143·5°, corresponding to $-31 \leq h \leq 31$, $0 \leq k \leq 8$, $0 \leq l \leq 32$. 3692 reflections satisfying $I \geq 2·5\,\sigma(I)$ were considered as observed. No correction was made for absorption, 62 standard reflections, 0·5% intensity variation. The *NRCVAX* system was used for all calculations (Gabe, Lee & LePage, 1985). The structure was solved by the application of direct methods and refined by full-matrix least squares on F. Anisotropic thermal parameters were refined for non-H atoms. The H atoms were located from a difference map, their positions and isotropic temperature factors were refined. The final residuals obtained at convergence* were $R = 0·044$ and $wR = 0·052$, $S = 2·03$. Weights based on counting statistics were used. The maximum Δ/σ ratio was 0·220. In the last D map, the deepest hole was $-0·390$ e Å^{-3}, and the highest peak 0·440 e Å^{-3}. Atomic scattering factors as stored in the *NRCVAX* program were those of Cromer & Waber (1974).

Discussion. Table 1 gives the final atomic parameters with their B values.† Bond lengths and angles are given in Tables 2(*a*) and 2(*b*). Selected torsion angles of the condensed rings skeleton are given in Table 2(*c*). Fig. 1 shows a perspective view and the atomic numbering of the molecule. The results of the structure determination indicate that (2) has a *CAC* relative stereochemistry. This observation confirms that during the Diels–Alder reaction, the macrocycle (1) leads to a conformationally mobile tricycle having a boat-like *B* ring and chair-like *A* and *C* rings. This transient conformer adopted a more stable conformation with a twisted boat *B* ring as observed in the crystal structure. It is interesting to notice here that the planes of both axial methoxycarbonyl groups symmetrically face the olefinic plane, as can be seen in Fig. 1. Such proximities between methoxycarbonyl and the olefinic moieties suggest further exploitation of the iodolactonization reaction and further desactivation leading to specific natural products. No abnormally short intermolecular contacts were noted in the crystal packing.

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* Function minimized: $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$.

† Lists of structure factors, anisotropic thermal parameters, H-atom parameters and all torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52678 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of 1-Methyl-2,4,4,6-tetraphenyl-1,4-dihydropyridine

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Abstract. $C_{30}H_{25}N$, $M_r = 399·54$, monoclinic, $P2_1/c$, $a = 12·581\,(5)$, $b = 13·955\,(5)$, $c = 12·885\,(4)$ Å, $\beta = 93·63\,(3)°$, $V = 2258\,(1)$ Å^3, $Z = 4$, $D_m = 1·17\,(1)$, $D_x = 1·176\,(1)$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0·7107$ Å, $\mu = 0·063$ mm^{-1}, $F(000) = 848$, $T = 296$ K, $R = 0·052$ for 2231 unique observed reflections. The planes of the phenyl rings at C1, C3, C3 and C5 make angles 51·5 (1), 56·9 (1), 75·6 (1) and 60·8 (1)° with the mean plane of the dihydropyridine ring, which is itself essentially planar. No significant intermolecular interactions are observed.

Introduction. The structure of the title compound has been studied in connection with the development of new materials suitable for recording media. The structure of the excited state may explain the differ-

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Table 1. *Final coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($Å^2 \times 10^4$)

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
C1	3543 (2)	2927 (2)	467 (2)	423 (8)
C2	2851 (2)	2211 (2)	464 (2)	493 (10)
C3	1932 (2)	2134 (2)	1169 (2)	479 (8)
C4	2010 (2)	2977 (2)	1899 (2)	497 (9)
C5	2726 (2)	3681 (2)	1886 (2)	430 (8)
C6	2752 (2)	4463 (2)	2659 (2)	482 (9)
C7	3665 (3)	4691 (2)	3258 (2)	636 (12)
C8	3660 (3)	5404 (3)	4009 (3)	810 (14)
C9	2745 (3)	5895 (3)	4155 (3)	912 (18)
C10	1836 (4)	5695 (3)	3569 (3)	915 (18)
C11	1839 (3)	4990 (2)	2821 (3)	681 (12)
C12	4412 (2)	2940 (2)	− 271 (2)	445 (9)
C13	5469 (2)	2976 (2)	80 (2)	611 (11)
C14	6270 (2)	2960 (2)	− 613 (3)	695 (13)
C15	6018 (3)	2929 (2)	− 1658 (3)	692 (12)
C16	4980 (3)	2897 (2)	− 2011 (3)	747 (13)
C17	4175 (3)	2903 (2)	− 1324 (2)	611 (11)
C18	898 (2)	2154 (2)	449 (2)	485 (9)
C19	302 (2)	2971 (3)	305 (3)	694 (12)
C20	− 572 (3)	3006 (3)	− 417 (3)	834 (16)
C21	− 843 (3)	2209 (3)	− 990 (3)	419 (13)
C22	− 274 (3)	1395 (3)	− 855 (3)	744 (14)
C23	585 (3)	1362 (3)	− 134 (2)	632 (12)
C24	1980 (2)	1205 (2)	1817 (2)	512 (10)
C25	1224 (3)	1036 (3)	2540 (2)	663 (12)
C26	1284 (3)	235 (3)	3171 (3)	811 (16)
C27	2080 (4)	− 429 (3)	3089 (3)	867 (17)
C28	2817 (3)	− 278 (3)	2375 (3)	848 (16)
C29	2778 (3)	532 (2)	1759 (3)	709 (13)
N30	3528 (2)	3695 (1)	1169 (2)	467 (7)
C31	3820 (4)	4643 (3)	770 (4)	878 (17)

ent photochromic properties of dihydropyridines having a variety of substitution patterns. The structure of the ground state, established here by X-ray diffraction, may be used as a starting point for quantum chemical calculation of absorption bands.

Experimental. Transparent, colorless rod-like crystals of 1-methyl-2,4,4,6-tetramethyl-1,4-dihydropyridine turn pink when exposed to daylight. During the intensity measurements the crystal became almost black, but no changes in intensitities were observed. The density was determined by flotation in aqueous KBr. When ground or cut the crystals split into slabs. Therefore, the measured crystal was only partly ground to an approximate ellipsoid of dimensions 0·35 × 0·45 × 0·80 mm. The crystal quality and the space group ($P2_1/c$) were checked by Weissenberg photographs. The lattice parameters, refined from 15 centered reflections ($10 < 2\theta < 21°$) and measured using two different crystals, were identical within one e.s.d. A total of 4002 symmetry-independent reflections were measured by ω–2θ scan ($2\theta < 50°$), h: − 14 → 14, k: 0 → 16, l: 0 → 14, using a Syntex $P2_1$ diffractometer. Three standard reflections (022, 040, 304) showed no significant fluctuations during the measurement. 2231 reflections with $I > 1{\cdot}96\sigma(I)$ were used for refinement. Both absorption and extinction were ignored. The phase problem was solved by *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), and the structure refined by *SHELX*76 (Sheldrick, 1976). The function minimized was $\sum w\Delta^2$, where $w = 2{\cdot}07[\sigma^2(F_o) + 0{\cdot}0009\ |F_o|^2]^{-1}$ and $\Delta = ||F_o| - |F_c||$. All non-H atoms were refined with anisotropic temperature parameters. All H atoms, localized on a difference map, were freely refined isotropically to acceptable positions [$\langle$C—H$\rangle$ = 0·98 (4) Å]. The refinement of 305 parameters in three blocks was stopped when all $\Delta/\sigma < 0{\cdot}15$. No significant correlations among refined parameters were observed. The resulting R = 0·052, wR = 0·053. Maximum and minimum peaks on a final difference map were 0·2 and −0·2 e Å^{-3}. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Geometry was calculated with *PARST* (Nardelli, 1983) and *IMC* (Hašek, 1981). Refined atomic parameters of non-H atoms are listed in Table 1.*

Discussion. The atomic numbering scheme and the conformation of the molecule are shown in Fig. 1 and bond lengths, valence angles and selected torsion angles are listed in Table 2. The 1,4-dihydropyridine ring is almost planar, $\chi^2 = 103$ [highest deviation 0·020 (3) Å]. The angle between the five-atom planes involving each of the double bonds (χ^2 = 36 and 62) is 2·5 (1)°. The 1,4-dihydropyridine ring here exhibits a greater degree of planarity than in other derivatives (Iwasaki, Watanabe & Maeda, 1987; see Table 3).

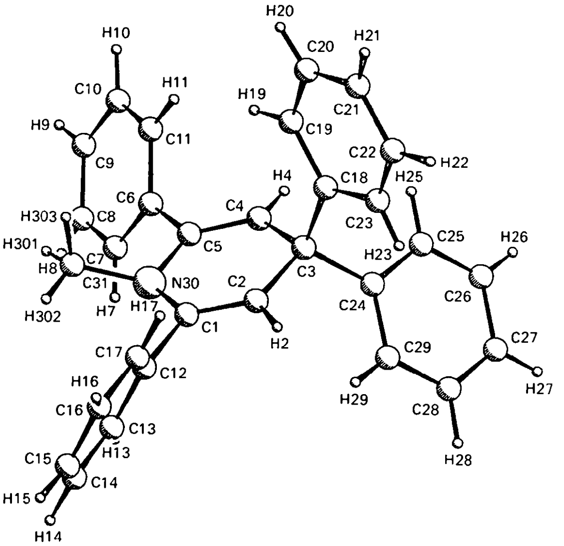

Fig. 1. A view of 1-methyl-2,4,4,6-tetraphenyl-1,4-dihydropyridine with the atomic numbering scheme.

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* Diagrams of the molecule showing bond distances and angles, and lists of anisotropic temperature parameters, H-atom coordinates and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52659 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å), *bond angles* (°) *and torsion angles* (°)

N1—C1	1·404 (3)	C24—C29	1·381 (4)
N1—C5	1·410 (3)	C7—C8	1·389 (5)
N1—C31	1·474 (4)	C10—C11	1·377 (5)
C1—C2	1·324 (4)	C13—C14	1·389 (5)
C4—C5	1·333 (4)	C16—C17	1·387 (5)
C3—C2	1·519 (4)	C19—C20	1·396 (5)
C3—C4	1·506 (4)	C22—C23	1·381 (4)
C5—C6	1·477 (3)	C25—C26	1·382 (5)
C1—C12	1·495 (3)	C28—C29	1·381 (5)
C3—C18	1·550 (3)	C9—C10	1·360 (6)
C3—C24	1·541 (4)	C9—C8	1·362 (6)
C6—C7	1·380 (4)	C15—C14	1·364 (5)
C6—C11	1·390 (4)	C15—C16	1·356 (5)
C12—C13	1·378 (4)	C21—C20	1·366 (6)
C12—C17	1·371 (4)	C21—C22	1·349 (6)
C18—C19	1·370 (4)	C27—C26	1·374 (6)
C18—C23	1·379 (4)	C27—C28	1·362 (6)
C24—C25	1·393 (4)		

C1—N1—C5	116·8 (2)	C7—C6—C11	117·5 (3)
C1—N1—C31	116·5 (2)	C13—C12—C17	118·1 (3)
C5—N1—C31	116·4 (2)	C19—C18—C23	117·3 (3)
N1—C1—C2	122·9 (2)	C25—C24—C29	116·8 (3)
N1—C1—C12	116·2 (2)	C6—C7—C8	120·9 (3)
C2—C1—C12	120·9 (2)	C10—C11—C6	121·4 (3)
C1—C2—C3	125·2 (3)	C12—C13—C14	120·8 (3)
C2—C3—C4	107·2 (2)	C12—C17—C16	120·7 (3)
C2—C3—C24	112·2 (2)	C18—C19—C20	121·4 (3)
C4—C3—C18	112·3 (2)	C18—C23—C22	121·6 (3)
C4—C3—C24	108·7 (2)	C24—C25—C26	121·1 (3)
C2—C3—C18	106·4 (2)	C24—C29—C28	121·7 (3)
C18—C3—C24	110·0 (2)	C7—C8—C9	119·9 (3)
C3—C4—C5	125·8 (2)	C9—C10—C11	119·7 (4)
C4—C5—N1	122·0 (2)	C13—C14—C15	120·2 (3)
N1—C5—C6	116·4 (2)	C15—C16—C17	120·8 (3)
C4—C5—C6	121·5 (2)	C19—C20—C21	119·4 (4)
C5—C6—C7	122·0 (2)	C21—C22—C23	120·1 (4)
C5—C6—C11	120·6 (2)	C25—C26—C27	120·9 (4)
C1—C12—C13	121·4 (2)	C27—C28—C29	120·9 (4)
C1—C12—C17	120·5 (2)	C8—C9—C10	120·6 (4)
C3—C18—C19	121·8 (2)	C14—C15—C16	119·4 (3)
C3—C18—C23	120·8 (2)	C20—C21—C22	120·2 (3)
C3—C24—C25	120·0 (2)	C26—C27—C28	118·6 (4)
C3—C24—C29	123·1 (2)		

N30—C1—C2—C3	2·7 (2)	C2—C1—N30—C31	37·3 (2)
C1—C2—C3—C4	−3·7 (2)	C1—N30—C31—H301	−168 (3)
C2—C3—C4—C5	3·0 (2)	C1—N30—C31—H302	−42 (4)
C3—C4—C5—N30	−1·3 (2)	C1—N30—C31—H303	80 (4)
C4—C5—N30—C1	−0·3 (2)	C2—C3—C24—C29	0·5 (2)
C5—N30—C1—C2	−0·4 (2)	C2—C3—C18—C23	75·1 (2)
N30—C1—C12—C13	57·0 (2)	C4—C3—C24—C29	−117·9 (2)
N30—C5—C6—C7	−51·0 (2)	C4—C3—C18—C23	−176·8 (2)

Table 3. *A comparison of* 1,4-*dihydropyridines*: *mean torsion angles of the phenyls around the* C1—C12 *and* C5—C6 *bonds and torsion angles of the* 1,4-*dihydropyridine ring*

E.s.d.'s are less than 0·2° in each case.

(I) 2,4,4,6-Tetraphenyl-1,4-dihydropyridine.[a]
(II) 1-Methyl-2,4,4,6-tetraphenyl-1,4-dihydropyridine. [b].
(III) 4-Benzyl-1-methyl-2,4,6-triphenyl-1,4-dihydropyridine.[c]

	(I)	(II)	(III)
Mean torsion around C1—C12	26·9	57·0	37·9
Mean torsion around C5—C6	−43·0	−50·5	−29·8
C1—C2—C3—C4	2·2	−3·7	−20·8
C2—C3—C4—C5	−4·5	3·0	21·6
C3—C4—C5—N	−0·7	−1·3	−6·9
C4—C5—N—C1	8·6	−0·3	−11·5
C5—N—C1—C2	−10·8	−0·4	12·3
N—C1—C2—C3	5·3	2·7	5·3

References: (*a,c*) Iwasaki, Watanabe & Maeda (1987); (*b*) This work.

The planes of the phenyl rings at C1, C3, C3 and C5 make angles of 51·5 (1), 56·9 (1), 75·6 (1) and 60·8 (1)° with the dihydropyridine plane. The respective χ^2 values are in the range 9–18. Rotation of the phenyl rings at C1 and C5 is much higher than in other derivatives (Table 3). The bonds C1—C12 and C5—C6 lie almost in the 1,4-dihydropyridine plane [at angles of 2·8 (2) and 0·8 (1)°, respectively], whilst C3—C18 and C3—C24 make angles of 58·0 (1) and 51·7 (1)° with this plane and the N—C(methyl) bond makes an angle of 32·3 (1)°. Normals to the C1 and C5 phenyl rings make angles of 23·0 (2) and 25·4 (2)° with the N—C(methyl) vector. Angles between the relevant phenyl planes and the bonds C5—C6, C1—C12, C3—C18 and C3—C24 are 2·1 (1), 1·1 (1), 4·9 (1) and 2·5 (1)°, respectively. The methyl group is staggered with H303 lying between C1, C5, and the lone pair at N30 situated between H301 and H302 in a Newman projection.

Bond distances and valence angles are normal. All bond angles adjacent to double bonds are enlarged; the average angles, ⟨C(sp^2)=C(sp^2)—C⟩ [125·5 (3)], ⟨C(sp^2)=C(sp^2)—N⟩ [122·4 (3)], ⟨C(sp^2)=C(sp^2)—C(benzene)⟩ [121·2 (3)°], are compensated by the average ⟨N30—C(sp^2)—C(benzene)⟩ [116·3 (3)°]. The three angles around N30 are, surprisingly, equal within one e.s.d., ⟨C—N—C⟩ = 116·6 (2)°. All the N30—C31—H angles are larger than H—C31—H angles. The inner angle C2—C3—C4 [107·3 (2)°] is significantly smaller than expected for sp^3 hybridization in contrast to C18—C3—C24 [110·0 (2)°]. Each C(sp^2)—C(sp^3) bond makes one smaller and one larger angle with the exocyclic C—C(phenyl) bonds: C2—C3—C24 = 112·2 (3), C4—C3—C18 = 112·3 (3)°, and C2—C3—C18 = 106·4 (2), C4—7 C3—C24 = 108·7 (2)°.

Atomic thermal motion increases significantly with distance from the molecular centre. The $U_{\rm eq}$ values range from $<0·05$ Å^2 for dihydropyridine and adjacent carbons, to 0·07 Å^2 in the next shell and up to 0·09 Å^2 for outer atoms and for C31. The ratio of the shortest:longest principal axis increases likewise, with a maximum asymmetry of 4·1 for C31. A systematic decrease [−1·9 (3) to −3·2 (3)°] of benzene internal

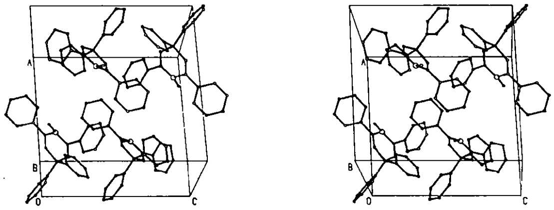

Fig. 2. Molecular packing of 1-methyl-2,4,4,6-tetraphenyl-1,4-dihydropyridine.

angles from 120° was found at C6, C12, C18 and C24 with a compensatory enlargement [0·7 (4) to 1·7 (4)°] at C7, C11, C13, C17, C19, C23, C25 and C29. This effect may be connected with the π-electron-releasing effect of the double bond on the phenyls at C1 and C5 (Domenicano & Vaciago, 1979). However, a similar effect is observed for both phenyls at C3. A more realistic explanation (valid for all four rings) is the effect of thermal libration and rotation. This accounts for the shortening of the outer two phenyl bonds in each ring, which range from 1·349 (6) to 1·374 (6) Å [⟨C—C⟩ = 1·362 (7) Å], whilst other phenyl bonds lie in the range 1·370 (4)–1·396 (4) [⟨C—C⟩ = 1·382 (8) Å]. Similar effects are observed in other structures and will be reviewed elsewhere.

Molecular packing (see Fig. 2) and the conformation of the phenyl rings are controlled only by van der Waals forces. The shortest intermolecular distance between non-H atoms is C14—C31^{i} (i = $1-x$, $1-y, -z$) [3·351 (1) Å]. No changes in the diffraction pattern were observed during coloration, either in the single crystal or in the powdered material. Probably only a small part of the molecule undergoes photochromic excitation and/or coloration causes insignificant geometrical changes. Differences in photochomic behaviour between compounds may be attributed to differences in planarity of the 1,4-dihydropyridine rings, related to the packing effects of the phenyl groups in positions C1 and C5, and to steric interactions of the benzyl group in the 4-benzyl-1-methyl derivative (see Table 3) (Iwasaki, Watanabe & Maeda, 1987).

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Structure of the Cyclohexapeptide Cleromyrine II Trihydrate

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Abstract. $C_{29}H_{40}N_6O_7.3H_2O$, $M_r = 638{\cdot}7$, trigonal, $P3_121$, $a = 14{\cdot}190\,(2)$, $c = 29{\cdot}833\,(4)$ Å, $V = 5202\,(1)$ Å^3, $Z = 6$, $D_x = 1{\cdot}22$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 7{\cdot}8$ cm^{-1}, $F(000) = 2052$, $T = 291$ K, $R = 0{\cdot}069$ for 1942 observed reflections. The new cyclohexapeptide cleromyrine II was isolated from *Clerodendrum myricoides*. Its structure was established by spectroscopic and X-ray diffraction methods as *cyclo*(-Gly-Tyr-Gly-Pro-Leu-Pro-). The conformation essentially consists of two β-turns including the Pro residues and one central very short antiparallel β-sheet stabilized by two intramolecular hydrogen bonds: N(Tyr2)···O(Leu5) = 2·94 (2) Å and N(Leu5)···O(Tyr2) = 3·02 (2) Å.

Introduction. Cleromyrine I and II are two new homodetic cyclohexapeptides isolated from *Clerodendrum myricoides* (Verbenaceae) as described in a preceding communication (Bashwira, Hootelé, Tourwé, Pepermans, Laus & van Binst, 1989); the

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