

Fig. 2. A plot of a unit cell viewed nearly down the *b* axis.

phenyldicoumarol is similar to dicoumarol and to the flavones obtusifolin (Narayanan, Zeichmeister, Rohrl & Hoppe, 1971) and urarinol (Hufford, Lasswell, Hirotsu & Clardy, 1979), all of which also contain dissymmetric intramolecularly H-bonded molecules.

Packing in phenyldicoumarol is related partly to the arrangements found in both dicoumarol and dibromodicoumarol. A unit-cell drawing (Johnson, 1976) is given in Fig. 2. Coumarins on different molecules related by the screw axes along *a* (the short axis) pack at the nominal 3.5 Å separation, as in dibromodicoumarol (*P*<sub>4</sub>,2<sub>1</sub>,2) where a similar intercoumarin spacing is found between screw-related molecules along one of the two short axes. In dicoumarol (*P*<sub>2</sub>,*c*), a similar intercoumarin spacing is found along the short axis but between glide-related molecules.

*Acta Cryst.* (1989). **C45**, 787–791

## Structure of 2,2,6,6-Tetramethylpiperidin-4-ol–Dodecanoic Acid (1/2) Complex

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(Received 25 January 1988; accepted 4 November 1988)

**Abstract.** C<sub>9</sub>H<sub>19</sub>NO·2C<sub>12</sub>H<sub>24</sub>O<sub>2</sub>, *M<sub>r</sub>* = 558.0, monoclinic, *P*<sub>2</sub>, *a* = 7.865 (4), *b* = 9.727 (7), *c* = 23.77 (2) Å, β = 99.54 (6)°, *V* = 1793.0 Å<sup>3</sup>, *Z* = 2, *D<sub>m</sub>* = 1.03, *D<sub>x</sub>* = 1.033 Mg m<sup>-3</sup>, λ(CuKα) = 1.54178 Å, μ = 0.53 mm<sup>-1</sup>, *F*(000) = 624, *T* = 293 K, final *R* = 0.066 for 1821 unique observed reflections.

Support under grant MS-86-G-4 from the Mississippi Affiliate of the American Heart Association is gratefully acknowledged.

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The solution of the structure showed that one of the two crystallographically independent acid molecules is deprotonated with the proton transferred to the piperidine N atom; the independent acid molecules have fully extended zigzag conformations and form tight H-bonded dimers. The cations are linked through H

bonds into infinite chains which are stacked along the *a* axis to form sheets parallel to the *ab* plane. The acid dimers are intercalated between the cation sheets and have an antiparallel arrangement, thus producing bilayers. The carboxylic group of the undissociated acid does not assume the usual synplanar conformation. The piperidine ring of the cation is a largely distorted chair owing to the steric repulsion between the intramolecular overcrowded atoms.

**Introduction.** 2,2,6,6-tetramethylpiperidin-4-ol (TMP) is a prime member of the group of derivatives containing the 2,2,6,6-tetramethylpiperidin-4-oxo moiety which has recently attracted considerable attention in view of the discovery that quaternary salts of many of these bases with fatty acids act as light stabilizers for polymers. A number of German, US and Soviet patents have been granted on this subject. Though highly desirable, detailed crystallographic reports on the bonding in these novel systems have not yet appeared in the literature. Therefore, as part of our serial studies on the interaction patterns between fatty acids and TMP bases, we report here a structure determination of a TMP-dodecanoic (lauric) acid (1/2) complex (T-5). It was prepared by mixing at room temperature equimolar amounts of TMP and lauric acid (LA) dissolved in diethyl ether.

Another interest focused on TMP derivatives follows from the fact that these are versatile intermediates in a number of organic syntheses of industrial interest (Scott, 1983; Jachontov, 1984). The bonding of four methyl groups to the piperidine ring results in a very crowded molecule whose steric strain is mainly relieved by considerable distortion of a 'chair' form or even by adopting twist or boat conformations. Thus, all three conformations have been found in the crystal structures of free-base forms of TMP and related analogues (Tamura, Sato & Yoshioka, 1969; Berliner, 1970; Bordeaux & Lajz rowicz, 1974; Sato, Yoshioka & Tamura, 1975; Cygler, Grabowski, Skolimowski & Skowroński, 1978).

**Experimental.** Single crystals of T-5 obtained by crystallization from acetone solvent; colourless plate-like crystal:  $0.40 \times 0.30 \times 0.05$  mm,  $D_m$  by flotation from bromoform/cyclohexane; systematic absences  $0k0$  for *k* odd from Weissenberg photographs; Syntex *P2*<sub>1</sub> diffractometer; accurate unit-cell parameters by least-squares refinement of 11 reflections,  $15 < \theta < 40^\circ$ ; intensity data ( $h = 0$  to 7,  $k = 0$  to 9,  $l = -23$  to 23) collected with Cu  $K\alpha$  radiation,  $\theta$ - $2\theta$  scan, each reflection scanned at variable rate from  $1^\circ$  (in  $2\theta$ ) below  $K\alpha_1$  peak to  $1^\circ$  above  $K\alpha_2$  maximum, background-to-scan-time ratio = 1.0; two standard reflections measured every 98 reflections: no significant systematic fluctuations; 1993 unique reflections,  $2 < \theta \leq 50^\circ$ , 1821 with  $I \geq 1.96\sigma(I)$  considered as observed and

included in the refinement; Lorentz-polarization but no absorption or extinction corrections.

Solution of the structure was not routine: during many initial attempts to solve the structure with several computerized direct-phasing multiple-solution methods (e.g. *MULTAN*, *MAGEX*, *RANTAN*) *E* maps uniformly showed only two 'infinite' parallel chains per asymmetric unit. Verification with the point-atom origin-removed Patterson function confirmed correct orientation of the chains but it was difficult to deduce their proper termination and relative positions. An advance in clarifying the structure was made when it was found that all phases based on the chain structure fitted relations  $\varphi(\mathbf{H}) = 2\pi\mathbf{H}\cdot\mathbf{r}_0$  or  $\varphi(\mathbf{H}) = 2\pi\mathbf{H}\cdot\mathbf{r}_0 + \pi$ , where  $\mathbf{r}_0 \approx (0, 0.315, 0)$ ; a centre of symmetry at  $\mathbf{r}_0$  was then apparent, i.e. the hydrocarbon chains formed a centrosymmetrical arrangement in a non-centrosymmetrical structure. Thus, as the hydrocarbon substructure dominated the phases, a relatively small number of strong *E*'s, used by *MULTAN*, combined only with each other and, as a consequence, sets of centric phases mixing both enantiomorphs were generated. Then it was considered that blocks of weaker reflections with correct phases had to be inserted to resolve details (such as oxygens of LA's and the TMP molecule) that did not fit into the chain lattice periodicity; consequently, the following procedure was adopted leading finally to the solution of the structure: (1) Based on chemical and packing considerations, the chains were cut to 12-atom lengths and subsequently shifted relative to one another in the *c* direction, while a low-resolution *R* factor [ $650$  low-angle data with  $(\sin\theta)/\lambda < 0.315 \text{ \AA}^{-1}$ ] was simultaneously monitored. The best chain model gave an *R* of 0.498. (2) To have better indication of reflections having phases other than 0 or  $\pi$ , the origin was shifted to  $\mathbf{r}_0$  and the partial structure factors,  $F_p$ , were calculated. (3) 69 of 93 reflections with  $|E| > 1.90$  were phased by applying the symbolic addition procedure (Karle & Karle, 1966, 1968). Two groups of reflections were identified: group (I), characterized by  $F_o/F_p \approx 1.0$ , comprised reflections which combined with each other to give phase indications of 0 or  $\pi$ , and group (II) of the reflections associated with  $F_o/F_p \geq 2.5$  and having probable phase values other than 0 or  $\pi$ . Symbols *a*-*d* were assigned to four reflections belonging to group (II), and they were evaluated at the end of the symbolic-phasing procedure as having values sufficiently different from 0 and  $\pi$ , a situation favourable for effective enantiomorph discrimination. (4) The 69 phases determined in the preceding step were used for phase extension and refinement by the tangent formula (program *NRC005*: Huber & Brisse, 1970) for 401 reflections with  $|E| > 1.2$ ; 39 centric phases [group (I)] were kept fixed throughout while 30 reflections of group (II) were only allowed to relax during a few final cycles of the refinement. An *E* map computed from these 401 phased

reflections showed positions of 35 of the 39 non-H atoms; the remaining atoms were located from subsequent Fourier synthesis.

Structure refined by iterated Fourier syntheses and isotropic block-diagonal least-squares refinement; difference Fourier map revealed H-atom positions of the TMP but not those of the LA's; refinement continued on all positional parameters, anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H atoms; in three final cycles two low-angle reflections (001 and 002) affected by secondary extinction were deleted from refinement; in final cycle  $R = 0.066$ ,  $wR = 0.085$  for observed reflections only, max. shift/e.s.d. 0.18, function minimized  $\sum w(\Delta F)^2$ , where  $w = 1$  if  $|F_o| < 8$  and  $w = 8/|F_o|$  if  $|F_o| \geq 8$ , max. and min. electron density difference peaks 0.23 and  $-0.18 \text{ e \AA}^{-3}$ ; scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974); all calculations performed with local version of the NRC system (Ahmed, Hall, Pippy & Huber, 1973).

**Discussion.** Atomic coordinates of non-H atoms and  $B_{\text{eq}}$  values for molecules LA1, LA2 and TMP are listed in Table 1,\* bond lengths and angles in Table 2. The molecular packing and the atom numbering in LA1 and LA2 are shown in Fig. 1. The numbering scheme for the TMP is shown in Fig. 2, which also displays the conformation of the molecule.

As mentioned above, the asymmetric unit contains two molecules of LA and one molecule of TMP. As two H atoms were found in the difference synthesis bonded to N(1) of the TMP, a proton transfer has occurred from one of the two LA's to N(1). Although H atoms of the LA's were not located, inspection of carboxyl-group dimensions clearly shows that it is the LA1 which is ionized [the C(1)–O(1) and C(1)–O(2) bond distances of 1.260 (4) and 1.248 (4) Å are equal within the limits of accuracy] while LA2 remains protonated with the proton bonded to O(3).

In the crystal (Fig. 1), the  $\text{TMP}^+$  cations are linked head-to-tail through an N(1)–H1...O(5) ( $1-x, \frac{1}{2}+y, -z$ ) hydrogen bond [N(1)–H1 = 0.79 (2), N(1)...O(5) = 2.868 (3), H1...O(5) = 2.09 (2) Å, N(1)–H1...O(5) = 171 (2)°] to form spiral chains along the *b* axis. The chains are stacked in the *a* direction by van der Waals forces acting between hydrophobic regions (mainly methyl groups) of the  $\text{TMP}^+$  cations. The stacks are separated by unit-cell translations along the *c* axis. The LA molecules are intercalated between these stacks and are oriented by their polar heads towards the hydrophilic regions of the  $\text{TMP}^+$  cations, but only one

Table 1. *Final atomic coordinates* ( $\times 10^4$ ) *with e.s.d.'s in parentheses and equivalent isotropic thermal parameters*  $B_{\text{eq}}$

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

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}(\text{\AA}^2)$
C(1)	-1733 (4)	3988 (3)	1046 (1)	4.43
C(2)	-1359 (5)	2928 (4)	1528 (1)	5.86
C(3)	-1926 (6)	3448 (5)	2071 (2)	7.27
C(4)	-1143 (7)	2569 (5)	2597 (2)	8.04
C(5)	-1597 (6)	3093 (6)	3140 (2)	8.20
C(6)	-581 (6)	2449 (6)	3675 (2)	8.34
C(7)	-1037 (7)	2952 (7)	4222 (2)	8.95
C(8)	38 (6)	2439 (6)	4761 (2)	8.55
C(9)	-423 (7)	2927 (7)	5303 (2)	9.63
C(10)	653 (6)	2491 (6)	5843 (2)	8.49
C(11)	165 (9)	2948 (9)	6384 (2)	11.83
C(12)	1147 (8)	2578 (9)	6922 (2)	11.98
O(1)	-963 (3)	5127 (2)	1115 (1)	5.44
O(2)	-2778 (3)	3710 (2)	606 (1)	5.21
C(13)	2757 (6)	5098 (6)	2091 (2)	8.05
C(14)	3973 (5)	5522 (7)	2620 (2)	8.76
C(15)	3412 (6)	5036 (6)	3161 (2)	7.94
C(16)	4584 (6)	5433 (6)	3698 (2)	8.32
C(17)	4046 (6)	5013 (7)	4242 (2)	8.72
C(18)	5189 (6)	5425 (8)	4782 (2)	9.19
C(19)	4691 (7)	4995 (7)	5336 (2)	9.36
C(20)	5797 (6)	5448 (8)	5865 (2)	9.04
C(21)	5269 (7)	5005 (7)	6418 (2)	10.00
C(22)	6496 (6)	5380 (7)	6945 (2)	8.51
C(23)	6039 (8)	4992 (9)	7502 (2)	11.95
C(24)	7380 (7)	5249 (8)	8016 (2)	10.33
O(3)	1439 (4)	5881 (4)	1945 (1)	8.48
O(4)	3017 (5)	4057 (5)	1829 (2)	12.50
N(1)	2866 (3)	2234 (3)	-534 (1)	3.43
C(25)	3510 (4)	3051 (3)	1002 (1)	4.18
C(26)	4313 (4)	4365 (3)	-736 (1)	4.10
C(27)	3124 (3)	5145 (3)	-401 (1)	3.78
C(28)	2692 (4)	4264 (3)	72 (1)	3.82
C(29)	1778 (3)	2918 (3)	-140 (1)	3.65
C(30)	4848 (4)	2135 (4)	1215 (1)	5.28
C(31)	2102 (5)	3326 (4)	1502 (1)	5.51
C(32)	1735 (4)	1933 (4)	350 (1)	5.29
C(33)	-48 (4)	3126 (4)	-445 (1)	4.91
O(5)	3985 (3)	6373 (2)	-165 (1)	4.74

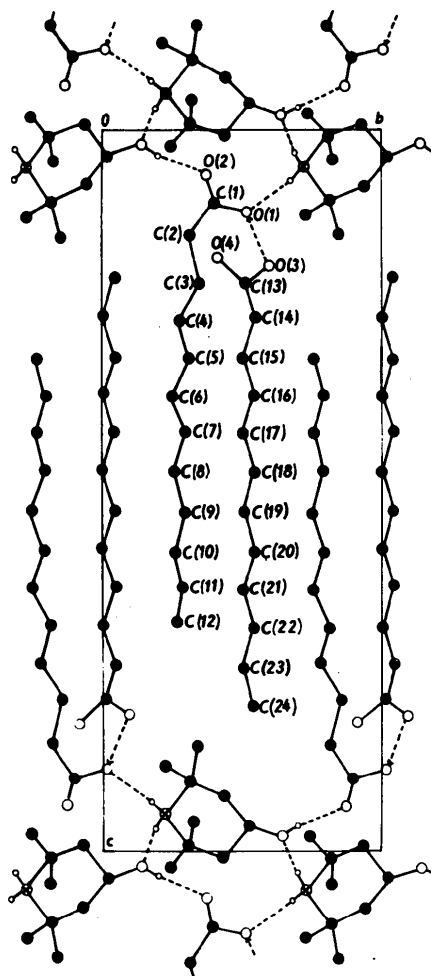
of the two LA's, namely LA1, directly participates in hydrogen-bonding interaction with the  $\text{TMP}^+$  cation, both O atoms of this ionized carboxylic group acting as acceptors of the protons; the details of the geometry of these H bonds are: N(1)–H2...O(1) ( $-x, \frac{1}{2}+y, -z$ ), N(1)–H2 = 0.59 (2), N(1)...O(1) = 2.768 (3), H2...O(1) = 2.19 (2) Å, N(1)–H2...O(1) = 170 (3)°; O(5)–H...O(2) ( $-x, \frac{1}{2}+y, -z$ ), O(5)–H = 0.71 (6), O(5)...O(2) = 2.614 (3), H...O(2) = 1.92 (6) Å, O(5)–H...O(2) = 164 (6)°. The undissociated LA2 associates with LA1 through the strong hydrogen bond O(4)...O(2) [2.600 (4) Å] which results in the formation of dimers. Thus, packing of two symmetry-independent molecules of LA within the dimers is parallel, while the dimers are packed in an antiparallel fashion which causes the formation of bilayers. Such an arrangement, which is reminiscent of molecular association in lipoidal membranes, gives rise to a pronounced interdigitation within the bilayer: many C...C contacts within the range 4.3–4.9 Å involving the methyl and methylenic groups stabilize the bilayer.

The C–C bond lengths within the alkyl chains of LA's are significantly shorter [on average 1.493 (7) Å] than 1.533 Å (Bartell, 1959) and the C–C–C angles

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51576 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

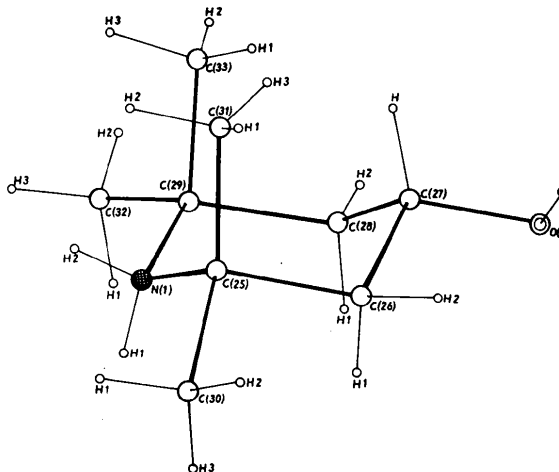
Table 2. Bond distances (Å) and angles (°) with *e.s.d.*'s in parentheses

C(1)—O(1)	1.260 (4)	C(17)—C(18)	1.495 (6)
C(1)—O(2)	1.248 (4)	C(18)—C(19)	1.494 (6)
C(1)—C(2)	1.533 (5)	C(19)—C(20)	1.473 (7)
C(2)—C(3)	1.522 (5)	C(20)—C(21)	1.495 (7)
C(3)—C(4)	1.555 (6)	C(21)—C(22)	1.484 (7)
C(4)—C(5)	1.486 (6)	C(22)—C(23)	1.476 (7)
C(5)—C(6)	1.518 (6)	C(23)—C(24)	1.497 (7)
C(6)—C(7)	1.489 (6)	N(1)—C(25)	1.521 (4)
C(7)—C(8)	1.497 (6)	C(25)—C(26)	1.516 (4)
C(8)—C(9)	1.474 (6)	C(25)—C(30)	1.529 (5)
C(9)—C(10)	1.478 (7)	C(25)—C(31)	1.508 (4)
C(10)—C(11)	1.471 (7)	C(26)—C(27)	1.527 (4)
C(11)—C(12)	1.425 (8)	C(27)—C(28)	1.496 (4)
C(13)—O(3)	1.287 (6)	C(27)—O(5)	1.440 (4)
C(13)—O(4)	1.223 (7)	C(28)—C(29)	1.537 (4)
C(13)—C(14)	1.506 (6)	C(29)—N(1)	1.523 (4)
C(14)—C(15)	1.502 (6)	C(29)—C(32)	1.511 (5)
C(15)—C(16)	1.496 (6)	C(29)—C(33)	1.525 (4)
C(16)—C(17)	1.483 (6)		
O(1)—C(1)—O(2)	122.3 (3)	C(19)—C(20)—C(21)	117.4 (5)
C(2)—C(1)—O(1)	117.7 (3)	C(20)—C(21)—C(22)	116.7 (5)
C(2)—C(1)—O(2)	119.9 (3)	C(21)—C(22)—C(23)	118.6 (5)
C(1)—C(2)—C(3)	111.3 (3)	C(22)—C(23)—C(24)	116.5 (5)
C(2)—C(3)—C(4)	111.5 (4)	C(25)—N(1)—C(29)	120.7 (2)
C(3)—C(4)—C(5)	112.9 (4)	N(1)—C(25)—C(26)	107.6 (2)
C(4)—C(5)—C(6)	114.6 (4)	N(1)—C(25)—C(30)	105.6 (2)
C(5)—C(6)—C(7)	115.3 (4)	N(1)—C(25)—C(31)	112.3 (3)
C(6)—C(7)—C(8)	117.0 (4)	C(26)—C(25)—C(30)	111.5 (3)
C(7)—C(8)—C(9)	117.0 (5)	C(26)—C(25)—C(31)	112.3 (3)
C(8)—C(9)—C(10)	118.5 (5)	C(30)—C(25)—C(31)	107.7 (3)
C(9)—C(10)—C(11)	118.6 (5)	C(25)—C(26)—C(27)	112.8 (3)
C(10)—C(11)—C(12)	121.8 (6)	C(26)—C(27)—C(28)	110.1 (2)
O(3)—C(13)—O(4)	123.2 (5)	C(26)—C(27)—O(5)	109.0 (2)
C(14)—C(13)—O(3)	115.8 (4)	C(28)—C(27)—O(5)	109.5 (2)
C(14)—C(13)—O(4)	121.0 (5)	C(27)—C(28)—C(29)	113.2 (2)
C(13)—C(14)—C(15)	113.0 (4)	N(1)—C(29)—C(28)	107.0 (2)
C(14)—C(15)—C(16)	114.9 (4)	N(1)—C(29)—C(32)	106.4 (2)
C(15)—C(16)—C(17)	116.6 (4)	N(1)—C(29)—C(33)	110.7 (2)
C(16)—C(17)—C(18)	117.2 (4)	C(28)—C(29)—C(32)	110.9 (2)
C(17)—C(18)—C(19)	118.3 (5)	C(28)—C(29)—C(33)	113.5 (2)
C(18)—C(19)—C(20)	117.6 (5)	C(32)—C(29)—C(33)	108.0 (3)

Fig. 1. The crystal structure projected along the *a* axis and numbering scheme for the two symmetry-independent molecules of LA. Only H atoms of the TMP<sup>+</sup> cations involved in hydrogen bonds (shown by broken lines) are drawn for clarity.

are significantly larger [on average 116.3 (5)°] than normal tetrahedral angles. Both of these deviations increase on approaching the methyl termini and could be due to systematic shifts in the apparent carbon positions caused by large libration about the long-chain axes but no corrections for libration were made. This is further supported by obvious correlation between these deviations from ideal geometry and the values of  $B_{eq}$  (Table 1), which also point to the stabilizing influence of the hydrogen bonds against libration of the LA's on the sides of their carboxylic heads. On the other hand, the O(4), which is the only oxygen not involved in the hydrogen bonding, has the largest value of  $B_{eq}$  (12.5 Å<sup>2</sup>).

In both molecules of LA the alkyl chains are in nearly fully extended conformations; the chain in LA2 is quite planar, the torsion angles being 180° with good approximation, while the chain in LA1 exhibits small, but significant, curving at C(2)—C(3) and C(4)—C(5) bonds [torsion angles 165.4 (3) and 168.3 (4)° respectively]. The conformation of the ionized carboxyl (LA1), as expressed in terms of the torsion angle  $\chi = \text{O}(1)\text{—C}(1)\text{—C}(2)\text{—C}(3)$ , is anticlinal [ $\chi = -63.3$  (4)°], while the plane of the carboxylic group of LA2 is nearly normal to the plane of the alkyl chain

Fig. 2. A perspective view of the TMP<sup>+</sup> cation.

$[\chi = \text{O}(4)\text{—C}(13)\text{—C}(14)\text{—C}(15) = 95.2(6)^\circ]$ . Thus, the conformation of the unionized carboxyl of LA2 is different from that usually encountered in  $\alpha,\beta$ -saturated carboxylic acids which prefer a synplanar placement of the 'carbonyl' oxygen ( $\chi \approx 0^\circ$ ; Leiserowitz, 1976).

Bond lengths and angles within the  $\text{TMP}^+$  cation reflect a strain resulting from crowding of the methyl groups on the piperidine ring. Thus, the  $\text{N}(1)\text{—C}(25)$  and  $\text{N}(1)\text{—C}(29)$  bonds are significantly stretched [the respective distances are 1.521(4) and 1.523(4) Å] with respect to the normal value of 1.499 Å reported for the  $\text{N}^+\text{—C}$  single bond (Birnbau, 1967), or to the value of 1.497 Å as observed for the similar bond in the parent, unstrained piperidine hydrochloride (Rérat, 1960). Similarly, the  $\text{C}(25)\text{—N}(1)\text{—C}(29)$  bond angle of  $120.7(2)^\circ$  is considerably wider than the usual value of about  $112^\circ$  and bond angles around C(25) and C(29) show marked deviations from normal tetrahedral angles, varying within  $106.4\text{—}113.5^\circ$ ; a narrowing of the endocyclic angles at C(25) and C(29) is accompanied by a widening of the angles at C(26) and C(28). Consequently, the chair conformation of the piperidine ring is flattened. The puckering angle on the side of the N is about  $48^\circ$ , while that on the side of the C(OH) group is about  $60^\circ$ . The flattening of the ring at N(1) is also illustrated by the asymmetry parameters (Duax & Norton, 1975),  $\Delta C_2[\text{C}(25), \text{C}(26)] = 12.6$  and  $\Delta C_5[\text{N}(1)] = 0.4^\circ$ , indicating loss of rotation symmetry with retention of the orthogonal mirror plane.

The above-mentioned bond-length, valence-angle and ring-torsional distortions have also been observed in the structure of 2,2,6,6-tetramethylpiperidinone hydrochloride (Rees & Weiss, 1971) and result from the need to relieve the very short intramolecular contact  $\text{H}1(\text{C}33)\cdots\text{H}3(\text{C}31)$  between the axial methyl substituents. In spite of all these adaptations of molecular geometry, this contact of distance 2.07(4) Å as

observed in the structure is still highly repulsive and should actually be even more severe considering that the diffraction experiment gives systematically shortened C—H distances with respect to the internuclear distance of about 1.09 Å. Other unfavourable  $\text{H}\cdots\text{H}$  steric contacts, significantly below the sum of van der Waals radii (2.40 Å) and separated by at least four bonds, are:  $\text{H}2(\text{C}32)\cdots\text{H}3(\text{C}33)$  2.15(5),  $\text{H}1(\text{C}33)\cdots\text{H}(\text{C}27)$  2.25(4) and  $\text{H}3(\text{C}30)\cdots\text{H}1(\text{C}26)$  2.26(4) Å.

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### Three Conformers in a Crystal of *N*-Ac-L-Leu-L-Tyr-OMe

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(Received 1 September 1988; accepted 28 November 1988)

**Abstract.**  $\text{C}_{18}\text{H}_{26}\text{N}_2\text{O}_5$ , three independent molecules with different conformations,  $M_r = 350.4$ , orthorhombic,  $P2_12_12_1$ ,  $a = 16.077(10)$ ,  $b = 28.935(18)$ ,  $c = 12.597(6)$  Å,  $V = 5860.0$  Å<sup>3</sup>,  $Z = 12$ ,  $D_x = 1.191$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54178$  Å,  $F(000) = 2256$ , room temperature, final  $R = 4.9\%$  for 4596 data with

$|F_o| > 3\sigma$  and 5.4% for all 4977 measured data. The three independent molecules have different conformations for the backbones and the side-chains, although each molecule is relatively flat and has an approximate H shape. The backbone in one of the conformations has  $\phi$ ,  $\psi$  angles near those for a  $\beta$ -turn. There is extensive