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Structure of 2,2,4,6-Tetraphenyldihydro-1,3,5-triazine Ethanol Solvate

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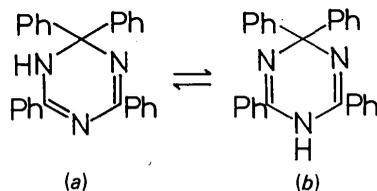
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Abstract. $C_{27}H_{21}N_3 \cdot C_2H_6O$, $M_r = 433.5$, monoclinic, $P2_1/a$, $a = 16.670$ (1), $b = 13.5270$ (8), $c = 10.7697$ (7) Å, $\beta = 100.520$ (8)°, $V = 2387.7$ (3) Å³, $Z = 4$, $D_x = 1.206$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54184$ Å, $\mu = 5.03$ cm⁻¹, $F(000) = 920$, $T = 293$ K, $R = 0.071$ for 3322 observed reflections. 2,2,4,6-Tetraphenyldihydro-1,3,5-triazine exists in the 2,3-dihydro form, one of the two possible tautomers. The triazine and ethanol molecules are connected alternately by N(3)–H...O and N(5)...H–O hydrogen bonds to form a ribbon along the b axis, which seems to be responsible for the fact that this inclusion compound does not show photocoloration, unlike the inclusion compounds composed of acetone or tetrahydrofuran.

Introduction. 2,2,4,6-Tetraphenyldihydro-1,3,5-triazine was reported to exhibit photochromism in the solid state (Lottermoser, 1896) but the structure of the colored species has not been determined. Previously, one of the authors reported that the triazine exists in an equilibrium mixture of 2,3-dihydro (*a*) and 2,5-dihydro (*b*) forms, which are prototropic tautomers, in solution and in the solid state (Maeda, Kihara & Ishimura, 1985). Recently we found that the triazine formed crystalline inclusion compounds with various solvent molecules with a molar ratio of 1:1 on recrystallization. For acetone, chloroform, and tetrahydrofuran the colorless inclusion compounds turned red on exposure to UV light and the red color faded gradually in the dark, while the inclusion compounds composed of ethanol or 2-propanol showed no color change even

under prolonged irradiation. In order to clarify a relationship between structure and photocoloration for both types of inclusion compound, we have determined the molecular and crystal structure of the title compound.



Experimental. The triazine was synthesized by the method of Lottermoser (1896). Colorless plate-like crystals from an ethanol solution; systematic absences: $h0l$ $h = 2n + 1$, $0k0$ $k = 2n + 1$; crystal dimensions $0.3 \times 0.2 \times 0.5$ mm, sealed in a glass capillary, Rigaku AFC-4 diffractometer, graphite monochromator; cell parameters refined by least squares on the basis of 16 independent 2θ values, Cu $K\alpha$ radiation ($45 < 2\theta < 59^\circ$); intensity measurement performed up to $2\theta = 125^\circ$ ($h = -21$ to 21 , $k = 0$ to 16 , $l = 0$ to 14); ω - 2θ scan technique, scan speed 4° min^{-1} in θ , scan width $(1.0 + 0.15 \tan \theta)^\circ$; background 5 s before and after each scan; three standard reflections (460, $\bar{9}21$, 006) monitored every 50 reflections, no significant variation in intensities; 3823 reflections measured, 3322 with $|F_o| > 3\sigma(|F_o|)$ considered as observed and used for structure determination; corrections for Lorentz and polarization effects, absorption ignored; direct methods (MULTAN78, Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and subsequent difference

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Table 1. Final atomic coordinates ($\times 10^4$) with their e.s.d.'s and equivalent isotropic thermal parameters, B_{eq} (\AA^2), for non-H atoms

$B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i \cdot a_j$. Occupancy factors for O(31)–C(32)–C(33) and O(31')–C(32')–C(33') are 0.58 and 0.42, respectively.

	x	y	z	B_{eq}
N(1)	6695 (1)	2659 (2)	7493 (2)	3.4
C(2)	6999 (2)	1717 (2)	7095 (2)	3.3
N(3)	6748 (1)	1612 (2)	5709 (2)	3.4
C(4)	6712 (2)	2413 (2)	4975 (2)	3.4
N(5)	6738 (1)	3312 (2)	5439 (2)	3.7
C(6)	6637 (2)	3366 (2)	6695 (2)	3.2
C(7)	6413 (2)	4365 (2)	7105 (3)	3.6
C(8)	6072 (2)	5068 (2)	6217 (3)	4.7
C(9)	5831 (2)	5987 (2)	6613 (4)	6.2
C(10)	5942 (3)	6200 (3)	7878 (4)	6.7
C(11)	6282 (2)	5519 (3)	8766 (4)	6.3
C(12)	6515 (2)	4599 (2)	8375 (3)	4.8
C(13)	6611 (2)	2301 (2)	3578 (2)	3.8
C(14)	6817 (2)	1455 (3)	3010 (3)	5.2
C(15)	6713 (3)	1407 (3)	1695 (3)	6.4
C(16)	6406 (2)	2188 (3)	959 (3)	6.2
C(17)	6196 (2)	3036 (3)	1537 (3)	6.2
C(18)	6296 (2)	3092 (2)	2824 (3)	5.0
C(19)	7935 (2)	1719 (2)	7456 (2)	3.3
C(20)	8320 (2)	2263 (2)	8465 (3)	4.6
C(21)	9169 (2)	2251 (3)	8800 (3)	5.4
C(22)	9628 (2)	1713 (3)	8139 (3)	5.0
C(23)	9247 (2)	1153 (3)	7146 (4)	6.7
C(24)	8407 (2)	1163 (3)	6801 (3)	5.9
C(25)	6605 (2)	877 (2)	7717 (2)	3.6
C(26)	5791 (2)	954 (2)	7798 (3)	4.9
C(27)	5390 (2)	211 (3)	8312 (4)	6.6
C(28)	5798 (3)	-625 (3)	8758 (4)	7.5
C(29)	6604 (3)	-702 (3)	8709 (4)	7.8
C(30)	7007 (2)	39 (3)	8178 (3)	5.6
O(31)	3047 (4)	379 (6)	5056 (10)	4.7
C(32)	3760 (5)	890 (9)	5673 (8)	7.8
C(33)	4103 (10)	1482 (11)	4704 (13)	11.5
O(31')	3029 (8)	610 (11)	4821 (12)	5.7
C(32')	3606 (6)	1399 (7)	4891 (22)	8.5
C(33')	4420 (5)	972 (14)	4745 (19)	8.6

Table 2. Selected bond distances (\AA) and angles ($^\circ$)

N(1)–C(2)	1.465 (3)	N(3)–C(4)	1.336 (3)
N(1)–C(6)	1.278 (3)	C(4)–N(5)	1.312 (3)
C(2)–N(3)	1.481 (3)	C(4)–C(13)	1.490 (4)
C(2)–C(19)	1.537 (4)	N(5)–C(6)	1.396 (3)
C(2)–C(25)	1.527 (4)	C(6)–C(7)	1.490 (4)
C(2)–N(1)–C(6)	116.2 (2)	N(3)–C(4)–N(5)	122.0 (2)
N(1)–C(2)–N(3)	109.2 (2)	N(3)–C(4)–C(13)	120.0 (2)
N(1)–C(2)–C(19)	108.3 (2)	N(5)–C(4)–C(13)	117.9 (2)
N(1)–C(2)–C(25)	108.6 (2)	C(4)–N(5)–C(6)	114.6 (2)
N(3)–C(2)–C(19)	110.0 (2)	N(1)–C(6)–N(5)	127.2 (2)
N(3)–C(2)–C(25)	107.8 (2)	N(1)–C(6)–C(7)	118.1 (2)
C(19)–C(2)–C(25)	112.8 (2)	N(5)–C(6)–C(7)	114.6 (2)
C(2)–N(3)–C(4)	119.5 (2)		

Fourier map calculations, full-matrix least squares (*SHELX76*, Sheldrick, 1976) with anisotropic thermal parameters for non-H atoms and isotropic ones for H atoms, the atoms of ethanol disordered between two sets of positions, treated as rigid molecules with usual geometry (C–C 1.510, C–O 1.430 \AA , C–C–O 108.0 $^\circ$), occupancy factors refined to 0.58 (2) and 0.42 (2), some H atoms located on difference Fourier map, other H-atom positions obtained geometrically, but no H atoms of ethanol included in the refinements, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = [\sigma^2(|F_o|) + 0.0040|F_o|^2]^{-1}$; final $R = 0.071$ and $wR = 0.084$ for 3322 observed reflections; $(\Delta/\sigma)_{\max} = 0.09$ for the triazine; final difference map showed $|\Delta\rho| \leq 0.3 \text{ e } \text{\AA}^{-3}$;

atomic scattering factors from *International Tables for X-ray Crystallography* (1974); calculations carried out on a HITAC M-280 computer at the Computer Center of the University of Tokyo.

Discussion. Atomic coordinates of non-H atoms are listed in Table 1.* Fig. 1 shows the molecular structure with the atom numbering. Selected bond distances and angles are listed in Table 2. The bond distances and angles for the ethanol molecules are omitted.

The dihydrotriazine was found to exist in the 2,3-dihydro form in crystals, which is one of the possible tautomers. The dihydrotriazine ring is in the boat conformation with C(2) and N(5) as the apexes. The dihedral angles between the least-squares plane of N(1), C(6), C(4) and N(3), and the planes N(1)–C(2)–N(3) and C(4)–N(5)–C(6) are 28.9 (2) and 11.5 (3) $^\circ$, respectively. The torsion angles of N(5)–C(6)–C(7)–C(8) and N(5)–C(4)–C(13)–C(18) are 20.3 (4) and -20.1 (4) $^\circ$, respectively. The two phenyl rings at the 2-position are almost perpendicular to the plane composed of N(1), C(6), C(4) and N(3): the dihedral angles are 96.4 (1) and 73.9 (1) $^\circ$. The significant difference between C(6)–N(1) and C(4)–N(3) indicates that N(1) and N(3) are non-equivalent in the crystalline state. The bond distance of C(6)–N(1) [1.278 (3) \AA] corresponds to a localized C=N double bond. It is consistent with the result that the H atom is bound not to N(1) but to N(3).

Fig. 2 shows the crystal structure. The ethanol molecules, which are surrounded by phenyl rings and

* Lists of anisotropic thermal parameters for non-H atoms, positional and thermal parameters for H atoms, bond distances and angles and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44629 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

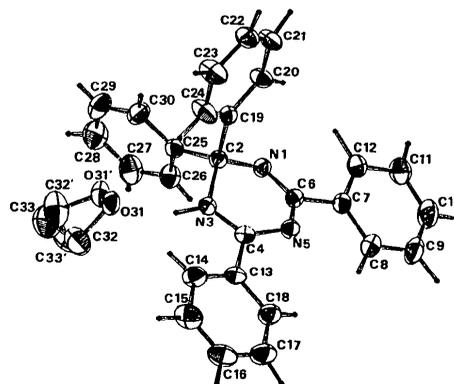


Fig. 1. ORTEP plot (Johnson, 1965) of the title compound with the numbering scheme. H atoms are shown as spheres of 0.05 \AA radius and the anisotropic ellipsoids enclose 30% probability.

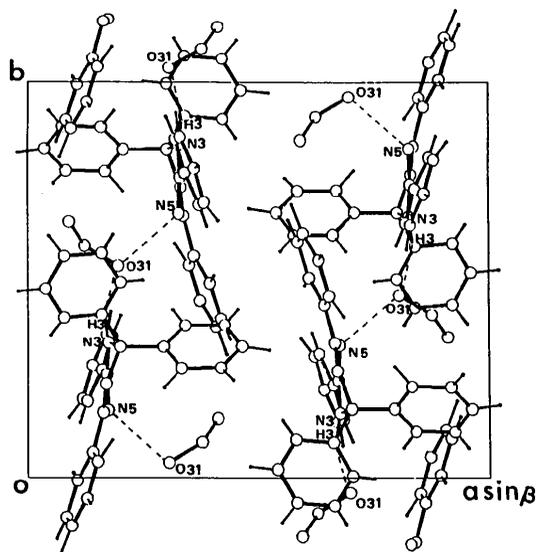


Fig. 2. Crystal structure viewed along the *c* axis. The hydrogen bonds are indicated by broken lines. The ethanol molecule with the lower occupancy factors is omitted.

triazine rings, are disordered. The triazine and ethanol molecules are alternately connected to form a ribbon along the *b* axis by the two types of intermolecular hydrogen bond: N(5)···H—O(31) and N(3)—H···O(31). The distances of N(5)···O(31), N(3)···O(31), N(5)···O(31'), and N(3)···O(31') are 2.90 (1),

2.86 (1), 2.78 (2), and 3.01 (3) Å, respectively. Except for the hydrogen bonds, there are no intermolecular distances less than the van der Waals distances. N(3) serves as a hydrogen-bond donor and H(3) is in the direction of the O atom of the ethanol [N(3)—H···O(31) = 157 (3), N(3)—H···O(31') = 155 (3)°], while N(5) serves as a hydrogen-bond acceptor. This hydrogen-bonding scheme suggests that the H atom could be partially bound to N(5). Although the mechanism of the photocoloration is still not clarified after the determination of the structure of the title compound, it could be proposed that the hydrogen-bonding scheme may inhibit the photocoloration for this inclusion compound.

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Structure of Naphtho[1,8-*de*][1,2]oxathiepin 3-Oxide

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Abstract. C₁₂H₁₀O₂S, *M_r* = 218.28, orthorhombic, *Pna*2₁, *a* = 11.574 (4), *b* = 5.794 (2), *c* = 30.128 (8) Å, *V* = 2020.4 Å³, *Z* = 8, *D_x* = 1.435 Mg m⁻³, λ(Mo Kα) = 0.71069 Å, μ = 0.28 mm⁻¹, *F*(000) = 912, *T* = 295 K, *R* = 0.035 and *wR* = 0.040 for 1442 observed reflections. The two molecules in the asymmetric unit are almost centrosymmetrically related. The —O—SO— group is incorporated in a seven-membered-ring system bridging the naphthalene moiety. The S=O bonds are 1.463 (3) and

1.485 (3) Å while the two intracyclic S—O bonds are 1.602 (3) and 1.610 (3) Å. For both molecules the three bond angles involving the S atom are in the range 98.7 (2) to 109.5 (2)°.

Introduction. The sulfinate functional group in a ring system was first reported by Baumann & Walter (1893) although to our knowledge its structure has never been verified. It was nearly 80 years before the next examples appeared by way of a thermolysis reaction (Dittmer,