

(Charbonnier, Faure & Loiseleur, 1977), 1,451 (3) et 1,460 (4) Å dans la glycyllaurine (Garrigou-Lagrange, Jensen & Cotrait, 1977). La liaison S—C [1,770 (4) Å] est aussi comparable aux liaisons S—C rencontrées dans les trois composés cités. Celles-ci sont comprises entre 1,748 (6) et 1,781 (4) Å. N(4)—C(5) [1,375 (4) Å] et N(4)—C(8) [1,384 (4) Å] expriment la conjugaison du doublet non partagé de N(4) avec les électrons π de C(8)—O(9) et de C(5)—O(13). La longueur de C(6)—N(14) [1,480 (5) Å], relativement grande par rapport à celle de C(3)—N(4) [1,442 (5) Å], paraît en relation avec la charge positive portée par le groupement —NH₃. La longueur moyenne calculée par Allen, Kennard, Watson, Brammer, Orpen & Taylor (1987) pour ce type de liaison est de 1,488 (13) Å. Les deux distances C—O et les différentes distances C—C peuvent être considérées comme normales.

Trois liaisons hydrogène N—H...O et deux liaisons O—H...O participent à la cohésion de la structure. Les premières sont réalisées par N(14), les secondes par O(15). Ces liaisons ont été représentées sur la Fig. 1. Leurs longueurs et leurs angles sont indiqués dans le Tableau 2. La Fig. 2 montre une vue suivant [001] de la structure.

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Structure of 6-Chloro-4,4,5,7-tetramethyldihydrocoumarin

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Abstract. C₁₃H₁₅ClO₂, $M_r = 238.71$, monoclinic, $P2_1/c$, $a = 18.818$ (1), $b = 8.6481$ (9), $c = 28.450$ (3) Å, $\beta = 93.181$ (8)°, $V = 4622.8$ (2) Å³, $Z = 16$, $D_x = 1.37$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 2.51$ cm⁻¹, $F(000) = 2016$, $T = 292$ K. The final $R = 0.048$ for 4285 observed reflections. The conformation of the lactone ring in the four independent molecules is intermediate between half-chair and sofa and very similar to the conformation observed in 4,4,5,7,8-pentamethyldihydrocoumarin and in 6-amino-4,4,5,7,8-pentamethyldihydrocoumarin. In both those compounds and in the four independent molecules of the title compound similar large distortions of valency angles occur in the phenyl rings, presumably to accommodate the overmethylation. Two of the four independent molecules show partial disorder in the conformations adopted by the lactone rings. A non-

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crystallographic pseudo-symmetry centre links molecule (a) with (b), and (c) with (d).

Introduction. The determination of the crystal structure of 6-chloro-4,4,5,7-tetramethyldihydrocoumarin [hereinafter referred to as (I)] continues the studies of the coumarin derivatives on the aspects of their conformation and of the influence of substituents and intermolecular interactions on minor conformational changes. Milstien & Cohen (1972) used this group of compounds for their studies on stereopopulation control and its role in enzyme-catalysed reactions. The rate of enhancement in such reactions often exceeds 10¹⁰ or even 10¹⁸. The restriction on conformational freedom – resulting from the interactions of the substrate with the enzyme – is one of the numerous factors which make such rate enhancement possible. The coumarin deriva-

tives were chosen as model structures to demonstrate the importance of conformational restrictions in the reactions of lactonization, by Milstien & Cohen (1972) and Borchardt & Cohen (1972*a,b*). They described the influence of substituents – the methyl groups at C(4) and C(5) (see Fig. 1)* – closely located in the molecule and restricting the conformational changes of the side chain, on the rate of lactonization of *o*-hydroxydihydrocinnamic acid. They found that these restrictions enhance the rate of the reaction by over 10^{11} . Two X-ray structure determinations have been carried out to support their experiments: of 4,4,5,7,8-pentamethyldihydrocoumarin and of pentamethyl-*o*-hydroxydihydrocinnamic alcohol (Karle & Karle, 1972), and it was found that the conformational restrictions imposed by the methyl groups at C(4) and C(5) are not as severe as it was originally expected; this conclusion was also confirmed by the structural study of 6-amino-4,4,5,7,8-pentamethyldihydrocoumarin (Katrusiak, 1989).

Experimental. Crystals of (I) used in this X-ray diffraction study were obtained from ethanol solution by slow evaporation. The space group and unit-cell parameters were determined by the precession method. The crystal used for data collection was a colourless plate $0.3 \times 0.3 \times 0.2$ mm; the measurements were performed with a CAD-4 diffractometer and Mo $K\alpha$ graphite-monochromated radiation. Unit-cell parameters from the least-squares fit to 20 automatically centred reflections ($11.0 < 2\theta < 22.0^\circ$). 2θ - θ scan method, variable scan speed 2.0 – $20.0^\circ \text{ min}^{-1}$ depending on reflection intensity. 6643 reflections up to $2\theta = 60^\circ$ ($\sin\theta/\lambda = 0.713 \text{ \AA}^{-1}$) were measured – the half-hemisphere of data comprising the reflections with indices $h - 20/20$, $k 0/10$, $l 0/37$; no systematic variation in intensity was observed for four control reflections measured every four hours. Only the Lp corrections were applied; 4285 reflections had $I \geq 1.96\sigma(I)$ and were considered observed. The structure was solved with *SHELX76* (Sheldrick, 1976) and refined with anisotropic thermal parameters; all H atoms were located from difference Fourier maps and included in the refinement with isotropic thermal parameters. This

* The atom labelling of the title compound has been adapted, for the sake of clarity, to other structures discussed in this paper.

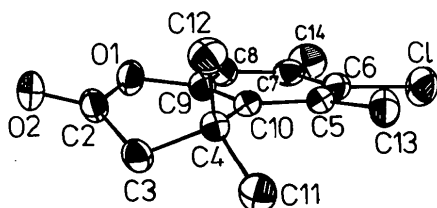


Fig. 1. An ORTEP (Johnson, 1970) view of molecule (a) at 50% probability level. The H atoms are omitted for clarity.

model converged to $R = 0.072$. Then it was noted that atoms C(3), C(11) and C(12) of molecules (c) and (d) [the four independent molecules of (I) are referred to as (a), (b), (c) and (d)] have large vibrational parameters perpendicular to their bonds and that in molecules (c) and (d) there were peaks opposite to C(3) with respect to the lactone ring plane; these peaks were about 1.5 \AA from C(2) and C(4) and it was assumed that they correspond to atoms C(3) of molecules (c) and (d) disordered into the opposite sides of the lactone ring – this was corroborated by finding additional ΔF peaks corresponding to the partly occupied positions of methyl C atoms C(11) and C(12), which are coupled with the positions of disordered C(3). The disordered atoms, corresponding to the ‘reverse’ conformation of the lactone rings of molecules (c) and (d), were included in the refinement with isotropic temperature factors. Their site-occupation factors, one for molecule (c) and one for molecule (d), were defined as $(1.0-k)$, where k is the site-occupation factor common for atoms C(3), C(11) and C(12) of one molecule. The k values refined to 0.059 (11) for molecule (c) and 0.185 (9) for molecule (d). As the site-occupation factors of the atoms of the ‘reverse’ conformation of the lactone rings were relatively small it was not attempted to refine them with anisotropic temperature factors or to insert the (disordered) H atoms for the ‘reverse’ conformation. It was not possible to distinguish any separate peaks on ΔF maps, which would correspond to the disordered positions of atoms O(1), C(2) and O(2) or to any other atoms in molecules (c) and (d). The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(F_o) + 0.000235F_o^2]^{-1}$. At final convergence: $R = 0.048$, $wR = 0.048$, $S = 1.1$, $(\Delta/\sigma)_{\text{max}} = 0.25$ for non-H atoms; highest and lowest peaks on the final ΔF map: 0.19 and -0.24 e \AA^{-3} , respectively. Most of the calculations were performed with *SHELX76* (Sheldrick, 1976) on an ICL2900 computer, the atomic scattering factors were from *International Tables for X-ray Crystallography* (1974). The final atomic parameters are listed in Table 1.*

Discussion. A view of the molecule of (I) is presented in Fig. 1. The asymmetric part of the unit cell contains four independent molecules, two of which, (c) and (d), have lactone rings disordered into two conformations with atoms C(3) stretching out at the opposite sides of the rings. In both these molecules the disordered atoms are well resolved and the site-occupation factors of one conformation are significantly larger than the other. The positions of the atoms with the site-occupation

* 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 51768 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates of the non-H atoms and their U_{eq}

The letters added to the atom numbers denote molecules (a), (b), (c) and (d); letters 'E' and 'F' denote the disordered atoms: U_{iso} and its e.s.d.'s are given for these atoms.

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	$U(\text{\AA}^2)$
O(1A)	0.35198 (10)	0.4488 (3)	0.20713 (7)	0.064
C(2A)	0.29274 (17)	0.4534 (4)	0.22904 (11)	0.060
O(2A)	0.29660 (12)	0.4720 (3)	0.27098 (7)	0.077
C(3A)	0.23121 (16)	0.4403 (4)	0.19763 (11)	0.060
C(4A)	0.23441 (15)	0.3116 (4)	0.16091 (10)	0.050
C(11A)	0.23502 (17)	0.1538 (4)	0.18567 (12)	0.068
C(12A)	0.16875 (15)	0.3288 (4)	0.12991 (11)	0.067
C(10A)	0.29974 (15)	0.3356 (4)	0.13563 (10)	0.045
C(5A)	0.31086 (15)	0.2854 (4)	0.08984 (10)	0.048
C(13A)	0.26179 (18)	0.1811 (4)	0.06203 (11)	0.071
C(6A)	0.37041 (17)	0.3280 (4)	0.07009 (11)	0.059
Cl(1A)	0.38387 (5)	0.2736 (1)	0.01179 (3)	0.094
C(7A)	0.42261 (16)	0.4085 (4)	0.09350 (11)	0.059
C(14A)	0.48661 (18)	0.4563 (5)	0.07059 (13)	0.089
C(8A)	0.41212 (16)	0.4476 (4)	0.13971 (12)	0.060
C(9A)	0.35241 (15)	0.4107 (4)	0.15921 (10)	0.051
O(1B)	0.15141 (10)	0.8145 (3)	0.29632 (7)	0.063
C(2B)	0.21040 (16)	0.8080 (4)	0.27486 (11)	0.055
O(2B)	0.20820 (11)	0.7895 (3)	0.23326 (7)	0.074
C(3B)	0.27174 (16)	0.8192 (4)	0.30679 (11)	0.059
C(4B)	0.26852 (15)	0.9432 (4)	0.34537 (10)	0.049
C(11B)	0.2688 (2)	1.1021 (4)	0.32154 (12)	0.072
C(12B)	0.33367 (16)	0.9207 (4)	0.37637 (12)	0.068
C(10B)	0.20258 (14)	0.9194 (3)	0.36989 (10)	0.045
C(5B)	0.18943 (16)	0.9661 (4)	0.41613 (10)	0.056
C(13B)	0.23847 (18)	1.0620 (5)	0.44525 (12)	0.079
C(6B)	0.12794 (17)	0.9238 (4)	0.43387 (10)	0.058
Cl(1B)	0.11436 (5)	0.9711 (2)	0.49237 (3)	0.098
C(7B)	0.07706 (16)	0.8457 (4)	0.40858 (11)	0.060
C(14B)	0.01186 (18)	0.8031 (5)	0.42862 (12)	0.087
C(8B)	0.08882 (15)	0.8116 (4)	0.36286 (11)	0.057
C(9B)	0.14907 (15)	0.8491 (4)	0.34457 (10)	0.049
O(1C)	0.10788 (11)	0.3410 (3)	0.28588 (7)	0.065
C(2C)	0.04979 (18)	0.3226 (4)	0.25956 (12)	0.063
O(2C)	0.05285 (12)	0.2749 (3)	0.22027 (8)	0.081
C(3C)	-0.0108 (2)	0.3770 (4)	0.28241 (12)	0.064
C(3F)	0.003 (2)	0.190 (6)	0.2908 (15)	0.036 (11)
C(4C)	-0.01563 (16)	0.3150 (4)	0.33304 (11)	0.058
C(11C)	-0.0255 (2)	0.1407 (5)	0.33129 (15)	0.088
C(11F)	-0.060 (3)	0.444 (7)	0.320 (2)	0.049 (14)
C(12C)	-0.0769 (2)	0.3996 (6)	0.35141 (15)	0.085
C(12F)	-0.076 (5)	0.237 (12)	0.372 (3)	0.14 (3)
C(10C)	0.05112 (15)	0.3585 (4)	0.35974 (10)	0.050
C(5C)	0.06051 (17)	0.3794 (4)	0.40846 (11)	0.060
C(13C)	0.0080 (2)	0.3388 (6)	0.44211 (12)	0.093
C(6C)	0.12210 (18)	0.4352 (4)	0.42658 (10)	0.062
Cl(1C)	0.13324 (5)	0.4746 (2)	0.48665 (3)	0.101
C(7C)	0.17729 (17)	0.4620 (4)	0.39970 (12)	0.062
C(14C)	0.2445 (2)	0.5180 (5)	0.42019 (13)	0.082
C(8C)	0.16826 (16)	0.4292 (4)	0.35246 (11)	0.057
C(9C)	0.10712 (16)	0.3794 (4)	0.33376 (10)	0.052
O(1D)	0.38758 (12)	0.9029 (3)	0.21310 (8)	0.071
C(2D)	0.4449 (2)	0.9281 (5)	0.23907 (13)	0.072
O(2D)	0.44211 (13)	0.9681 (3)	0.27850 (9)	0.092
C(3D)	0.5075 (2)	0.8736 (5)	0.21651 (15)	0.068
C(3E)	0.4885 (10)	1.0371 (24)	0.2069 (7)	0.067 (5)
C(4D)	0.50938 (16)	0.9378 (4)	0.16517 (12)	0.059
C(11D)	0.5185 (3)	1.1098 (6)	0.1678 (2)	0.090
C(11E)	0.5404 (15)	0.807 (4)	0.1882 (10)	0.116 (9)
C(12D)	0.5723 (2)	0.8536 (7)	0.1474 (2)	0.092
C(12E)	0.5502 (11)	1.079 (3)	0.1374 (8)	0.078 (6)
C(10D)	0.44361 (16)	0.8932 (4)	0.13909 (11)	0.052
C(5D)	0.43332 (17)	0.8699 (4)	0.08958 (11)	0.061
C(13D)	0.4879 (2)	0.9131 (6)	0.05663 (13)	0.109
C(6D)	0.3711 (2)	0.8163 (4)	0.07207 (11)	0.065
Cl(1D)	0.36065 (6)	0.7785 (2)	0.01161 (3)	0.106
C(7D)	0.31645 (17)	0.7881 (4)	0.09913 (12)	0.058
C(14D)	0.2499 (2)	0.7260 (5)	0.07878 (13)	0.084
C(8D)	0.32607 (15)	0.8167 (4)	0.14618 (11)	0.056
C(9D)	0.38732 (16)	0.8686 (4)	0.16488 (10)	0.051

factors closer to unity have been determined with similar accuracy to those of the non-disordered atoms in this structure.

Table 2. Bond lengths (\AA) and valency angles ($^\circ$) for four symmetry independent molecules

	(a)	(b)	(c)	(d)
O(1)–C(2)	1.360 (4)	1.350 (4)	1.348 (4)	1.339 (4)
O(1)–C(9)	1.403 (4)	1.409 (4)	1.403 (4)	1.404 (4)
C(2)–O(2)	1.203 (4)	1.193 (4)	1.197 (4)	1.179 (5)
C(2)–C(3)	1.476 (4)	1.480 (4)	1.474 (5)	1.504 (6)
C(3)–C(4)	1.531 (5)	1.539 (5)	1.546 (5)	1.565 (6)
C(4)–C(11)	1.536 (5)	1.533 (5)	1.520 (6)	1.500 (6)
C(4)–C(12)	1.539 (4)	1.535 (4)	1.535 (5)	1.552 (6)
C(4)–C(10)	1.530 (4)	1.530 (4)	1.536 (4)	1.514 (4)
C(10)–C(5)	1.403 (4)	1.415 (4)	1.400 (4)	1.427 (4)
C(10)–C(9)	1.373 (4)	1.389 (4)	1.379 (4)	1.386 (5)
C(5)–C(4)	1.517 (5)	1.494 (5)	1.495 (5)	1.518 (5)
C(5)–C(6)	1.385 (5)	1.394 (5)	1.386 (5)	1.385 (5)
C(6)–C(1)	1.759 (3)	1.750 (3)	1.745 (3)	1.752 (3)
C(6)–C(7)	1.387 (5)	1.382 (5)	1.389 (5)	1.385 (5)
C(7)–C(14)	1.516 (5)	1.488 (5)	1.504 (5)	1.510 (5)
C(7)–C(8)	1.385 (5)	1.367 (5)	1.376 (5)	1.365 (5)
C(8)–C(9)	1.373 (5)	1.368 (4)	1.366 (4)	1.374 (4)
C(2)–O(1)–C(9)	120.3 (2)	121.8 (2)	120.9 (3)	122.1 (3)
O(1)–C(2)–C(3)	115.2 (3)	115.0 (3)	114.2 (3)	114.2 (3)
O(1)–C(2)–O(2)	116.8 (3)	118.1 (3)	118.3 (3)	119.4 (3)
O(2)–C(2)–C(3)	128.1 (3)	127.0 (3)	127.4 (3)	125.7 (4)
C(2)–C(3)–C(4)	113.9 (3)	114.8 (3)	113.3 (3)	110.6 (3)
C(3)–C(4)–C(10)	106.9 (3)	107.6 (3)	106.3 (3)	107.7 (3)
C(3)–C(4)–C(12)	104.8 (3)	104.8 (3)	104.1 (3)	101.5 (3)
C(3)–C(4)–C(11)	109.5 (3)	108.0 (3)	109.2 (3)	108.4 (3)
C(11)–C(4)–C(10)	115.4 (2)	115.8 (3)	113.1 (3)	114.0 (3)
C(11)–C(4)–C(12)	110.6 (3)	110.4 (3)	111.4 (3)	112.0 (3)
C(11)–C(4)–C(12)	109.6 (3)	110.2 (3)	112.5 (3)	112.7 (4)
C(4)–C(10)–C(9)	118.4 (3)	118.1 (3)	117.7 (3)	118.5 (3)
C(4)–C(10)–C(5)	125.2 (3)	126.4 (3)	125.9 (3)	126.4 (3)
C(5)–C(10)–C(9)	116.6 (3)	115.7 (3)	116.6 (3)	115.3 (3)
C(10)–C(5)–C(6)	118.5 (3)	118.2 (3)	118.7 (3)	118.6 (3)
C(10)–C(5)–C(13)	122.7 (3)	121.9 (3)	123.1 (3)	120.5 (3)
C(13)–C(5)–C(6)	118.9 (3)	120.1 (3)	118.3 (3)	120.8 (3)
C(5)–C(6)–C(7)	124.7 (3)	124.6 (3)	124.0 (3)	124.6 (3)
C(5)–C(6)–C(1)	119.3 (3)	117.9 (3)	119.6 (3)	118.1 (3)
Cl(1)–C(6)–C(7)	116.1 (3)	117.7 (2)	116.6 (2)	117.4 (3)
C(6)–C(7)–C(8)	115.6 (3)	116.4 (3)	116.1 (3)	116.3 (3)
C(6)–C(7)–C(14)	123.4 (3)	123.1 (3)	123.3 (3)	122.9 (3)
C(14)–C(7)–C(8)	121.1 (3)	120.7 (3)	120.7 (3)	120.9 (3)
C(7)–C(8)–C(9)	120.4 (3)	120.7 (3)	120.7 (3)	120.8 (3)
C(10)–C(9)–C(8)	124.2 (3)	124.4 (3)	123.8 (3)	124.5 (3)
O(1)–C(9)–C(8)	113.0 (3)	113.4 (3)	113.4 (3)	113.8 (3)
O(1)–C(9)–C(10)	122.8 (3)	122.3 (3)	122.9 (3)	121.8 (3)

Table 2 lists the bond lengths and valency angles in the molecules. The lengths of the corresponding bonds in the independent molecules show differences up to 4.8 e.s.d.'s [see C(4)–C(11), C(5)–C(10)]; even larger differences are observed for the valency angles – up to 10 e.s.d.'s. These differences sum up the random experimental errors, the systematic errors caused by the disorder of the lactone rings in molecules (c) and (d), and the changes in conformation of the independent molecules caused by their different environments in the crystal lattice. The conformation of the four independent molecules is similar – the largest differences in the torsion angles [up to 8.5 (7)° – about 12 e.s.d.'s] are observed in the least rigid part of the molecule, the lactone ring. Selected torsion angles in the independent molecules are given in Table 3.

The lactone rings have conformations intermediate between half-chair and sofa – their asymmetry parameters (Duax & Norton, 1975) for molecules (a), (b), (c) and (d) are: $\Delta C_s^2 = 12.4$, 13.1, 9.6, 7.0° and $\Delta C_2^2 = 14.1$, 12.3, 17.4, 15.1°, respectively. A similar conformation of the lactone ring was observed in the structures of 4,4,5,7,8-pentamethyldihydrocoumarin

Table 3. Selected torsion angles ($^{\circ}$)

	(a)	(b)	(c)	(d)
C(2)–O(1)–C(9)–C(10)	-18.4 (9)	18.7 (9)	19.2 (9)	-14.6 (9)
C(9)–O(1)–C(2)–C(3)	-8.6 (9)	8.3 (9)	12.5 (9)	-15.9 (9)
O(1)–C(2)–C(3)–C(4)	46.4 (8)	-42.8 (8)	-49.1 (9)	51.6 (9)
O(2)–C(2)–C(3)–C(4)	-136.0 (8)	139.7 (8)	136.0 (8)	-139.8 (9)
C(2)–C(3)–C(4)–C(10)	-51.8 (8)	51.2 (8)	54.8 (8)	-53.5 (9)
C(3)–C(4)–C(10)–C(9)	26.6 (8)	-25.5 (8)	-24.9 (8)	26.2 (9)
C(12)–C(4)–C(10)–C(5)	-38.1 (9)	39.7 (9)	41.5 (9)	-40.5 (9)
C(11)–C(4)–C(10)–C(5)	86.8 (8)	-86.1 (8)	-86.2 (9)	88.8 (9)
C(4)–C(10)–C(9)–O(1)	8.7 (9)	-6.2 (9)	-9.0 (9)	8.9 (9)
C(4)–C(10)–C(5)–C(13)	-7.9 (9)	7.1 (9)	9.9 (10)	-9.1 (10)
C(5)–C(10)–C(9)–C(8)	5.1 (9)	-5.6 (9)	-4.4 (9)	4.2 (9)
C(9)–C(10)–C(5)–C(6)	-5.9 (9)	7.3 (9)	7.4 (9)	-3.5 (9)
C(10)–C(5)–C(6)–C(7)	5.2 (10)	-3.0 (10)	-4.2 (10)	2.8 (10)
C(13)–C(5)–C(6)–C(11)	5.8 (9)	-5.3 (9)	-6.0 (9)	7.9 (9)
C(5)–C(6)–C(7)–C(8)	0.1 (10)	-0.7 (10)	0.2 (10)	0.8 (10)
Cl(1)–C(6)–C(7)–C(14)	3.6 (9)	1.5 (9)	2.1 (9)	1.0 (9)
C(6)–C(7)–C(8)–C(9)	-1.3 (9)	2.8 (9)	3.1 (9)	-0.4 (9)
C(7)–C(8)–C(9)–C(10)	0.2 (10)	2.0 (10)	0.5 (10)	-0.8 (10)

[hereinafter (II)] (Karle & Karle, 1972) and 6-amino-4,4,5,7,8-pentamethyldihydrocoumarin (III) (Katrusiak, 1989). The distances of C(11), C(12) and C(13) from the least-squares plane fitted to the atoms of the phenyl ring, differ only slightly in molecules (a), (b), (c) and (d): C(11) 1.277 (4), 1.287 (4), 1.230 (5) and 1.223 (5) Å; C(12) -1.017 (4), -1.008 (4), -1.072 (5) and -1.088 (6) Å; and C(13) 0.198 (4), 0.174 (4), 0.280 (5) and 0.235 (5) Å, respectively. These distances in structure (II) (disordered structure) are 1.35 Å for C(11), -0.85 Å for C(12) and 0.125 Å for C(13); in two symmetry-independent molecules of (III), C(11) is 1.141 (3) and 1.033 (4) Å off the phenyl-ring plane, C(12) -1.160 (4) and -1.164 (4) Å, and C(13) -0.151 (3) and -0.226 (4) Å, for molecules (IIIa) and (IIIb) respectively. In all these structures atom C(13) is on the same side of the phenyl ring as the methyl C atom at C(4) which is more distant from the plane. In most of the structures, except for molecule (IIIa), atom C(4) inclines to the opposite side of the ring. Molecule (IIIa) has both atoms C(4) and C(13) on the same side of the ring – in that case atoms C(11) and C(12) are almost equidistant from the plane. Similar systematic observations, concerning the positions of the atoms with respect to the phenyl-ring plane, can also be made for other corresponding atoms in these structures – for example it has been noted that atom O(1) in all these structures is on the same side of the phenyl ring as C(13).

Significant deformations have been observed in the valency angles within and without the phenyl ring. They are almost identical in all four independent molecules of (I) and very similar – at least in the directions of departure from ideal 120° – to those observed for (II) and (III). As suggested by Karle & Karle (1972), these angular distortions occur in the phenyl ring to accommodate the overmethylation. The χ^2 values for the phenyl rings of molecules (a), (b), (c) and (d) are 87.7, 106.4, 94.7 and 31.9, respectively.

The *PLUTO* (Motherwell & Clegg, 1978) stereodiagram in Fig. 2 presents the arrangement of the

molecules in the unit cell (half of the unit-cell contents). There are no short intermolecular contacts in this structure. A pseudo-symmetry operation – a non-crystallographic centre of symmetry at 0.25, 0.63, 0.25 – links molecule (a) with (b) and molecule (c) with (d). The departures of the positions of the corresponding atoms transformed through this centre are relatively small, though statistically strongly significant. For example, the dihedral angle between the planes fitted to the phenyl-ring atoms is $1.82 (9)^{\circ}$ for molecules (a) and (b) and $0.85 (12)^{\circ}$ for molecules (c) and (d) – a centre of symmetry would constrain this angle to 0° . The dihedral angles for the molecules not 'related' by the pseudo-centre [molecule (a) and (c) or (d), and molecule (b) and (c) or (d)] are larger than 10° . Interestingly, this pseudo-centre of symmetry relates the ordered [(a) and (b)] and disordered [(c) and (d)] molecules. No similar pseudo-symmetry operation linking molecules (a) or (b) with (c) or (d) could be found.

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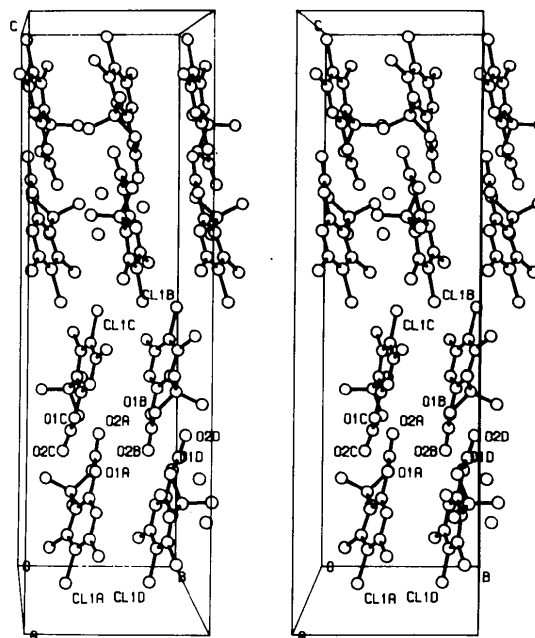


Fig. 2. A *PLUTO* stereodiagram of the structure down a. Half of the molecules contained in the unit cell have been included in this drawing to avoid overlapping of the molecules. H atoms have been omitted for clarity. The sites with small occupation factors of disordered atoms C(3), C(11) and C(12) of molecule (d) have been indicated as unconnected circles.

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New Refinement of the Room-Temperature Structure of LiCuVO_4

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Abstract. Lithium copper(II) vanadate, $M_r = 207.43$, orthorhombic, *Imma*, $a = 5.662$ (1), $b = 5.809$ (1), $c = 8.758$ (2) Å, $V = 288.0$ (2) Å³, $Z = 4$, $D_x = 4.78$ Mg m⁻³, $\text{Mo K}\alpha$, $\lambda = 0.71069$ Å, $\mu = 10.4$ mm⁻¹, $F(000) = 348$, $R = 0.040$ for 461 unique reflections. The sample was prepared by hydrothermal growth ($T = 919$ K, $P = 190$ MPa, 48 h) of 1.5 g of a powder of LiCuVO_4 in 1.65 cm³ of 0.1 M NaF aqueous solution. LiCuVO_4 is an orthorhombic distortion of the cubic spinel structure, with V^{5+} on tetrahedral sites and Li^+ and Cu^{2+} distributed in an ordered way on the octahedral sites. This leads to edge-sharing chains of Li^+ and Cu^{2+} octahedra running along [100] and [010], respectively.

Experimental. Powder sample prepared as previously described (Joubert, Grenier & Durif, 1965). Hydrothermal growth (919 K, 190 MPa, 48 h) performed in a platinum tube (1.5 g LiCuVO_4 powder, 1.65 cm³ of 0.1 M NaF aqueous solution). Dark-brown platelet (0.14 × 0.08 × 0.03 mm). Data collected on a Siemens AED-2 four-circle diffractometer. ω -2 θ step-scan

mode in N steps of $\Delta\omega^\circ$, $38 \leq N \leq 47$, $0.023 \leq \Delta\omega \leq 0.045^\circ$; time per step 2 s. Profile-fitting data analysis (Clegg, 1981); isotropic linewidth $\Gamma = (1.15 + 0.32 \tan\theta)^\circ$. Aperture $D = 4.5$ mm.

Lattice constants based on 28 reflections measured in double step-scan mode at $\pm(2\theta \approx 30^\circ)$; absorption correction by the Gaussian method, $A_{\text{max}} = 0.70$, $A_{\text{min}} = 0.40$. Intensity measurement to $2\theta \leq 90^\circ$ of five independent sets of reflections within range $|h| \leq 11$, $|k| \leq 11$, $|l| \leq 16$. Standard reflections ($\bar{2}20$, 220 , 004), intensity variation 1.0%; 3458 reflections measured, 461 independent reflections used for refinements [$|F| > 6\sigma(|F|)$], $R_{\text{int}} = 0.050$.

Structure solved by direct methods with *TANG* option of *SHELX76* (Sheldrick, 1976). F magnitudes used in least-squares refinements, 23 parameters refined; max. $|A/\sigma| = 0.001$; secondary-extinction factor $x = 2.1 \times 10^{-7}$; atomic scattering factors for Li, Cu, V and O from *International Tables for X-ray Crystallography* (1974); calculations with *SHELX76* program (Sheldrick, 1976); all atoms, except Li, refined anisotropically [$R = 0.040$, $wR = 0.035$, $w = 1/\sigma^2(F)$].