

Structure of 2,4,4,6-Tetraphenyl-3,4(1,4)-dihydropyrimidine 2-Propanol Solvate

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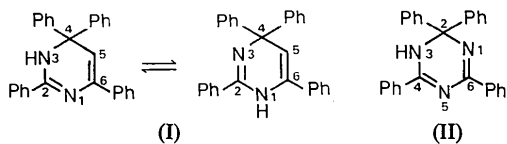
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(Received 25 October 1990; accepted 4 January 1991)

Abstract. $C_{28}H_{22}N_2 \cdot C_3H_8O$, $M_r = 446.6$, monoclinic, $C2/c$, $a = 21.894$ (9), $b = 13.547$ (1), $c = 21.133$ (4) Å, $\beta = 125.68$ (1)°, $V = 5091$ (2) Å³, $Z = 8$, $D_x = 1.165$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54184$ Å, $\mu = 4.72$ cm⁻¹, $F(000) = 1904$, $T = 293$ K, $R = 0.068$ for 2241 observed reflections. 2,4,4,6-Tetraphenyldihydropyrimidine (I) exists in the 3,4-dihydro form in the crystal. The crystal structure is isomorphous with that of 2,2,4,6-tetraphenyldihydro-1,3,5-triazine 2-propanol solvate. The pyrimidine and 2-propanol molecules are connected alternately by $N(1)\cdots H-O$ and $N(3)-H\cdots O$ hydrogen bonds to construct a ribbon-like structure around the 2₁ axis.

Introduction. Previously we reported the crystal structures and photochemical behavior of 2,2,4,6-tetraphenyldihydro-1,3,5-triazine (II) and its solvated crystals (Mori, Ohashi & Maeda, 1988, 1989). On the basis of the X-ray and photochemical studies, it was clarified that hydrogen bonds which alternately connected the triazine and the solvent molecules inhibit the photocoloration reaction of (II) in the crystals including an alcoholic or amine solvent. To our knowledge this is the first example



for control of photochromic property in the solid state by hydrogen bonds. As one of the candidates which were expected to show a similar relationship between the hydrogen-bonding scheme in the crystal and solid-state photochemical behavior, we have synthesized 2,4,4,6-tetraphenyl-3,4(1,4)-dihydropyrimidine (I). (I) showed photocoloration both in solution and in the solid state. Furthermore, (I) formed

crystals including ethanol or 2-propanol on recrystallization. However, in contrast to the case of (II), the crystals including an alcoholic solvent did show photocoloration which was similar to that of the unsolvated crystal. In order to compare the structures of (I) and (II) and to clarify what makes the difference in photochemical behavior in the solid state between the two heterocycles, the crystal structure of (I) 2-propanol solvate was determined.

Experimental. (I) was synthesized by the method of van der Stoep & van der Plas (1979) for the preparation of 4,4,6-triphenyldihydropyrimidine from 2,4,6-triphenylpyrimidine. Colorless plate-like crystals from a 2-propanol solution; crystal dimensions 0.5 × 0.2 × 0.1 mm, sealed in a glass capillary, Rigaku AFC-4 diffractometer, graphite-monochromated Cu $K\alpha$ radiation; cell parameters refined by least squares on the basis of 18 independent 2θ values ($44 < 2\theta < 55^\circ$); intensity measurement performed up to $2\theta = 125^\circ$ ($h - 26 \rightarrow 26$, $k - 15 \rightarrow 0$, $l 0 \rightarrow 25$); ω - 2θ scan technique, scan speed 2° min^{-1} in θ , scan width $(1.0 + 0.15 \tan \theta)^\circ$, background 5 s before and after each scan; three standard reflections (067 , 1028 , 028) monitored every 50 reflections, no significant variation in intensities; 4073 reflections measured, 2248 with $|F_o| > 5\sigma(|F_o|)$ considered observed and used for structure determination; corrections for Lorentz and polarization effects, absorption ignored. Direct methods (*MULTAN*78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and subsequent difference Fourier map calculations, full-matrix least squares (*SHELX*76; Sheldrick, 1976) with anisotropic thermal parameters for non-H atoms and isotropic ones for H atoms; some H atoms located on difference Fourier map, other H-atom positions obtained geometrically; one of two methyl groups in 2-propanol molecule disordered between two positions, the occupancy factors fixed to 0.8 and 0.2, the two methyl groups with occupancy factors of 1.0 and

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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

$$B_{\text{eq}} = (4/3) \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}/B
N(1)	6658 (2)	2984 (3)	1782 (2)	4.0
C(2)	6952 (2)	3832 (3)	1788 (2)	3.7
N(3)	6686 (2)	4709 (3)	1806 (2)	3.9
C(4)	6159 (2)	4821 (3)	2019 (2)	3.8
C(5)	5716 (2)	3881 (3)	1786 (2)	4.2
C(6)	5974 (2)	3033 (3)	1705 (2)	3.7
C(7)	7591 (2)	3800 (3)	1723 (2)	4.0
C(8)	7644 (3)	3018 (4)	1324 (3)	4.8
C(9)	8232 (3)	2970 (4)	1262 (3)	5.8
C(10)	8789 (3)	3668 (5)	1615 (4)	6.5
C(11)	8748 (3)	4435 (5)	2013 (3)	6.0
C(12)	8157 (3)	4506 (4)	2067 (3)	4.7
C(13)	5643 (2)	5697 (3)	1557 (2)	4.1
C(14)	5778 (3)	6646 (4)	1857 (3)	6.4
C(15)	5315 (4)	7418 (5)	1406 (3)	7.6
C(16)	4721 (3)	7264 (5)	645 (3)	7.0
C(17)	4586 (3)	6352 (4)	340 (3)	6.0
C(18)	5037 (3)	5568 (4)	784 (3)	5.2
C(19)	6582 (2)	4987 (3)	2901 (3)	4.2
C(20)	7348 (3)	5101 (4)	3395 (3)	5.7
C(21)	7709 (4)	5199 (5)	4190 (3)	7.2
C(22)	7330 (4)	5195 (5)	4502 (4)	7.2
C(23)	6560 (5)	5120 (6)	4016 (4)	8.7
C(24)	6198 (3)	5017 (5)	3228 (3)	7.1
C(25)	5556 (2)	2088 (3)	1473 (2)	4.2
C(26)	4928 (3)	1954 (4)	1475 (4)	6.0
C(27)	4538 (3)	1047 (5)	1216 (4)	7.2
C(28)	4766 (3)	301 (5)	977 (3)	6.6
C(29)	5380 (3)	422 (4)	977 (3)	6.0
C(30)	5781 (3)	1303 (3)	1224 (3)	5.0
O(31)	7336 (2)	6655 (2)	1893 (2)	5.7
C(32)	7159 (3)	7230 (4)	1236 (3)	6.9
C(33)	7804 (4)	7290 (6)	1192 (4)	10.9
C(34)*	6510 (5)	6744 (7)	525 (4)	10.7
C(34)†	6620 (19)	7973 (25)	1027 (19)	9.2 (8)

* The occupancy factor is 0.8.

† The occupancy factor is 0.2; isotropic refinement.

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

N(1)—C(2)	1.314 (6)	C(4)—C(5)	1.499 (7)
N(1)—C(6)	1.410 (6)	C(4)—C(13)	1.534 (7)
C(2)—N(3)	1.333 (6)	C(4)—C(19)	1.539 (7)
C(2)—C(7)	1.484 (7)	C(5)—C(6)	1.334 (7)
N(3)—C(4)	1.469 (7)	C(6)—C(25)	1.481 (7)
C(2)—N(1)—C(6)	116.2 (4)	C(5)—C(4)—C(13)	110.6 (4)
N(1)—C(2)—N(3)	124.0 (4)	C(5)—C(4)—C(19)	109.8 (4)
N(1)—C(2)—C(7)	117.2 (4)	C(13)—C(4)—C(19)	110.9 (4)
N(3)—C(2)—C(7)	118.7 (4)	C(4)—C(5)—C(6)	122.2 (5)
C(2)—N(3)—C(4)	122.3 (4)	N(1)—C(6)—C(5)	121.8 (4)
N(3)—C(4)—C(5)	106.5 (4)	N(1)—C(6)—C(25)	113.9 (4)
N(3)—C(4)—C(13)	107.6 (4)	C(5)—C(6)—C(25)	124.2 (5)
N(3)—C(4)—C(19)	111.2 (4)		

0.8 treated as rigid groups, the other methyl C atom refined isotropically without H atoms; intense reflections with low 2θ angle (020, 111, $\bar{1}11$, 132, $\bar{1}32$, $\bar{2}02$, $\bar{2}04$, $\bar{4}04$) seemed to suffer from extinction and thus were not used in the refinement; final $R = 0.068$ and $wR = 0.075$ for 2241 observed reflections, $w = [\sigma^2(|F_o|) + 0.0040|F_o|^2]^{-1}$; $(\Delta/\sigma)_{\text{max}} = 0.15$; final difference map showed $|\Delta\rho| < 0.24 \text{ e \AA}^{-3}$; atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV); calculations carried out on an IBM 4381-R24 computer at Ochanomizu University.

Discussion. Final atomic coordinates for non-H atoms are listed in Table 1 and selected bond distances and angles in Table 2.* Fig. 1 shows the molecular structure of the pyrimidine with the atom numbering. In the crystals (I) was found to exist as the 3,4-dihydro form; but in solutions and in the solid state without any solvent it exists in an equilibrium mixture of the two tautomers, 3,4-dihydro and 1,4-dihydro forms. As is seen in Table 2, the C(2)—N(3) bond is shorter than a normal C—N single bond, and the difference between the bond lengths of N(1)—C(2) and C(2)—N(3) is rather small, which can account for the fact that the prototropic tautomerization occurs easily even in the solid state. The molecular structure as a whole resembles that of (II). The pyrimidine ring is almost planar except for C(4), which deviates by 0.37 \AA from the least-squares plane (plane *A*) composed of N(1), C(2), N(3), C(5) and C(6). The two phenyl rings at the 4-position markedly rotate from the pyrimidine ring; the dihedral angles with plane *A* are 71.4 (2) and 81.5 (2) $^\circ$. On the other hand, the torsion angles N(1)—C(2)—C(7)—C(8) and C(5)—C(6)—C(25)—C(26) are 28.7 (7) and -13.8 (8) $^\circ$, respectively.

The crystal structure is isomorphous with that of (II) 2-propanol solvate, and these structures are characterized by an identical hydrogen-bonding scheme. As is schematically shown in Fig. 2, (I) and 2-propanol molecules are alternately connected to form a ribbon-like structure around the 2_1 axis by

* Lists of anisotropic thermal parameters for non-H atoms, positional and thermal parameters for H atoms, bond distances and angles, least-squares-planes data and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53903 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

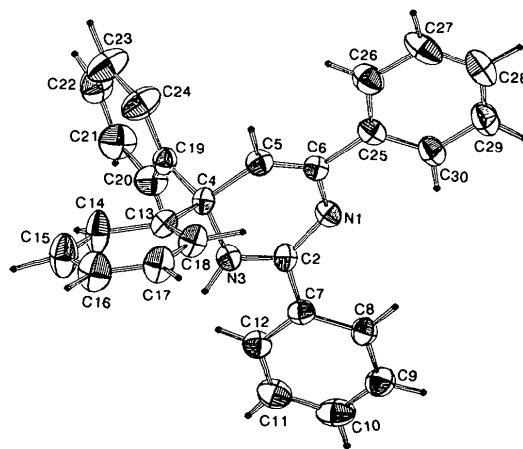


Fig. 1. ORTEP (Johnson, 1965) plot of (I) with the atom numbering. The anisotropic ellipsoids enclose 30% probability.

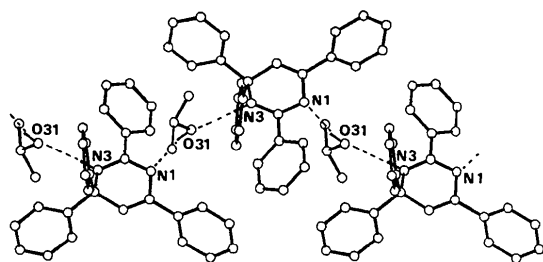


Fig. 2. Schematic drawing of the hydrogen bonding.

the two types of intermolecular hydrogen bonds: N(3)—H(3)···O(31) and N(1)···H(31)—O(31). The distances and angles for the hydrogen bonds are N(3)···O(31) = 2.951 (6), N(1)···O(31) = 2.955 (6) Å, N(3)—H(3)···O(31) = 163 (6) and N(1)···H(31)—O(31) = 165 (6)°. (I) partially tautomerizes to the 1,4-dihydro form on the loss of the solvent molecules, suggesting that the hydrogen bonds with the 2-propanol molecules can stabilize the 3,4-dihydro form. There are no unusually short contacts except for the hydrogen bonds. From these results it seems that the replacement of N(1) in (II), which was not involved in any hydrogen bonds, by a CH group has little influence on the molecular and crystal structure.

The colorless crystals of the (I) 2-propanol solvate turned red on exposure of UV light in spite of the structural similarity with (II) 2-propanol solvate, in which photocoloration was inhibited by the hydro-

gen bonds. The different photochemical behaviors of the triazine and (I) cannot be explained in terms of any differences in crystal structures between the two heterocycles. A different pathway of photocoloration reaction which is not inhibited by the hydrogen bonds connecting (I) and 2-propanol molecules alternately, is suggested for the solvated crystal of (I). The details of the photochemical reactions of (I) will be discussed elsewhere.

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture (No. 63628505). YM thanks the Hayashi Memorial Foundation for Female Natural Scientists for financial support.

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Acta Cryst. (1991). **C47**, 1658–1662

Structures of *N*²-Acetyl-DL-alaninamide and *N*²-Acetyl-DL-leucinamide

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(Received 1 August 1990; accepted 8 January 1991)

Abstract. *N*²-Acetyl-DL-alaninamide (NAAA), C₅H₁₀N₂O₂, *M_r* = 130.15, monoclinic, *P*2₁/*c*, *a* = 5.9798 (4), *b* = 16.690 (2), *c* = 7.7615 (4) Å, β = 107.18 (2)°, *V* = 740.1 (1) Å³, *Z* = 4, *D_x* = 1.168 Mg m⁻³, λ(Cu *Kα*) = 1.54178 Å, μ = 0.73 mm⁻¹, *F*(000) = 280, room temperature, final *R* = 0.045 for 1386 reflections with *I* > 3σ(*I*). *N*²-Acetyl-DL-leucinamide (NALA), C₈H₁₆N₂O₂, *M_r* = 172.23, monoclinic, *P*2₁/*c*, *a* = 16.807 (2), *b* =

7.2188 (8), *c* = 8.9716 (9) Å, β = 102.61 (1)°, *V* = 1062.2 (4) Å³, *Z* = 4, *D_x* = 1.077 Mg m⁻³, λ(Cu *Kα*) = 1.54178 Å, μ = 0.60 mm⁻¹, *F*(000) = 376, room temperature, final *R* = 0.041 for 1423 reflections with *I* > 3σ(*I*). In both structures the packing is ruled by two-dimensional networks of three intermolecular hydrogen bonds, which involve all the polar groups and interconnect L and D molecules, giving rise to characteristic structures arranged in layers. In the