(4)	6.4	N(31″)	8214(7)	153(9)	462(12)	7.4(3)
C(19)	2996(2)	1863(3)	12578(3)	4.0	C(32″)	8806(8)	545(10)	−272(13)	7.1(3)
C(20)	3476(3)	1320(4)	11942(5)	6.4	C(33″)	9138(18)	1500(15)	135(27)	19.1(12)
C(21)	4288(3)	1281(5)	12308(6)	7.6	C(34″)	9740(11)	1737(12)	−781(18)	9.2(5)

a) $B_{\mathrm{eq}}=\frac{4}{3}\sum_i\sum_j B_{ij}a_ia_j$. b) All the occupancy factors for the three propylamine molecules, N(31)-C(34), N(31′)-C(34′) and N(31″)-C(34″), are fixed to be 0.33333. c) For the atoms of propylamine isotropic temperature factors are listed instead of B_{eq}.

Table 4. Selected Bond Distances (l/Å) and Angles (ϕ/°) for **1**—**5**

	1	**2**	**3**[a]	**4**[b]	**5**[b]
N(1)-C(2)	1.466(4)	1.464(5)	1.465(3)	1.453(4)	1.460(4)
C(2)-N(3)	1.468(4)	1.481(5)	1.481(3)	1.488(4)	1.474(4)
N(3)-C(4)	1.346(3)	1.323(5)	1.336(3)	1.327(4)	1.329(4)
C(4)-N(5)	1.311(3)	1.303(5)	1.312(3)	1.314(4)	1.299(4)
N(5)-C(6)	1.389(3)	1.386(5)	1.396(3)	1.387(4)	1.393(4)
C(6)-N(1)	1.287(3)	1.273(5)	1.278(3)	1.282(4)	1.274(4)
C(2)-C(19)	1.529(4)	1.519(6)	1.537(4)	1.530(5)	1.535(4)
C(2)-C(25)	1.535(4)	1.529(6)	1.527(4)	1.540(5)	1.544(4)
C(4)-C(13)	1.475(3)	1.501(6)	1.490(4)	1.486(4)	1.489(4)
C(6)-C(7)	1.488(4)	1.495(5)	1.490(4)	1.489(5)	1.493(4)
N(1)-C(2)-N(3)	109.1(2)	109.6(3)	109.2(2)	110.1(2)	110.4(2)
C(2)-N(3)-C(4)	118.7(2)	119.6(3)	119.5(2)	119.4(3)	121.6(3)
N(3)-C(4)-N(5)	121.3(2)	124.0(4)	122.0(2)	123.1(3)	123.0(3)
C(4)-N(5)-C(6)	114.9(2)	114.1(1)	114.6(2)	115.0(3)	114.9(2)
N(5)-C(6)-N(1)	126.9(2)	128.0(4)	127.2(2)	126.4(3)	127.7(3)
C(6)-N(1)-C(2)	115.2(2)	117.1(3)	116.2(2)	117.9(3)	117.8(2)

a) Ref. 3. b) Ref. 4.

ces and angles of **1** and **2** are listed in Table 4, together with those of **3**, **4**, and **5**, and some torsion angles and dihedral angles are in Table 5. Figure 2 shows the molecular structure of TPDT with the atom numbering in the crystal of **1**. For **2** the same numbering scheme is used. The molecular structure of TPDT in **1** and **2** is similar to that in **3**, **4**, or **5**. During the refinements the difference maps showed that a hydrogen atom is bound to N(3), not N(5), that is, TPDT exists in 2,3-dihydro (a) form in both **1** and **2**, as it does in **3**, **4**, or **5**. However, the differences between N(3)-C(4) and C(4)-N(5) were found to be rather small in both **1** and **2**, as was reported for the other three inclusion compounds.[3,4] The bond distance of N(3)-C(4) for the five crystals **1**—**5** (1.323—1.346 Å) is similar to a typical C-N distance of six-membered N-containing aromatic rings. The sums of bond angles around N(3) are 359 and 360° for **1** and **2** respectively, that is, N(3) is planar rather than pyramidal. These results suggest that lone pair electrons on N(3) is effectively conjugated with the π system of C(4)=N(5)-C(6)=N(1). Further inspection of Table 4 reveals that

Table 5. Some Torsion Angles (ϕ/°) and Dihedral Angles (ϕ/°)[a] for **1** and **2**

	1	**2**
N(3)-C(4)-C(13)-C(14)	6.4(4)	−30.2(7)
N(5)-C(6)-C(7)-C(8)	19.8(4)	11.9(6)
N(3)-C(4)-N(5)-C(6)	13.0(3)	−8.0(6)
C(4)-N(5)-C(6)-N(1)	−18.0(4)	11.3(6)
N(5)-C(6)-N(1)-C(2)	−7.8(4)	7.9(6)
[1][a]	53.7(1)	77.4(2)
[2][a]	86.5(1)	78.9(2)
[3][a]	32.2(3)	24.8(4)
[4][a]	12.7(3)	7.7(4)

a) [1]: the dihedral angle between the least-squares plane of N(1), N(3), C(4), and N(6) (plane A) and the least-squares plane of C(19)-C(24). [2]: the dihedral angle between plane A and the least-squares plane of C(25)-C(30). [3]: the dihedral angle between plane A and the plane of N(1), C(2), and N(3). [4]: the dihedral angle between plane A and the plane of C(4), N(5), and C(6).

the bond distance of N(3)-C(4) in **2** is shorter than that in **1**. The corresponding bond distance in **3**, **4**, or **5** is also slightly shorter than that in **1**, suggesting that the hydrogen bond involving N(3) has an effect on N(3)-C(4) bond. The shortening of N(3)-C(4) tends to enlarge N(3)-C(4)-N(5) bond angle in **2**—**5**. The bond distance of C(4)-C(13) in **2** is larger than that in **1**, which may also result from the shortening of N(3)-C(4). No other significant differences in bond distances or angles were observed for the five crystals **1**—**5**. 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 reported in **3**, **4**, or **5**. The torsion angles of N(3)-C(4)-N(5)-C(6) and C(4)-N(5)-C(6)-N(1) in **2** are smaller than the corresponding angles in **1** respectively, indicating that the N(3)-C(4)-N(5)-C(6)-N(1) system in **2** is more planar than that in **1**. The torsion angles of N(5)-C(6)-C(7)-C(8) and N(3)-C(4)-C(13)-C(14) and the dihedral angles between the plane composed of N(1), N(3), C(4), and C(6) and that composed of the phenyl ring C(19)-C(24) or that composed of the ring C(25)-C(30) in **1** and **2** are similar to the corresponding angles in **3**, **4**, or **5**: the two phenyl rings at 4- and 6-positions are nearly coplanar with the dihydrotriazine ring, while the two at 2-position are almost perpendicular to it.

Figure 3 shows the crystal structures of **1** and **2**. In **2** the nitrogen atom of the propylamine is involved in two types of hydrogen bond: N(3)-H(3)···N(31) and N(5)···H-N(31). The distances of N(3)···N(31), N(3)···N(31′), and N(3)···N(31″) are 2.92(1), 3.07(1), and 3.05(1) Å respectively. The distances of N(5)···N(31) [3.18(1) Å], N(5)···N(31′) [3.25(1) Å], and N(5)···N(31″)[3.31(1) Å] are slightly longer. By these hydrogen bonds TPDT and the solvent molecules are alternately connected to form a ribbon-like structure along the two-fold screw axis, as is shown in Fig. 3(b). This hydrogen bonding scheme was also seen in **3** and **4**, where oxygen atoms of the solvent molecules were involved in the hydrogen bonds. No other short contacts were found between TPDT and the solvent molecules in **2**, which seemed to allow the solvent molecules to take a disordered structure. In **1** there are no unusually short contacts. Thus, comparison of crystal structures of **1**—**5** revealed that the hydrogen bonding scheme constructing the ribbon-like structure is characteristic of **2**, **3**, and **4**, which are photostable. On the other hand in **1** and **5**, which exhibit photocoloration, each TPDT molecule is isolated. It is, therefore, confirmed that the hydrogen bonds observed in **2**, **3**, and **4** inhibit the photocoloration of the crystals.

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