The molecules are held together by N—H···Cl hydrogen bonds. The geometry of this bond is N(1)···Cl(25)$(1-x,y,z)$ = 3·169 (4), H(201)···Cl(25) = 2·27 (4) Å, N(1)—H(201)···Cl(25) = 164 (4)°.

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Structure of 6-Amino-4,4,5,7,8-pentamethyldihydrocoumarin

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Abstract. $C_{14}H_{19}NO_2$, $M_r = 233·3$, triclinic, $P\bar{1}$, $a = 9·925$ (2), $b = 11·193$ (3), $c = 11·915$ (3) Å, $\alpha = 95·39$ (2), $\beta = 91·09$ (2), $\gamma = 97·38$ (2)°, $V = 1304·7$ (3) Å^3, $Z = 4$, $F(000) = 480$, $D_x = 1·19$ (1), $D_m = 1·18$ (1) g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 0·43 cm^{-1}, $T = 292$ K. Final $R = 0·045$ for 3099 observed reflections. The statistically significant difference in bond length C(6)—N between the two independent molecules can be explained in terms of the differences in the intermolecular interactions of the N atoms. The conformation of the lactone ring in both independent molecules is intermediate between half-chair and sofa and very similar to that observed in 4,4,5,7,8-pentamethyldihydrocoumarin. In both these compounds similar large distortions of valency angles occur in the phenyl rings to accommodate the overmethylation.

Introduction. The crystal structure of the title compound (hereafter referred to as I) opens a series of papers on our studies of structural properties of coumarin derivatives. Similar compounds were synthesized and used by Milstien & Cohen (1972) who introduced the concept of stereopopulation control to show the importance of conformational restrictions in enzyme-catalysed reactions. The enzyme enhancements of such reactions often range from 10^{10} to 10^{18}. Among a number of factors which make such rate enhancement possible Milstien & Cohen (1972) indicated the importance of the restrictions in conformational freedom of the substrate resulting from its interactions with the enzyme. The coumarin derivatives were the model compounds chosen to demonstrate this process. Milstien & Cohen (1972) and Borchardt & Cohen (1972) described the influence of substituents – three methyl groups – restricting the freedom of conformational changes of a side chain with acid group and so promoting rapid lactonization. To support their work, two X-ray diffraction studies on the structures of pentamethyl-*o*-hydroxydihydrocinnamyl alcohol and of 4,4,5,7,8-pentamethyldihydrocoumarin were carried out by Karle & Karle (1972). The present study was intended to supply additional structural data for the studies on stereopopulation control as well as to study the influence of substituents on minor conformational changes.

Experimental. Crystals suitable for X-ray analysis were obtained from an ethanol–acetone solution. They were colourless elongated prisms. The crystal used for data collection was a piece cut off a larger crystal, its dimensions being 0·3 × 0·3 × 0·3 mm. It was mounted on a CAD-4 diffractometer, and graphite-monochromated Mo $K\alpha$ radiation was used. The unit-cell parameters were determined by a least-squares fit to 16 automatically centred reflections ($12·0 \le 2\theta \le 31·0°$). The 2θ–θ scan method was applied with a variable scan speed ranging between 2·0 and 20·0° min^{-1} depending

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on reflection intensity. Out to $2\theta = 54{\cdot}0°$ $[(\sin\theta)/\lambda = 0{\cdot}64\ \text{Å}^{-1}]$ 5188 reflections were measured including equivalent and control reflections, Miller indices: h 0/12, k −13/13, l −14/14. Two intensity control reflections monitored every 2 h showed no systematic variation in intensity. 3105 unique reflections with $I \geq 1{\cdot}96\sigma(I)$ were considered observed; they were corrected for Lp effects only.

The structure was solved by direct methods (Sheldrick, 1984), refined isotropically to $R = 0{\cdot}15$ and anisotropically to $R = 0{\cdot}075$, then all the H atoms of two independent molecules were located on a difference Fourier map; the H atoms were included in the refinement with isotropic temperature factors. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = \sigma^{-1}(F_o)$. Six strong low-angle reflections with $(F_o - F_c)/\sigma(F_o) \geq 6{\cdot}0$ were excluded from the final cycles of the refinement. For 3099 reflections final $R = 0{\cdot}045$, $wR = 0{\cdot}039$ and $S = 1{\cdot}5$. The maximum and minimum peaks on the difference Fourier map for the final model were 0·17 and −0·17 e Å^{-3}, the largest change in the last cycle of refinement was 0·009 Å in the y coordinate of H(143) corresponding to shift/σ of 0·25, the largest shift/σ for non-hydrogen atoms was 0·05. The structure was refined using *SHELX*76 (Sheldrick, 1976) on an ICL-2900 computer; atomic scattering factors from *International Tables for X-ray Crystallography* (1974) were applied. The final atomic parameters are listed in Table 1.*

Discussion. The asymmetric part of the unit cell of the crystal contains two independent molecules, hereafter referred to as molecules (*a*) and (*b*). A stereoscopic view of molecule (*a*) with its atom labelling is presented in Fig. 1. The bond lengths and valency angles of the two molecules are listed in Table 2. All the corresponding bond lengths in molecules (*a*) and (*b*) are in good agreement, except for bond C(6)—N, for which the standardized difference $[d(a) - d(b)]/\sigma$ is 3·73 [here $d(a)$ and $d(b)$ are corresponding bond lengths in molecule (*a*) and (*b*) and σ is the combined standard deviation of their difference]. No statistically significant differences between molecules (*a*) and (*b*) were found for the valency angles. The torsion angles, describing the conformation of the molecules, are listed in Table 3. They show differences of up to almost 7° between the corresponding torsion angles of the two molecules reflecting the influence of intermolecular forces on their geometry (Katrusiak & Kałuski, 1981). These differences are highly statistically significant and provide valuable additional information about the

Table 1. *Fractional coordinates of atoms with e.s.d.'s, and isotropic or equivalent isotropic thermal parameters*

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

	x	y	z	U/U_{eq}(Å^2)
Molecule (*a*)				
O(1)	0·69170 (16)	0·23952 (15)	0·67973 (13)	0·057
C(2)	0·8067 (3)	0·30314 (23)	0·72806 (22)	0·058
O(2)	0·81656 (20)	0·31763 (18)	0·82884 (15)	0·083
C(3)	0·9075 (3)	0·34902 (23)	0·64773 (21)	0·059
C(4)	0·93246 (23)	0·25304 (20)	0·55208 (18)	0·048
C(11)	1·0313 (3)	0·3214 (3)	0·4749 (3)	0·068
C(12)	0·9985 (4)	0·1528 (3)	0·6017 (3)	0·075
C(10)	0·79394 (23)	0·20348 (18)	0·49662 (18)	0·044
C(5)	0·77209 (25)	0·15298 (19)	0·38486 (19)	0·049
C(13)	0·8849 (3)	0·1241 (3)	0·30821 (25)	0·066
C(6)	0·6381 (3)	0·12419 (20)	0·34146 (20)	0·056
N	0·6201 (4)	0·07571 (23)	0·22722 (21)	0·075
C(7)	0·5261 (3)	0·13708 (21)	0·40820 (22)	0·057
C(14)	0·3841 (4)	0·1035 (4)	0·3577 (4)	0·082
C(8)	0·54713 (25)	0·17872 (20)	0·52145 (20)	0·053
C(15)	0·4314 (3)	0·1911 (4)	0·5995 (3)	0·074
C(9)	0·68008 (24)	0·20964 (19)	0·56154 (19)	0·048
Molecule (*b*)				
O(1)	0·19860 (14)	0·38391 (14)	0·21536 (12)	0·050
C(2)	0·09377 (24)	0·39024 (20)	0·14431 (20)	0·050
O(2)	−0·01381 (16)	0·40470 (16)	0·18437 (15)	0·068
C(3)	0·1242 (3)	0·3785 (3)	0·02316 (21)	0·058
C(4)	0·21464 (23)	0·28048 (23)	−0·00927 (18)	0·051
C(11)	0·2407 (4)	0·2887 (5)	−0·13478 (25)	0·090
C(12)	0·1394 (4)	0·1572 (3)	0·0088 (4)	0·080
C(10)	0·34215 (21)	0·30918 (19)	0·06736 (17)	0·040
C(5)	0·47227 (22)	0·28332 (20)	0·03991 (17)	0·045
C(13)	0·5012 (3)	0·2020 (4)	−0·0628 (3)	0·073
C(6)	0·58334 (21)	0·32926 (20)	0·11289 (18)	0·043
N	0·71256 (21)	0·30411 (21)	0·08159 (20)	0·060
C(7)	0·56486 (21)	0·38994 (18)	0·21818 (17)	0·039
C(14)	0·6841 (3)	0·4343 (3)	0·29855 (25)	0·054
C(8)	0·43394 (21)	0·40593 (19)	0·25017 (17)	0·039
C(15)	0·4065 (3)	0·4600 (3)	0·36658 (22)	0·056
C(9)	0·32820 (20)	0·36749 (19)	0·17357 (17)	0·039
Molecule (*a*): H atoms				
H(31)	0·9914 (22)	0·3856 (18)	0·6880 (18)	0·054 (6)
H(32)	0·8671 (21)	0·4197 (20)	0·6122 (18)	0·060 (7)
H(111)	1·106 (3)	0·3705 (23)	0·5232 (21)	0·082 (9)
H(112)	0·987 (3)	0·371 (3)	0·425 (3)	0·105 (12)
H(113)	1·081 (3)	0·259 (3)	0·4262 (24)	0·097 (10)
H(121)	0·932 (3)	0·1125 (22)	0·6566 (21)	0·074 (7)
H(122)	1·016 (3)	0·0913 (24)	0·5409 (24)	0·096 (10)
H(123)	1·083 (3)	0·1857 (23)	0·6439 (23)	0·087 (9)
H(131)	0·859 (3)	0·0484 (23)	0·2602 (21)	0·080 (9)
H(132)	0·907 (3)	0·1862 (23)	0·2570 (22)	0·081 (9)
H(133)	0·972 (3)	0·1131 (22)	0·3517 (21)	0·078 (9)
H(N1)	0·538 (3)	0·076 (3)	0·205 (3)	0·099 (12)
H(N2)	0·691 (3)	0·109 (3)	0·175 (3)	0·138 (15)
H(141)	0·372 (3)	0·029 (3)	0·320 (3)	0·111 (13)
H(142)	0·368 (3)	0·152 (3)	0·295 (3)	0·131 (14)
H(143)	0·314 (4)	0·112 (3)	0·411 (3)	0·144 (17)
H(151)	0·380 (4)	0·126 (3)	0·610 (3)	0·124 (15)
H(152)	0·455 (4)	0·235 (4)	0·665 (4)	0·172 (20)
H(153)	0·361 (4)	0·239 (3)	0·567 (3)	0·136 (14)
Molecule (*b*): H atoms				
H(31)	0·0362 (23)	0·3621 (19)	−0·0201 (19)	0·063 (7)
H(32)	0·1734 (25)	0·4613 (22)	0·0036 (20)	0·078 (9)
H(111)	0·308 (4)	0·354 (3)	−0·146 (3)	0·124 (16)
H(112)	0·156 (3)	0·3011 (24)	−0·1720 (23)	0·095 (10)
H(113)	0·268 (3)	0·213 (3)	−0·173 (3)	0·101 (12)
H(121)	0·120 (3)	0·1489 (24)	0·0838 (23)	0·079 (8)
H(122)	0·192 (3)	0·0927 (24)	−0·0158 (22)	0·084 (11)
H(123)	0·052 (3)	0·1450 (23)	−0·0419 (23)	0·096 (10)
H(131)	0·424 (3)	0·1513 (22)	−0·0896 (20)	0·068 (8)
H(132)	0·571 (3)	0·1464 (23)	−0·0450 (22)	0·092 (10)
H(133)	0·533 (3)	0·258 (3)	−0·127 (3)	0·111 (12)
H(N1)	0·7274 (24)	0·3013 (21)	0·0083 (21)	0·066 (8)
H(N2)	0·7878 (25)	0·3452 (20)	0·1191 (20)	0·067 (8)
H(141)	0·680 (3)	0·512 (3)	0·3377 (25)	0·108 (11)
H(142)	0·700 (3)	0·381 (3)	0·353 (3)	0·136 (14)
H(143)	0·766 (4)	0·453 (3)	0·266 (3)	0·133 (15)
H(151)	0·313 (3)	0·4510 (23)	0·3839 (22)	0·087 (10)
H(152)	0·451 (3)	0·422 (3)	0·425 (3)	0·115 (12)
H(153)	0·439 (3)	0·540 (3)	0·3749 (25)	0·100 (12)

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* Lists of structure factors, anisotropic thermal parameters and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51292 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

flexibility of the molecule – the largest changes occur for the torsion angles involving the O atoms and methyl C atom C(15), which is the least rigid part of the molecule. No significant differences between the torsion angles involving the N atoms were found; moreover, even the torsion angles involving the H atoms bonded to N are almost the same: C(5)—C(6)—N—H(N2) is −36 (2)° for molecule (*a*) and −35 (2)° for molecule (*b*) and C(7)—C(6)—N—H(N2) is 15 (2) and 18 (2)° for molecules (*a*) and (*b*), respectively. A distinct difference, however, has been found in the intermolecular contacts of these N atoms. While the shortest intermolecular contacts of atom N(*a*) ['*a*' denotes the atoms of molecule (*a*), '*b*' of molecule (*b*)] are: N(*a*)···N(*b*) 3·268 (4) and N(*a*)···C(6*b*) 3·319 (4) Å, and so indicate only van der Waals interactions, the intermolecular contacts of the H atoms of N(*b*) are significantly shorter than the sums of the appropriate van der Waals radii (Bondi, 1964; Nyburg & Faerman, 1985). Distance N(*b*)···O($2b^{\mathrm{i}}$) (superscript 'i' denotes translation [100]) at 2·995 (3) Å is only slightly shorter than the sum of the van der Waals radii for O and N and the distance between N(*b*) and O(2*a*), 3·213 (3) Å, is only slightly longer than this sum. However, the H···O distances, H(N1*b*)···O(2*a*) of 2·34 (2) and H(N2*b*)···O($2b^{\mathrm{i}}$) of 2·11 (2) Å, are shorter than the sum of the van der Waals radii for H and O and clearly can be regarded as hydrogen bonds (Taylor & Kennard, 1983). This conclusion is corroborated by obtuse angles N(*b*)—H(N1*b*)···O(2*a*) of 167 (1) and N(*b*)—H(N2*b*)···O($2b^{\mathrm{i}}$) of 165 (1)°. Because no hydrogen bonds are observed for N(*a*), any statistically significant difference in the lengths of the C(6)—N bonds can be attributed to differences in the intermolecular interactions of these two N atoms. C(6*b*)—N(*b*) is shorter by 0·018 (5) Å than C(6*a*)—N(*a*), where, as explained above, N(*b*) is involved in hydrogen bonding whereas N(*a*) is not. The arrangement of the molecules in the crystal is shown in Fig. 2.

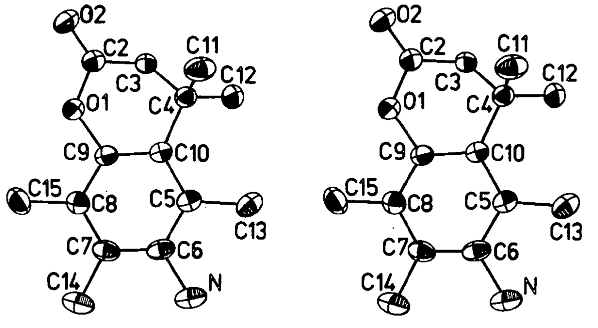

Fig. 1. *ORTEP* (Johnson, 1970) stereodiagram of molecule (*a*) viewed perpendicular to the phenyl ring. H atoms have been omitted for clarity. The thermal ellipsoids are drawn at 50% probability level.

Table 2. *Bond distances* (Å) *and valency angles* (°)

	(*a*)	(*b*)		(*a*)	(*b*)
O(1)—C(2)	1·353 (3)	1·342 (3)	C(10)—C(9)	1·387 (3)	1·386 (3)
O(1)—C(9)	1·416 (3)	1·416 (2)	C(5)—C(13)	1·506 (4)	1·509 (4)
C(2)—O(2)	1·197 (3)	1·201 (3)	C(5)—C(6)	1·404 (4)	1·403 (3)
C(2)—C(3)	1·476 (4)	1·478 (3)	C(6)—N	1·416 (3)	1·398 (3)
C(3)—C(4)	1·537 (3)	1·532 (4)	C(6)—C(7)	1·394 (4)	1·396 (3)
C(4)—C(11)	1·539 (4)	1·532 (5)	C(7)—C(14)	1·510 (5)	1·510 (3)
C(4)—C(12)	1·529 (4)	1·519 (4)	C(7)—C(8)	1·388 (3)	1·390 (3)
C(4)—C(10)	1·528 (3)	1·528 (3)	C(8)—C(15)	1·503 (4)	1·505 (3)
C(10)—C(5)	1·399 (3)	1·398 (3)	C(8)—C(9)	1·384 (3)	1·376 (3)
C(2)—O(1)—C(9)	120·7 (2)	120·6 (2)	C(10)—C(5)—C(6)	118·9 (2)	119·7 (2)
O(1)—C(2)—O(2)	118·3 (2)	117·8 (2)	C(13)—C(5)—C(6)	117·5 (2)	116·7 (2)
O(1)—C(2)—C(3)	114·8 (2)	115·5 (2)	C(5)—C(6)—N	117·3 (2)	118·2 (2)
O(2)—C(2)—C(3)	126·9 (2)	126·7 (2)	C(5)—C(6)—C(7)	122·1 (2)	121·2 (2)
C(2)—C(3)—C(4)	113·2 (2)	113·5 (2)	N—C(6)—C(7)	120·6 (3)	120·4 (2)
C(3)—C(4)—C(11)	104·6 (2)	105·1 (3)	C(6)—C(7)—C(14)	120·0 (3)	121·0 (2)
C(3)—C(4)—C(12)	109·1 (2)	109·6 (2)	C(6)—C(7)—C(8)	119·2 (2)	119·1 (2)
C(3)—C(4)—C(10)	106·9 (2)	106·7 (2)	C(14)—C(7)—C(8)	120·8 (2)	119·9 (2)
C(11)—C(4)—C(12)	110·5 (2)	110·3 (2)	C(7)—C(8)—C(15)	122·2 (2)	121·4 (2)
C(11)—C(4)—C(10)	114·4 (2)	114·4 (2)	C(7)—C(8)—C(9)	117·6 (2)	118·3 (2)
C(12)—C(4)—C(10)	111·0 (2)	110·6 (2)	C(15)—C(8)—C(9)	120·1 (2)	120·2 (2)
C(4)—C(10)—C(5)	125·3 (2)	126·0 (2)	O(1)—C(9)—C(10)	121·5 (2)	121·3 (2)
C(4)—C(10)—C(9)	117·7 (2)	117·2 (2)	O(1)—C(9)—C(8)	113·5 (2)	114·0 (2)
C(5)—C(10)—C(9)	117·0 (2)	116·8 (2)	C(10)—C(9)—C(8)	124·8 (2)	124·5 (2)
C(10)—C(5)—C(13)	123·6 (2)	123·6 (2)			

Table 3. *Torsion angles* (°)

The signs of all the tabulated values within either column may be reversed due to the centrosymmetry of the space group $P\bar{1}$.

	(*a*)	(*b*)
C(9)—O(1)—C(2)—O(2)	−173·8 (2)	−179·7 (2)
C(9)—O(1)—C(2)—C(3)	6·9 (3)	0·2 (3)
C(2)—O(1)—C(9)—C(10)	23·6 (3)	−27·1 (3)
C(2)—O(1)—C(9)—C(8)	−161·3 (2)	157·4 (2)
O(1)—C(2)—C(3)—C(4)	−46·7 (3)	41·7 (3)
O(2)—C(2)—C(3)—C(4)	134·0 (3)	−138·4 (3)
C(2)—C(3)—C(4)—C(11)	176·1 (2)	−176·6 (2)
C(2)—C(3)—C(4)—C(12)	−65·7 (3)	64·9 (3)
C(2)—C(3)—C(4)—C(10)	54·4 (3)	−54·8 (3)
C(3)—C(4)—C(10)—C(5)	153·6 (2)	−149·5 (2)
C(3)—C(4)—C(10)—C(9)	−25·8 (3)	29·7 (3)
C(11)—C(4)—C(10)—C(5)	38·4 (3)	−33·7 (3)
C(11)—C(4)—C(10)—C(9)	−141·1 (3)	145·5 (3)
C(12)—C(4)—C(10)—C(5)	−87·5 (3)	91·5 (3)
C(12)—C(4)—C(10)—C(9)	93·1 (3)	−89·3 (3)
C(4)—C(10)—C(5)—C(13)	9·2 (4)	−11·8 (4)
C(4)—C(10)—C(5)—C(6)	−172·6 (2)	171·5 (2)
C(9)—C(10)—C(5)—C(13)	−171·3 (2)	169·0 (2)
C(9)—C(10)—C(5)—C(6)	6·9 (3)	−7·7 (3)
C(4)—C(10)—C(9)—O(1)	−11·4 (3)	9·0 (3)
C(4)—C(10)—C(9)—C(8)	174·0 (2)	−176·1 (2)
C(5)—C(10)—C(9)—O(1)	169·1 (2)	−171·7 (2)
C(5)—C(10)—C(9)—C(8)	−5·5 (3)	3·2 (3)
C(10)—C(5)—C(6)—N	178·6 (2)	−178·5 (2)
C(10)—C(5)—C(6)—C(7)	−4·2 (4)	6·7 (3)
C(13)—C(5)—C(6)—N	−3·0 (4)	4·5 (3)
C(13)—C(5)—C(6)—C(7)	174·1 (2)	−170·3 (2)
C(5)—C(6)—C(7)—C(14)	−179·3 (3)	177·3 (2)
C(5)—C(6)—C(7)—C(8)	−0·5 (4)	−0·7 (3)
N—C(6)—C(7)—C(14)	−2·2 (4)	2·6 (3)
N—C(6)—C(7)—C(8)	176·5 (2)	−175·4 (2)
C(6)—C(7)—C(8)—C(15)	−178·0 (3)	174·2 (2)
C(6)—C(7)—C(8)—C(9)	2·2 (4)	−3·9 (3)
C(14)—C(7)—C(8)—C(15)	0·8 (4)	−3·8 (3)
C(14)—C(7)—C(8)—C(9)	−179·0 (3)	178·1 (2)
C(7)—C(8)—C(9)—O(1)	−174·1 (2)	177·9 (2)
C(7)—C(8)—C(9)—C(10)	0·8 (4)	2·6 (3)
C(15)—C(8)—C(9)—O(1)	6·1 (3)	−0·1 (3)
C(15)—C(8)—C(9)—C(10)	−179·0 (3)	−175·4 (2)

The torsion angles for the molecules of (I) are listed in Table 3. The conformation of the lactone ring can be described as strongly distorted and intermediate between half-chair and sofa. The asymmetry parameters (Duax & Norton, 1975) help to classify it as a sofa strongly distorted towards half-chair for molecule (*a*) –

$\Delta C_s^3 = 13{\cdot}7$, $\Delta C_2^{3,4} = 19{\cdot}6°$ – and as a half-chair strongly distorted towards sofa for molecule (*b*) – $\Delta C_2^{3,4} = 10{\cdot}4$, $\Delta C_s^3 = 21{\cdot}6°$. A similar conformation, intermediate between half-chair and sofa, was also observed for the lactone ring in the structure of 4,4,5,7,8-pentamethyldihydrocoumarin (hereafter referred to as II) described by Karle & Karle (1972). The distortions from the ideal value of 120° of the valency angles within the phenyl ring are very similar in both molecules (*a*) and (*b*) of (I) – they agree within 0·7° – and similar (in the same direction but somewhat smaller in magnitude) to those observed in the phenyl ring of (II). Also the distortions of valency angles outside the phenyl ring are very similar in (I) and (II). As was suggested by Karle & Karle (1972) these distortions provide additional space to accommodate the overcrowded methyl groups C(11), C(12) and C(13). Despite the strong angular distortions in the phenyl rings their planarity has been relatively little affected: the χ^2 values for the least-squares planes fitted to the atoms in the phenyl ring are 320·6 for molecule (*a*) and 499·3 for molecule (*b*), the largest departure from planarity being 0·056 (2) Å for C(10*a*) and 0·055 (2) Å for C(10*b*). Atoms O(1), C(4), C(13), N, C(14) deviate by 0·001 (3) [C(14*b*)] to 0·226 (4) Å [C(13*b*)] from the plane of the phenyl ring. Atom C(4*a*) is 0·205 (2) Å and C(4*b*) 0·200 (2) Å above this plane and atom C(13*a*) is –0·151 (3) Å and C(13*b*) –0·226 (4) Å below it. The significance of the restrictions imposed on the conformation of the molecule by the interlocking of the two CH_3 groups at C(11) and C(12) with the CH_3 group at C(13) can be assessed by comparing the displacements of atoms C(11) and C(12) from the phenyl-ring plane. In structure (I) atoms C(11) and C(12) are almost equidistant from this plane: C(11*a*) and C(12*a*) are displaced from it by 1·141 (3) and –1·160 (4) Å and C(11*b*) and C(12*b*) by 1·033 (4) and –1·164 (4) Å, respectively. However, in the structure of (II) the distances of atoms C(11) and C(12) to the phenyl-ring plane are 0·85 and –1·35 Å, respectively, thus significantly different for each of these atoms [the relevant torsion angles are C(5)–C(10)–C(4)–C(11) –45 and C(5)–C(10)–C(4)–C(12) 94°]. Even larger differences in the distances of C(11)* and C(12)* from the phenyl-ring plane were observed in the structure of pentamethyl-*o*-hydroxyhydrocinnamic acid (hereafter III). Its four symmetry-independent molecules in the crystal have a very similar conformation in which atom C(12)* is from 1·28 to 1·54 Å above the plane and C(11)* is much closer to this plane: from –0·365 to –0·116 Å below it (Karle & Karle, 1972). Thus the comparison of structures (I), (II) and (III) confirms the conclusion of Karle & Karle (1972) that the barrier imposed by the 'trialkyl lock' [C(11), C(12) and C(13)] is not severe and allows some conformational freedom in these structures.

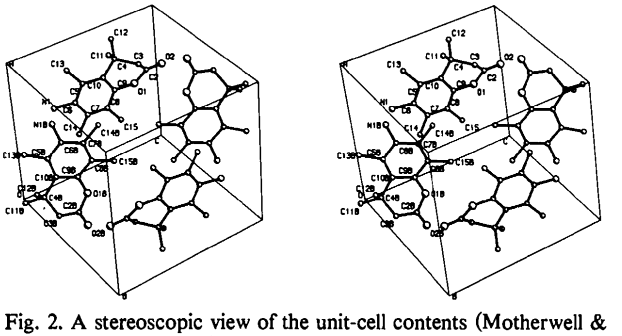

Fig. 2. A stereoscopic view of the unit-cell contents (Motherwell & Clegg, 1978). H atoms are omitted for clarity.

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* The atom-numbering of (I) has been adapted, for the sake of clarity, to other compounds discussed and compared in this paper.

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