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The Crystal and Molecular Structures of 2,4,4,6-Tetraphenyl-1,4-dihydropyridine and 4-Benzyl-1-methyl-2,4,6-triphenyl-1,4-dihydropyridine

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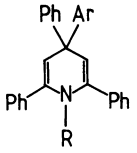
(Received October 15, 1986)

The crystal structures of 2,4,4,6-Tetraphenyl-1,4-dihydropyridine (**1**) and 4-benzyl-1-methyl-2,4,6-triphenyl-1,4-dihydropyridine (**2**) have been determined by the X-ray method. The crystals of **1** are monoclinic, $P2_1/a$, $a=12.883(1)$, $b=12.953(1)$, $c=12.575(1)$ Å, $\beta=94.95(1)°$, $V=2090.7(2)$ Å^3, $Z=4$, $D_x=1.225$ Mg m^{-3}. **2** is triclinic $P\bar{1}$, $a=7.786(1)$, $b=14.324(1)$, $c=10.759(1)$ Å, $\alpha=90.51(1)$, $\beta=106.89(1)$, $\gamma=92.02(1)°$, $V=1147.2(2)$ Å^3, $Z=2$, $D_x=1.196$ Mg m^{-3}. The final R values are 0.037 and 0.044 for **1** and **2**, respectively. The 1,4-dihydropyridine ring of **1** is a flat twisted boat, while that of **2** has a boat conformation with the apexes at N(1) and C(4). For **1** the dihedral angles of the phenyl rings and the plane of four C atoms, C(2), C(3), C(5), and C(6), of the pyridine ring are 46.6, 106.4, 62.3, and 30.5° for 2-, 4-, 4-, and 6-phenyl rings, respectively. The corresponding angles of **2** are 30.4, 50.2, and 39.1° for 2-, 4-, and 6-phenyl rings. The phenyl ring of benzyl group covers to the pyridine ring making the dihedral angle between these planes of 133.7°. The bond between C(4) and the methylene carbon is 1.576 Å, which is longer than the normal Csp^2–Csp^3 length.

2,4,4,6-Tetraphenyl-1,4-dihydropyridine (**1**) crystallized as colorless needles from an oxygen free benzene solution. The crystals and deaerated solutions of **1** exhibit a violet color on irradiation with UV light. The color of crystals was retained in deaerated media for a long time at room temperature, whereas in deaerated solutions the color was stable at only 77 K but at higher temperatures it gradually faded even under irradiation.[1] In solutions with oxygen the coloration does not occur and oxygenated products, *N*-(2-hydroperoxy-4-oxo-1,3,3-triphenylbutylidene)benzamide and 2,4,4,6-tetraphenyl-3,4-dihydro-3-pyridinol, were produced in benzene whereas 2,4,4,6-tetraphenyl-3-(4*H*)-pyridinone was given in acetone.[2] 4-Benzyl-1-methyl-2,4,6-triphenyl-1,4-dihydropyridine (**2**) also showed change of color from colorless to pale greenish



(1) R = H Ar = Ph
(2) R = Me Ar = Ch_2Ph

Table 1. Crystal Data, Experimental Conditions and Details of Refinements

	1 $C_{29}H_{23}N$	**2** $C_{31}H_{27}N$
M_w	385.51	413.56
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/a$	$P\bar{1}$
a/Å	12.883(1)	7.786(1)
b/Å	12.953(1)	14.324(1)
c/Å	12.575(1)	10.759(1)
α/°	90.0	90.51(1)
β/°	94.95(1)	106.89(1)
γ/°	90.0	92.02(2)
V/Å^3	2090.7(2)	1147.2(2)
Z	4	2
D_x/Mgm^{-3}	1.225	1.196
μ(Cu $K\alpha$)/mm^{-1}	0.543	0.526
F(000)	816	440
T/K	293	293
Crystal size/mm	0.20×0.20×0.25	0.2×0.2×0.15
2θ max./°	130	130
Range of h,k,l	$\bar{1}5$—15, 0—15, 0—14	0—9, $\bar{1}6$—16, $\bar{1}2$—12
Scan width $\Delta\omega$/°	1.2+0.5tanθ	1.15+0.4tanθ
Number of reflections		
Measured	3769	4457
Unique	3439	4142
Observed	3138	3222
R	0.037	0.044
R_w	0.036	0.061
S	0.758	1.151
g	9.6×10^{-7}	4.3×10^{-7}

yellow in crystals and in deaerated solutions under irradiation. In order to investigate a relationship between structures and photocoloration structures of **1** and **2** have been determined by the X-ray method.

Experimental

Crystal data and some experimental conditions are listed in Table 1. Intensities were collected on a Rigaku automatic

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors for Non-H Atoms

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
(a) **1**					(b) **2**				
N(1)	1458(1)	1182(1)	8650(1)	3.5	N(1)	6707(2)	2637(1)	1555(1)	3.0
C(2)	2086(1)	1164(1)	7801(1)	3.1	C(2)	6304(2)	3063(1)	2619(2)	2.9
C(3)	1993(1)	1865(1)	7031(1)	3.6	C(3)	7379(2)	3006(1)	3831(2)	3.1
C(4)	1209(1)	2740(1)	6971(1)	3.3	C(4)	8993(2)	2405(1)	4205(2)	2.8
C(5)	519(1)	2610(1)	7879(1)	3.5	C(5)	9545(2)	2220(1)	2994(2)	2.9
C(6)	622(1)	1870(1)	8615(1)	3.0	C(6)	8444(2)	2299(1)	1792(2)	2.8
C(21)	2876(1)	327(1)	7842(1)	3.3	C(11)	5249(3)	2079(1)	643(2)	4.1
C(22)	3450(1)	75(1)	8792(1)	4.3	C(21)	4698(2)	3647(1)	2277(2)	3.1
C(23)	4173(1)	−725(1)	8810(2)	5.4	C(22)	4198(2)	4112(1)	1103(2)	3.6
C(24)	4322(1)	−1260(1)	7897(2)	5.9	C(23)	2734(3)	4678(1)	793(2)	4.4
C(25)	3757(1)	−1019(1)	6961(1)	5.6	C(24)	1748(3)	4794(2)	1647(2)	4.9
C(26)	3035(1)	−228(1)	6930(1)	4.4	C(25)	2215(3)	4338(2)	2812(2)	5.1
C(411)	481(1)	2698(1)	5933(1)	3.3	C(26)	3680(3)	3767(2)	3126(2)	4.3
C(412)	−124(1)	3548(1)	5610(1)	4.1	C(41)	8495(2)	1468(1)	4800(2)	3.3
C(413)	−846(1)	3492(1)	4736(1)	4.9	C(411)	6966(2)	880(1)	3926(2)	3.1
C(414)	−975(1)	2595(1)	4158(1)	5.0	C(412)	7270(3)	219(1)	3074(2)	4.0
C(415)	−376(1)	1752(1)	4460(1)	5.2	C(413)	5881(3)	−341(2)	2299(2)	5.0
C(416)	342(1)	1803(1)	5345(1)	4.5	C(414)	4150(3)	−248(2)	2368(2)	5.0
C(421)	1808(1)	3769(1)	7042(1)	3.5	C(415)	3825(3)	401(2)	3208(2)	4.8
C(422)	1672(1)	4503(1)	7817(1)	4.6	C(416)	5221(3)	968(1)	3979(2)	3.9
C(423)	2235(1)	5419(1)	7853(1)	5.6	C(421)	10603(2)	2877(1)	5236(2)	3.0
C(424)	2952(1)	5610(1)	7141(1)	5.5	C(422)	12186(2)	2401(1)	5708(2)	3.6
C(425)	3107(1)	4885(1)	6374(2)	5.5	C(423)	13680(3)	2811(2)	6603(2)	4.4
C(426)	2536(1)	3980(1)	6320(1)	4.6	C(424)	13626(3)	3713(2)	7042(2)	5.3
C(61)	−92(1)	1753(1)	9469(1)	3.0	C(425)	12077(3)	4193(2)	6600(2)	5.3
C(62)	241(1)	1346(1)	10458(1)	3.9	C(426)	10576(3)	3785(1)	5698(2)	4.1
C(63)	−429(1)	1284(1)	11260(1)	4.4	C(61)	9046(2)	2111(1)	627(2)	3.0
C(64)	−1440(1)	1624(1)	11087(1)	4.4	C(62)	8619(3)	2706(1)	−424(2)	4.3
C(65)	−1786(1)	2003(1)	10102(1)	4.9	C(63)	9275(3)	2556(2)	−1475(2)	5.1
C(66)	−1127(1)	2058(1)	9297(1)	4.2	C(64)	10353(3)	1817(2)	−1492(2)	4.7
					C(65)	10754(3)	1214(2)	−472(2)	4.4
					C(66)	10097(3)	1361(1)	578(2)	3.8

The e.s.d's in parentheses refer to last digits. $B_{eq}=4/3\sum_i\sum_j\beta_{ij}a_ia_j$.

Table 3. Bond Length and Angles for Non-H Atoms with Estimated Standard Deviations

Distance	**1** l/Å	**2** l/Å	Distance	**1** l/Å	**2** l/Å
N(1)-C(2)	1.394(2)	1.411(2)	C(411)-C(412)	1.390(2)	1.385(3)
N(1)-C(6)	1.396(2)	1.406(2)	C(411)-C(416)	1.378(2)	1.387(3)
N(1)-C(11)		1.471(3)	C(412)-C(413)	1.379(2)	1.383(3)
C(2)-C(3)	1.325(2)	1.334(3)	C(413)-C(414)	1.374(3)	1.383(4)
C(2)-C(21)	1.485(2)	1.487(3)	C(414)-C(415)	1.372(3)	1.370(4)
C(3)-C(4)	1.515(2)	1.507(3)	C(415)-C(416)	1.386(2)	1.390(3)
C(4)-C(5)	1.516(2)	1.510(2)	C(421)-C(422)	1.383(2)	1.394(3)
C(4)-C(41)		1.576(3)	C(421)-C(426)	1.388(2)	1.392(3)
C(4)-C(411)	1.542(2)		C(422)-C(423)	1.390(3)	1.384(3)
C(4)-C(421)	1.539(2)	1.542(3)	C(423)-C(424)	1.363(3)	1.378(3)
C(5)-C(6)	1.332(2)	1.337(2)	C(424)-C(425)	1.373(3)	1.373(4)
C(6)-C(61)	1.481(2)	1.486(3)	C(425)-C(426)	1.383(2)	1.390(3)
C(21)-C(22)	1.389(2)	1.392(3)	C(61)-C(62)	1.385(2)	1.390(3)
C(21)-C(26)	1.385(2)	1.385(3)	C(61)-C(66)	1.390(2)	1.383(3)
C(22)-C(23)	1.392(2)	1.385(3)	C(62)-C(63)	1.384(2)	1.387(4)
C(23)-C(24)	1.369(3)	1.371(3)	C(63)-C(64)	1.375(2)	1.378(4)
C(24)-C(25)	1.366(3)	1.378(4)	C(64)-C(65)	1.370(2)	1.373(3)
C(25)-C(26)	1.382(2)	1.389(3)	C(65)-C(66)	1.377(2)	1.386(3)
C(41)-C(411)		1.508(3)			

Table 3. (Continued)

Angle	θ/°	θ/°	Angle	θ/°	θ/°
C(2)-N(1)-C(6)	118.9(1)	116.5(1)	C(4)-C(41)-C(411)		115.7(2)
C(2)-N(1)-C(11)		116.8(1)	C(4)-C(411)-C(412)	120.3(1)	
C(6)-N(1)-C(11)		116.2(1)	C(4)-C(411)-C(416)	121.7(1)	
N(1)-C(2)-C(3)	121.8(1)	121.9(2)	C(41)-C(411)-C(412)		121.1(2)
N(1)-C(2)-C(21)	115.3(1)	115.2(1)	C(41)-C(411)-C(416)		120.8(2)
C(3)-C(2)-C(21)	122.9(1)	122.6(2)	C(412)-C(411)-C(416)	117.8(1)	118.1(2)
C(2)-C(3)-C(4)	124.5(1)	123.6(2)	C(411)-C(412)-C(413)	121.0(1)	121.3(2)
C(3)-C(4)-C(5)	108.2(1)	107.5(1)	C(412)-C(413)-C(414)	120.6(2)	119.9(2)
C(3)-C(4)-C(41)		109.5(1)	C(413)-C(414)-C(415)	119.2(2)	119.6(2)
C(3)-C(4)-C(411)	111.7(1)		C(414)-C(415)-C(416)	120.3(2)	120.4(2)
C(3)-C(4)-C(421)	108.5(1)	112.8(1)	C(411)-C(416)-C(415)	121.2(1)	120.7(2)
C(5)-C(4)-C(41)		111.5(1)	C(4)-C(421)-C(422)	122.9(1)	119.8(2)
C(5)-C(4)-C(411)	106.3(1)		C(4)-C(421)-C(426)	119.7(1)	122.6(2)
C(5)-C(4)-C(421)	112.1(1)	108.4(1)	C(422)-C(421)-C(426)	117.4(1)	117.5(2)
C(41)-C(4)-C(421)		107.1(1)	C(421)-C(422)-C(423)	120.8(2)	121.6(2)
C(411)-C(4)-C(421)	110.2(1)		C(422)-C(423)-C(424)	121.0(2)	119.9(2)
C(4)-C(5)-C(6)	125.0(1)	123.5(2)	C(423)-C(424)-C(425)	119.0(2)	119.6(2)
N(1)-C(6)-C(5)	120.8(1)	122.1(2)	C(424)-C(425)-C(426)	120.4(2)	120.7(2)
N(1)-C(6)-C(61)	116.0(1)	116.1(1)	C(421)-C(426)-C(425)	121.4(2)	120.7(2)
C(5)-C(6)-C(61)	123.2(1)	121.6(2)	C(6)-C(61)-C(62)	121.8(1)	120.7(2)
C(2)-C(21)-C(22)	120.9(1)	120.8(2)	C(6)-C(61)-C(66)	120.4(1)	121.0(2)
C(2)-C(21)-C(26)	120.1(1)	121.3(2)	C(62)-C(61)-C(66)	117.8(1)	118.3(2)
C(22)-C(21)-C(26)	119.0(1)	117.9(2)	C(61)-C(62)-C(63)	120.8(1)	120.3(2)
C(21)-C(22)-C(23)	119.7(1)	121.1(2)	C(62)-C(63)-C(64)	120.5(1)	120.5(2)
C(22)-C(23)-C(24)	120.3(2)	120.3(2)	C(63)-C(64)-C(65)	119.2(1)	119.7(2)
C(23)-C(24)-C(25)	120.3(2)	119.5(2)	C(64)-C(65)-C(66)	120.6(2)	119.9(2)
C(24)-C(25)-C(26)	120.0(2)	120.4(2)	C(61)-C(66)-C(65)	121.0(1)	121.3(2)
C(21)-C(26)-C(25)	120.7(1)	120.8(2)			

diffractometer with graphite-monochromated Cu $K\alpha_1$ (λ= 1.54051 Å) radiation, using the ω-2θ scan technique with a scanning rate of 4° min^{-1} in 2θ. At both ends of the scan range 10 s background counts were taken for each reflection. Three reflections were monitored for every 50 reflections. Variations of intensities of the monitored reflections were within 3% for both **1** and **2**. Reflections of $|F_o| \geq 3\sigma(F_o)$ were used for structure determination. No absorption correction was applied.

Although the colorless crystals of **1** changed to be blue during an irradiation with X-rays, the intensities of the monitored reflections have not changed. After the intensity measurement a check on the unit cell dimensions and the space group was carried out, but no change was observed. For **2** color change could not be observed.

The structures were solved by the direct method with the program MULTAN 78.[3] All non-hydrogen atoms were refined by the block-diagonal least-squares with anisotropic temperature factors. A difference map showed the all hydrogen atoms. Further refinement with anisotropic temperature factors for non-hydrogen atoms and isotropic ones for H gave the final R values of 0.037 and 0.044 for **1** and **2**, respectively. The quantity minimized was $\sum w(|F_o|-k^{-1}|F_c|)^2$. For **1**, $w=1/(0.8208-0.0710|F_o|+0.002|F_o|^2)$ and for **2**, $w=1/(0.0617+0.0147|F_o|+0.0002|F_o|^2)$. Atomic scattering factors were taken from "International Tables for X-ray Crystallography."[4] All computations were performed on a HITAC M180 Computer of the Data Processing Center of the University of Electro-Communications with the programs UNICS III,[5] MULTAN 78, and ORTEP II.[6] The final atomic parameters are given in Table 2.[7]

Table 4. Torsion Angles

Angle	**1** τ/°	**2** τ/°
C(6)-N(1)-C(2)-C(3)	8.6(2)	−11.5(2)
C(2)-N(1)-C(6)-C(5)	−10.8(2)	12.3(2)
N(1)-C(2)-C(3)-C(4)	−0.7(2)	−6.9(2)
N(1)-C(6)-C(5)-C(4)	5.3(2)	5.3(2)
C(2)-C(3)-C(4)-C(5)	−4.5(2)	21.6(2)
C(3)-C(4)-C(5)-C(6)	2.2(2)	−20.8(2)
N(1)-C(2)-C(21)-C(22)	−42.4(2)	−30.4(2)
N(1)-C(2)-C(21)-C(26)	136.4(1)	151.3(1)
N(1)-C(6)-C(61)-C(62)	27.1(1)	39.0(2)
N(1)-C(6)-C(61)-C(66)	−153.3(1)	−143.3(1)
C(11)-N(1)-C(2)-C(21)		−53.2(2)
C(11)-N(1)-C(6)-C(61)		53.5(2)
H(1)-N(1)-C(2)-C(21)	−25(1)	
H(1)-N(1)-C(6)-C(61)	24(1)	
C(3)-C(4)-C(411)-C(412)	−165.1(1)	
C(3)-C(4)-C(411)-C(416)	20.3(2)	
C(3)-C(4)-C(421)-C(422)	−122.8(1)	178.4(1)
C(3)-C(4)-C(421)-C(426)	55.8(1)	−3.8(2)
C(2)-C(3)-C(4)-C(41)		−99.7(2)
C(2)-C(3)-C(4)-C(421)		141.1(1)
C(4)-C(41)-C(411)-C(412)		88.3(2)
C(4)-C(41)-C(411)-C(416)		−93.6(2)
C(3)-C(4)-C(41)-C(411)		58.8(2)
C(3)-C(4)-C(41)-H(41)		−178(1)
C(3)-C(4)-C(41)-H(42)		62(1)

Discussion

The molecular structures with the atom-numbering are shown in Fig. 1. Bond distances and angles are listed in Table 3. The torsion angles are listed in

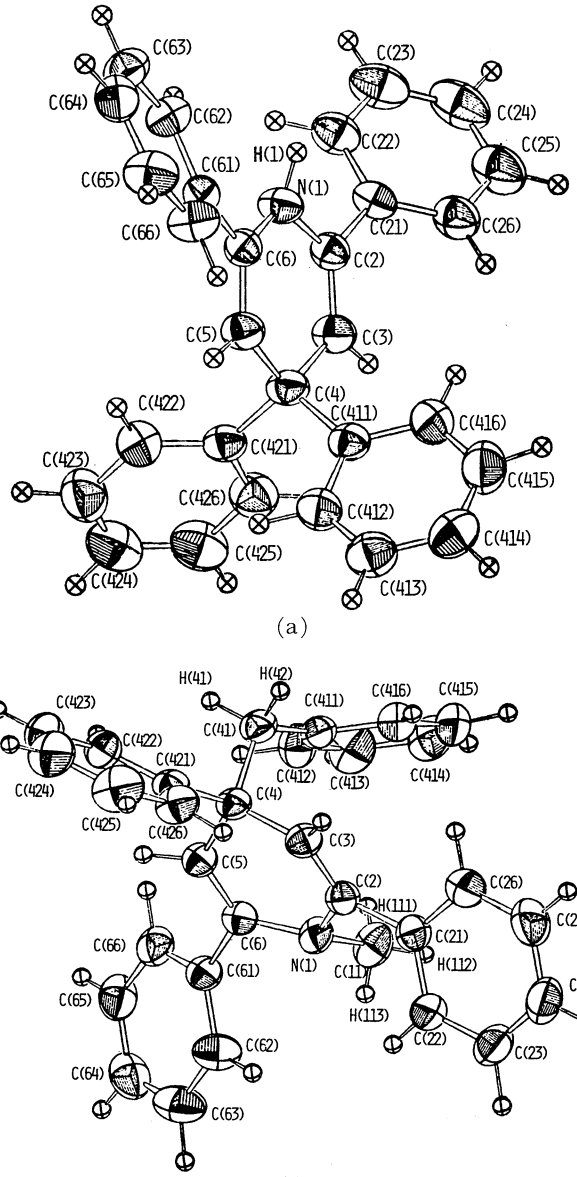


Fig. 1. Atomic numbering of the molecules. (a) **1** and (b) **2**. The thermal ellipsoids for non-H atoms are drawn at 50% probability.

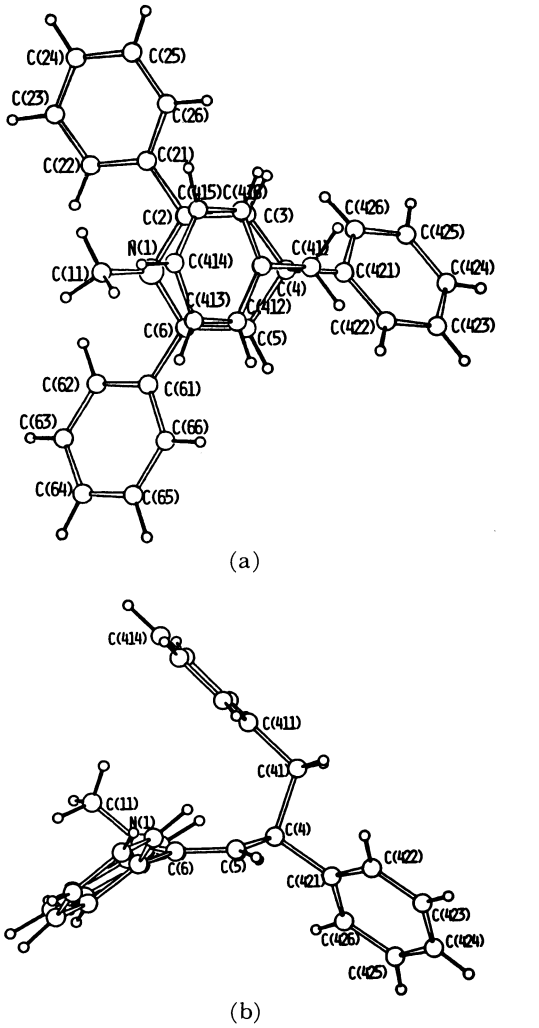


Fig. 2. (a) Projection of the molecule **2** on the dihydropyridine ring. (b) Side view of the molecule **2**.

Table 4. **2** shows a boat conformation with the apexes of C(4) and N(1). The torsion angles about C(4) ring bonds are larger than those about the N(1) bonds. The dihedral angles (boat angles) between the plane **A** defined by four atoms, C(2), C(3), C(5), and C(6), and the planes C(2)-N(1)-C(6) and C(3)-C(4)-C(5) are 10.1 and 17.5°, respectively. The dihedral angle (fold angle) between two N-C=C-C planes is 18.5°. The degree of the ring distorsions at N(1) and C(4) is the same order with those of 4-aryl-3,5-bis(methoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridine.[8] For **1** the torsion angles about the N(1) and C(4) ring bonds are smaller than the corresponding angles of **2** and the other 1,4-dihydropyridines and C(4) is less distorted than N(1).

The lengths of C(2)-C(3) and C(5)-C(6) show the double bond character and are shorter than the corresponding values (1.345—1.369 Å) of the other 1,4-dihydropyridines.[8] The difference of these bond lengths may be attributed to the two methoxycarbonyl groups at 3 and 5 positions. The lengths of N(1)-C(2) and N(1)-C(6) for **2** are slightly longer than those of **1** and the others because of the 1-methyl substituent. The endocyclic angles of **1** and **2** are different from those of the others. The angles C(2)-N(1)-C(6) and C(3)-C(4)-C(5) of **1** and **2** are smaller and the other angles of **1** and **2** are larger than the corresponding angles of 3,5-bis(methoxycarbonyl) derivatives. The lengths of C(2)-C(21) and C(6)-C(61) show typical Csp^2-Csp^2 length while C(4)-C(411) and C(4)-C(421) are longer than the typical Csp^2-Csp^3 length, especially C(4)-C(411) of **2**.

For **1** the dihedral angles between the plane **A** and the four phenyl planes are 46.6, 106.4, 62.3 and 30.5° for 2-, 4-, 4-, and 6-positions, respectively. The corresponding angles of **2** are 30.4, 50.2, and 39.1° for 2-, 4-, and 6-positions, respectively.

The phenyl ring of benzyl group of **2** is trans to the

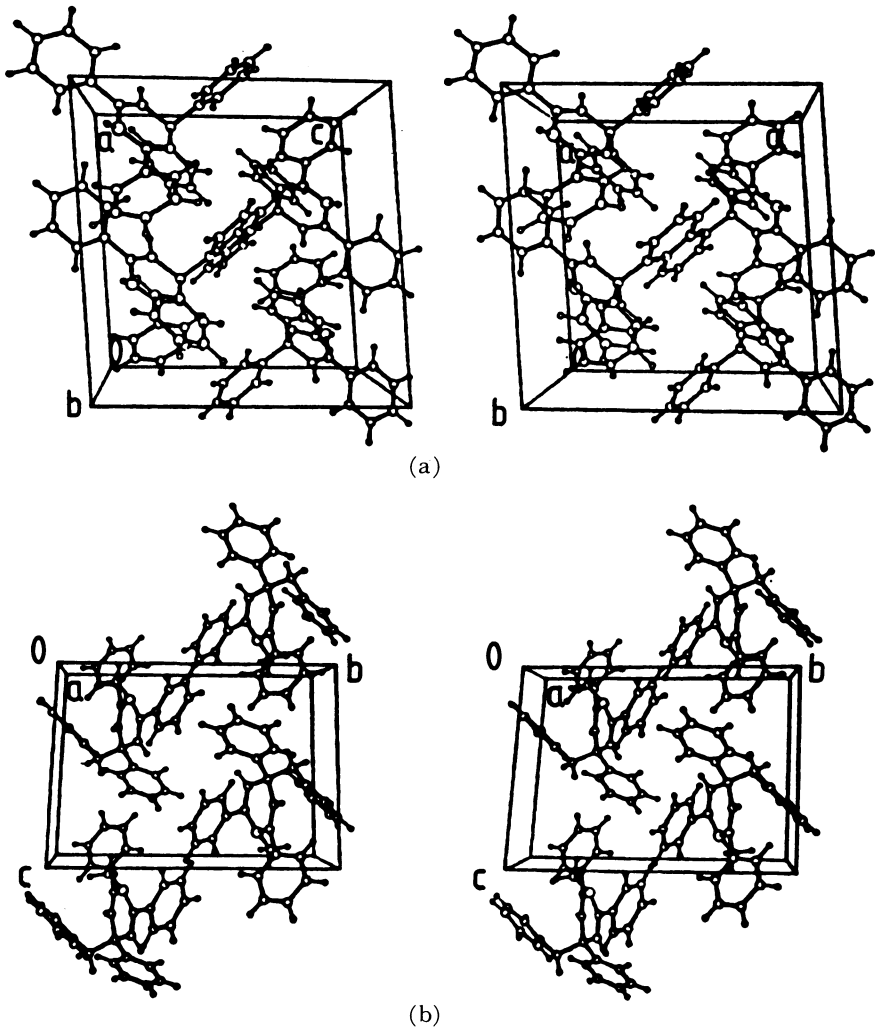


Fig. 3. Stereoscopic view of the crystal structure. (a) **1** and (b) **2**.

4-phenyl ring about the C(4)-C(41) bond and gauche to C(3) and C(5). This conformation of the benzyl group is quite interesting. Figure 2 shows the projection of **2** on the plane of the pyridine ring. The benzyl group covers the pyridine ring far from the phenyl group. The dihedral angles between the phenyl plane (C(411)—C(416)) and the plane **A** is 133.7°. Some intramolecular contacts between the phenyl ring of benzyl group and the pyridine ring, N(1)··· C(411), C(2)··· C(411), C(6)··· C(411), C(3)··· C(416), and C(5)··· C(412), are 3.569(2), 3.434(3), 3.491(3), 3.344(3), and 3.332(3) Å, respectively.

Figure 3 is the stereoscopic view of the crystal packing. There are no significant contacts shorter than the sum of the van der Waals' radii.

In spite of a color changing of the crystal of **1** during an irradiation with X-rays for intensitiy measurement, the intensities, the dimensions of the unit cell and so the crystal structure have been retained. This result suggests the coloration may be attributed to an electronic effect. A slight difference of photochemical behavior between **1** and **2** may relate to the planality of the 1,4-dihydropyridine and the steric retention of the benzyl group of **2**.

We thank Miss Junko Shibuya for preparing the compounds.

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