

as the cavity changes shape with changes in the chalcogen van der Waals radius.

The host molecules are planar, with dimensions similar to those determined for the pure compounds (Truter, 1967; Rutherford & Calvo, 1969). However, the bond lengths found here for selenourea [C–Se = 1.914 (15), C–N = 1.300 (15) Å compared with 1.86 (3) and 1.37 (2) Å found previously] suggest that the ionic contributions to the electronic structure must be considerable.

The structures confirm the general features of the inclusion complexes as described by Lenné (1954). The guest molecules in the 1:3 rational adducts lie in the vicinity of the 32 symmetry point in the structure, and the channel is constricted around the $\bar{3}$ point by $-\text{NH}_2$ groups. The host molecules are hydrogen-bonded to one another, the $\text{N}\cdots\text{X}$ distances being 3.462 (7) and 3.496 (5) Å for (I), and 3.51 (2) and 3.65 (2) Å for (II), for the hydrogen bonds between chains and within chains respectively. The distances for the thiourea host fall between those found by Truter (1967) for thiourea itself (3.42, 3.54 Å), while those for (II) almost precisely reverse those for selenourea, where the average distances are 3.64 (2) between chains and 3.51 (2) Å within chains. The greater variability in the length of the weaker $\text{N}-\text{H}\cdots\text{Se}$ bonds, together with an ability to adjust the position of the selenourea molecule within the chain to promote efficient packing, would appear to explain van Bekkum *et al.*'s (1969) observation of a larger variation in cell dimensions for the selenourea complexes. With regard to the packing of

the selenourea molecules, in selenourea itself, on average, the Se atom projects 0.81 (7) Å beyond the chain axis, while in the adamantane complex the Se atom is pushed back out of the cavity to project only 0.56 (1) Å.

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A *cis* and a *trans* 4'-Methyl Cyclopentamethylenemercaptopropionic Acid (Pmp)

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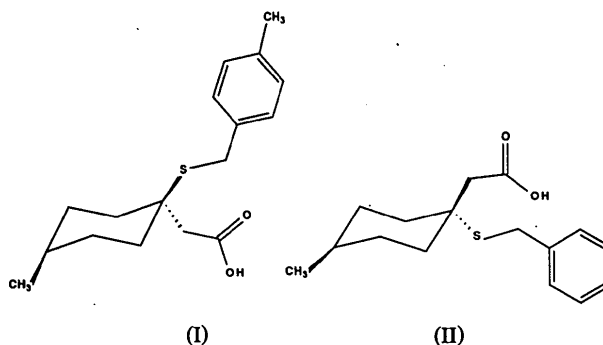
Abstract. (I): *trans*-4-Methyl-1-[(4-methylphenyl)methyl]thio)cyclohexaneacetic acid, $\text{C}_{17}\text{H}_{24}\text{O}_2\text{S}$, $M_r = 292.44$, monoclinic, $P2_1/n$, $a = 8.588$ (3), $b = 9.812$ (3), $c = 19.696$ (9) Å, $\beta = 91.90$ (3)°, $V = 1658.8$ (19) Å³, $Z = 4$, $D_x = 1.171$ Mg m⁻³, $\lambda(\text{Mo } K\alpha)$

$= 0.71073$ Å, $\mu = 0.1856$ cm⁻¹, $F(000) = 632$, $T = 295$ K, $R = 0.046$, $wR = 0.060$ for 2015 observations. (II): *cis*-4-Methyl-1-[(phenylmethyl)thio]cyclohexaneacetic acid, $\text{C}_{16}\text{H}_{22}\text{O}_2\text{S}$, $M_r = 278.42$, monoclinic, $P2_1/n$, $a = 15.884$ (3), $b = 9.391$ (4), $c = 22.429$ (4) Å, $\beta = 109.95$ (2)°, $V = 3145.0$ (29) Å³, $Z = 8$, $D_x = 1.176$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu =$

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0.1928 cm⁻¹, $F(000) = 1200$, $R = 0.054$, $wR = 0.064$ for 2166 observations. The two molecules are geometrical isomers of cyclopentamethylenemercaptopropionic acid (Pmp), a commonly used substitute for cysteine in position 1 of antagonists of neurohypophysial hormones. Crystals of (I), a *trans* isomer, and (II), a *cis* isomer, were examined to verify the geometrical isomerism obtained from two different synthetic paths to the Pmp nucleus. Despite the geometrical isomerism, the two molecules display striking conformational similarity. In both structures the methyl group at C4 occupies a pseudoequatorial position relative to the cyclohexane ring. The cyclohexane rings in both structures adopt chair conformations. Crystals of (II) contain two crystallographically independent molecules which differ only slightly in conformational detail. There is a 7° difference in the orientation of the phenyl ring relative to the carboxyl group in each molecule. Both structures display hydrogen-bonded intermolecular carboxylic acid dimers.

receptor antagonists as determined in the dog model (Albrightson, Caldwell, Brennan, DePalma & Kinter, 1987). As part of our studies directed toward understanding the conformational ramifications of modifications at position 1 in V2-receptor antagonists, we undertook to verify the *cis* and *trans* geometries of protected 4'-methyl Pmp molecules *via* single-crystal X-ray diffraction studies.



Introduction. Considerable effort has been devoted in these (Huffman *et al.*, 1985; Ali *et al.*, 1986; Yim *et al.*, 1986) and other (Manning, Klis, Olma, Seto & Sawyer, 1982; Manning, Lammek, Kruszynski, Seto & Sawyer, 1982; Manning, Olma, Klis, Kolodziejczyk, Seto & Sawyer, 1982; Sawyer, Pang, Seto, McEnroe, Lammek & Manning, 1981) laboratories toward the development of clinically useful vasopressin V2-receptor antagonists. These efforts have succeeded in identifying SK&F 101926 as a novel potent *in vivo* and *in vitro* aquaretic although the molecule shows agonist activity upon clinical evaluation in normal volunteers (Dubb, Allison, Tatioan, Blumberg, Lee & Stote, 1987; Allison *et al.*, 1988). During the search for V2-receptor antagonists it appeared that certain chemical modifications facilitated the initial conversion of full agonists to antagonists. Among these modifications was the cyclopentamethylenemercaptopropionic acid (Pmp) residue substituted for cysteine at position 1 of vasopressin (Manning, Lammek, Kolodziejczyk, Seto & Sawyer, 1981). du Vigneaud and co-workers first prepared the Pmp residue and incorporated it into oxytocin (Nestor, Ferger & du Vigneaud, 1975). During early work with vasopressin antagonists in this laboratory a synthesis of Pmp was developed which allowed preparation of a variety of substituted analogs to test design hypotheses with regard to steric bulk and electronic factors (Yim & Huffman, 1983). Modification of this synthesis led to improved control over the stereochemical outcome (Yim *et al.*, 1986) with the result that both *trans* (I) and *cis* (II) isomers can be prepared in the case of substitution at position 4 of the ring. The apparently minor structural modification imposed by this isomerism about residue 1 can dramatically alter the partial agonist activity of V2-

Experimental. For (I) colorless parallelepiped from hexane, approximate dimensions 0.40 × 0.70 × 0.30 mm, mounted with epoxy resin on a glass fiber. Cell constants from a least-squares refinement of 25 reflections [$30 \leq 2\theta(\text{Mo}) \leq 35^\circ$] measured on the diffractometer; Enraf-Nonius CAD-4 equipped with a graphite monochromator; variable-speed ω - θ scans, max. = 6.7, min. = 2.5° min⁻¹. Systematic absences: $h0l$ for $h+l$ odd; $0k0$ for k odd. 4253 measured intensities, $2\theta \leq 56^\circ$, $0 \leq h \leq 11$, $0 \leq k \leq 12$, $-26 \leq l \leq 26$, Lorentz-polarization correction, intensity decay correction (maximum loss in intensity = 3.1%; correction factors 1.00 min., 1.016 max.); no absorption correction. Symmetry-equivalent reflections in the quadrant collected were averaged, $R_{\text{int}} = 0.028$ on F_o . Structure solution using *MULTAN*11/82 (Main *et al.*, 1980) and difference Fourier syntheses; anisotropic vibrational parameters for non-hydrogen atoms, all H atoms located from difference maps and refined with isotropic temperature factors. Full-matrix least-squares refinement (on F); function minimized was $\sum w(|F_o| - |F_c|)^2$; $w = 4F_o^2/s^2(I)$ with $s(I) = [\sigma^2(I) + 0.06(F_o)^2]^{1/2}$. No evidence for secondary extinction. Final $R = 0.046$, $wR = 0.060$ for 2015 observations with $I \geq 3.0\sigma(I)$, 277 variables, $S = 1.536$; convergence indicated by max. $\Delta/\sigma = 0.30$, final difference map showed maximum positive and negative excursions of 0.219 and $-0.215 \text{ e } \text{\AA}^{-3}$, respectively. Refinement using 3058 observations with $I \geq 0.01\sigma(I)$ gave $R = 0.070$, $wR = 0.071$.

For (II), colorless elongated plate from ether/hexane, approximate dimensions 0.6 × 0.2 × 0.1 mm, mounted with epoxy resin on a glass fiber. Cell constants from a least-squares refinement of 25 reflections [$30 \leq 2\theta(\text{Mo}) \leq 35^\circ$] measured on the diffractometer; Enraf-

Nonius CAD-4 equipped with a graphite monochromator, variable-speed ω - θ scans. Systematic absences: $h0l$ for $h+l$ odd, $0k0$ for k odd. 7930 measured intensities, $2\theta \leq 55^\circ$, $0 \leq h \leq 20$, $0 \leq k \leq 12$, $-29 \leq l \leq 29$, Lorentz-polarization correction, intensity decay correction (maximum intensity loss = 3.6%; correction factors 1.000 min., 1.018 max.); no absorption correction. Symmetry-equivalent reflections in the quadrant collected were averaged, $R_{\text{int}} = 0.030$ on F_o . Structure solution from *MULTAN*11/82 and difference Fourier syntheses; anisotropic vibrational parameters for non-hydrogen atoms, all H-atom positions, except those of the carboxyl protons, were calculated from geometrical considerations, assigned isotropic temperature coefficients 1.3 times the equivalent isotropic temperature factor of the atoms to which they were bonded, and held fixed at the calculated positions. Carboxyl protons were held fixed at the positions indicated from a difference Fourier map and were assigned fixed isotropic temperature coefficients. Full-matrix least-squares refinement (on F); function minimized was $\sum w(|F_o| - |F_c|)^2$; $w = 4F_o^2/s^2(I)$ with $s(I) = [\sigma^2(I) + p(F_o)^2]^{1/2}$, $p = 0.05$. No evidence for secondary extinction. Final $R = 0.054$, $wR = 0.064$ for 2166 observations with $I \geq 3.0\sigma(I)$, 343 variables, $S = 1.280$; convergence indicated by max. $\Delta/\sigma = 0.00$; final difference map showed maximum positive and negative excursions of 0.230 and $-0.385 \text{ e } \text{\AA}^{-3}$, respectively. Refinement using 4537 observations with $I \geq 0.01\sigma(I)$ gave $R = 0.125$, $wR = 0.084$. Other computer programs used: Enraf-Nonius (1986) *SDP*. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Tables 1 and 2 present the positional parameters and their standard deviations as estimated from the least-squares matrix for (I) and (II), respectively.* *ORTEP* (Johnson, 1976) diagrams of (I) and (II) are presented as Figs. 1 and 2, respectively. There are two crystallographically independent molecules comprising the asymmetric unit for (II); only one of these molecules has been illustrated in Fig. 2. Geometrical relationships are listed in Tables 3 and 4.

Both the geometrical isomerism of (I) and (II) and their conformational similarities are readily apparent from the figures. In both (I) and (II) the methyl group at C4 occupies a pseudoequatorial position relative to the cyclohexane ring which in turn adopts a chair conformation for all three molecules. Atoms C2, C3, C5 and C6 describe a plane from which none of the four atoms deviates by more than 0.013 (3), 0.004 (5) or

Table 1. Table of positional parameters and their e.s.d.'s for compound (I)

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)^*$
S	0.85230 (8)	0.23866 (7)	0.67233 (4)	5.34 (1)
O1	0.9270 (3)	-0.0413 (2)	0.5807 (1)	8.22 (5)
O2	0.8275 (3)	0.0762 (2)	0.49375 (9)	8.85 (5)
C1	0.6727 (3)	0.2021 (2)	0.6233 (1)	4.48 (5)
C2	0.5295 (3)	0.2144 (3)	0.6671 (1)	5.30 (6)
C3	0.3763 (3)	0.2160 (3)	0.6268 (2)	6.13 (7)
C4	0.3717 (3)	0.3257 (3)	0.5727 (1)	5.40 (6)
C5	0.5118 (3)	0.3100 (3)	0.5275 (1)	5.25 (6)
C6	0.6643 (3)	0.3133 (2)	0.5687 (1)	4.75 (5)
C7	0.2187 (4)	0.3278 (4)	0.5319 (2)	8.05 (9)
C8	0.8600 (3)	0.1077 (3)	0.7376 (2)	7.01 (7)
C9	1.0181 (3)	0.1124 (3)	0.7720 (1)	5.29 (6)
C10	1.1356 (3)	0.0259 (3)	0.7531 (1)	5.47 (6)
C11	1.2806 (3)	0.0293 (3)	0.7838 (1)	5.32 (6)
C12	1.3157 (3)	0.1192 (3)	0.8354 (1)	5.26 (6)
C13	1.2000 (4)	0.2070 (3)	0.8547 (1)	6.22 (7)
C14	1.0536 (3)	0.2037 (3)	0.8241 (1)	6.36 (7)
C15	1.4745 (4)	0.1239 (4)	0.8688 (2)	8.05 (9)
C16	0.6793 (3)	0.0575 (3)	0.5924 (1)	5.86 (6)
C17	0.8207 (4)	0.0316 (3)	0.5525 (1)	6.67 (7)

* For anisotropically refined atoms the isotropic equivalent displacement parameters are given, defined as $B_{\text{eq}} = \frac{1}{3} \sum_i \beta_i \beta_i a_i^2$.

Table 2. Table of positional parameters and their e.s.d.'s for compound (II)

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
S	0.68372 (9)	0.2178 (2)	0.72010 (6)	3.68 (3)
S'	0.7795 (1)	0.2101 (2)	0.33700 (7)	4.60 (4)
O1	0.9178 (3)	0.2179 (5)	0.7006 (2)	6.4 (1)
O1'	0.5392 (3)	0.2468 (5)	0.3592 (2)	7.1 (1)
O2	0.9029 (3)	0.1075 (5)	0.7834 (2)	6.3 (1)
O2'	0.5533 (3)	0.1343 (5)	0.2769 (2)	7.2 (1)
C1'	0.7459 (3)	0.1540 (7)	0.4043 (3)	4.3 (1)
C1	0.7116 (3)	0.1325 (6)	0.6553 (2)	3.2 (1)
C2'	0.7397 (4)	0.2921 (7)	0.4388 (3)	5.0 (2)
C2	0.7188 (3)	0.2554 (6)	0.6117 (2)	3.5 (1)
C3'	0.8310 (4)	0.3564 (7)	0.4757 (3)	5.3 (2)
C3	0.6300 (4)	0.3263 (6)	0.5761 (2)	4.0 (1)
C4'	0.8934 (4)	0.2528 (8)	0.5201 (3)	6.0 (2)
C4	0.5597 (4)	0.2179 (7)	0.5385 (2)	4.5 (1)
C5'	0.9024 (4)	0.1205 (8)	0.4841 (3)	5.7 (2)
C5	0.5494 (3)	0.1017 (7)	0.5828 (3)	4.5 (2)
C6'	0.8129 (4)	0.0516 (7)	0.4494 (3)	5.2 (2)
C6	0.6381 (4)	0.0286 (6)	0.6179 (2)	4.0 (1)
C7'	0.6546 (4)	0.0757 (7)	0.3801 (3)	5.4 (2)
C7	0.7996 (4)	0.0485 (6)	0.6817 (3)	4.2 (1)
C8'	0.5779 (4)	0.1586 (7)	0.3356 (3)	5.0 (2)
C8	0.8785 (3)	0.1310 (7)	0.7248 (3)	4.5 (2)
C9'	0.7865 (5)	0.0446 (7)	0.2969 (3)	6.9 (2)
C9	0.6767 (4)	0.0694 (6)	0.7702 (3)	5.4 (2)
C10'	0.8042 (4)	0.0857 (6)	0.2380 (3)	4.9 (2)
C10	0.6571 (3)	0.1294 (6)	0.8259 (2)	3.8 (1)
C11'	0.8913 (5)	0.0879 (8)	0.2359 (3)	6.6 (2)
C11	0.7258 (4)	0.1682 (6)	0.8806 (3)	4.3 (2)
C12'	0.9058 (5)	0.1288 (9)	0.1807 (3)	7.3 (2)
C12	0.7081 (4)	0.2256 (7)	0.9317 (3)	5.2 (2)
C13'	0.8350 (5)	0.1668 (8)	0.1281 (3)	6.9 (2)
C13	0.6224 (4)	0.2450 (7)	0.9297 (3)	5.3 (2)
C14'	0.7503 (5)	0.1604 (7)	0.1296 (3)	6.4 (2)
C14	0.5532 (4)	0.2070 (8)	0.8753 (3)	6.2 (2)
C15'	0.7352 (4)	0.1237 (7)	0.1841 (3)	5.9 (2)
C15	0.5699 (4)	0.1498 (7)	0.8241 (3)	5.4 (2)
C16'	0.9841 (5)	0.318 (1)	0.5564 (4)	8.7 (3)
C16	0.4717 (4)	0.2900 (8)	0.5025 (3)	6.9 (2)

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51388 (74 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0.010 (6) \AA , respectively in (I), (II) and (II'). Atoms C1 and C4 are disposed on opposite sides of this plane by 0.655 (2) and 0.654 (3) \AA respectively for (I), by 0.631 (5) and 0.676 (6) \AA respectively for (II), and by 0.616 (6) and 0.659 (6) \AA respectively for (II').

The *p*-methylbenzyl mercaptan group substituted at C1 is *transoid* to the 4-methyl substituent in (I) and thus it also occupies an equatorial position relative to the cyclohexane ring. In (II) and (II'), however, this stereochemistry is reversed; the two independent molecules both have the 4-methyl and 1-benzylmercaptan groups in a *cisoid* relationship. The phenyl rings in both structures are rigorously planar.

Conformational differences between the two crystallographically independent molecules of (II) are observed although the differences are small in magnitude. In particular there is a 7° difference in the orientation of the phenyl rings relative to the carboxyl group in each molecule as indicated by the dihedral angles between the four-atom plane of the carboxyl group and the six-atom phenyl plane. For (II) and (II') these dihedral angles are 122.5 (2) and 129.8 (3)° respectively; however, the analogous angle in (I) is 117.4 (2)°. There is also a 3° difference in orientation of the carboxyl groups in (II) and (II') with the dihedral angles between

Table 3. Bond distances (Å) and angles (°) for (I)

S—C1	1.827 (2)	C5—C6	1.518 (4)
S—C8	1.817 (3)	C8—C9	1.498 (4)
O1—C17	1.272 (4)	C9—C10	1.378 (4)
O2—C17	1.240 (3)	C9—C14	1.389 (4)
C1—C2	1.531 (3)	C10—C11	1.367 (4)
C1—C6	1.532 (3)	C11—C12	1.372 (4)
C1—C16	1.546 (3)	C12—C13	1.378 (4)
C2—C3	1.514 (4)	C12—C15	1.495 (4)
C3—C4	1.515 (4)	C13—C14	1.376 (4)
C4—C5	1.528 (4)	C16—C17	1.490 (4)
C4—C7	1.517 (4)		
C1—S—C8	104.2 (1)	C8—C9—C10	121.3 (2)
S—C1—C2	111.5 (2)	C8—C9—C14	121.8 (2)
S—C1—C6	104.5 (2)	C10—C9—C14	116.9 (2)
S—C1—C16	110.3 (2)	C9—C10—C11	122.0 (2)
C2—C1—C6	108.6 (2)	C10—C11—C12	121.2 (2)
C2—C1—C16	109.5 (2)	C11—C12—C13	117.6 (2)
C6—C1—C16	112.3 (2)	C11—C12—C15	121.4 (3)
C1—C2—C3	114.0 (2)	C13—C12—C15	121.0 (3)
C2—C3—C4	112.2 (2)	C12—C13—C14	121.4 (3)
C3—C4—C5	109.6 (2)	C9—C14—C13	120.9 (3)
C3—C4—C7	112.6 (2)	C1—C16—C17	113.9 (2)
C5—C4—C7	112.2 (2)	O1—C17—O2	123.3 (3)
C4—C5—C6	111.6 (2)	O1—C17—C16	116.9 (2)
C1—C6—C5	112.3 (2)	O2—C17—C16	119.8 (3)
S—C8—C9	108.0 (2)		

Table 4. Bond distances (Å) and angles (°) for (II)

S—C1	1.841 (6)	C4—C5	1.522 (9)
S—C9	1.818 (6)	C4—C16	1.514 (8)
S'—C1'	1.841 (6)	C5'—C6'	1.513 (8)
S'—C9'	1.818 (7)	C5—C6	1.523 (7)
O1—C8	1.258 (8)	C7'—C8'	1.502 (8)
O1'—C8'	1.252 (8)	C7—C8	1.510 (7)
O2—C8	1.256 (7)	C9'—C10'	1.49 (1)
O2'—C8'	1.261 (7)	C9—C10	1.496 (9)
C1'—C2'	1.531 (9)	C10'—C11'	1.40 (1)
C1'—C6'	1.533 (8)	C10'—C15'	1.373 (8)
C1'—C7'	1.550 (8)	C10—C11	1.384 (6)
C1—C2	1.543 (7)	C10—C15	1.386 (9)
C1—C6	1.532 (7)	C11'—C12'	1.39 (1)
C1—C7	1.537 (7)	C11—C12	1.378 (9)
C2'—C3'	1.528 (8)	C12'—C13'	1.371 (8)
C2—C3	1.517 (7)	C12—C13	1.359 (9)
C3'—C4'	1.500 (9)	C13'—C14'	1.36 (1)
C3—C4	1.533 (7)	C13—C14	1.382 (7)
C4'—C5'	1.52 (1)	C14'—C15'	1.37 (1)
C4'—C16'	1.520 (9)	C14—C15	1.37 (1)
C1—S—C9	103.7 (3)	C1—C6—C5	113.2 (5)
C1'—S'—C9'	104.1 (3)	C1'—C7'—C8'	115.9 (5)
S'—C1'—C2'	105.1 (4)	C1—C7—C8	115.5 (5)
S'—C1'—C6'	113.0 (4)	O1'—C8'—O2'	122.7 (5)
S'—C1'—C7'	110.3 (4)	O1'—C8'—C7'	117.8 (5)
C2'—C1'—C6'	110.3 (4)	O2'—C8'—C7'	119.5 (6)
C2'—C1'—C7'	111.4 (5)	O1—C8—O2	122.9 (5)
C6'—C1'—C7'	106.8 (5)	O1—C8—C7	118.8 (5)
S—C1—C2	105.3 (4)	O2—C8—C7	118.2 (6)
S—C1—C6	111.4 (4)	S'—C9'—C10'	106.2 (5)
S—C1—C7	110.6 (3)	S—C9—C10	107.5 (4)
C2—C1—C6	109.7 (4)	C9'—C10'—C11'	121.3 (5)
C2—C1—C7	111.9 (5)	C9'—C10'—C15'	120.8 (6)
C6—C1—C7	107.9 (4)	C11'—C10'—C15'	117.8 (6)
C1'—C2'—C3'	113.2 (5)	C9—C10—C11	120.9 (5)
C1—C2—C3	113.9 (5)	C9—C10—C15	121.3 (4)
C2'—C3'—C4'	113.1 (6)	C11—C10—C15	117.8 (5)
C2—C3—C4	111.7 (5)	C10'—C11'—C12'	120.0 (5)
C3'—C4'—C5'	109.7 (5)	C10—C11—C12	121.2 (5)
C3'—C4'—C16'	112.6 (6)	C11'—C12'—C13'	120.2 (7)
C5'—C4'—C16'	111.8 (6)	C11—C12—C13	120.8 (5)
C3—C4—C5	109.7 (4)	C12'—C13'—C14'	119.7 (7)
C3—C4—C16	111.3 (5)	C12—C13—C14	118.7 (6)
C5—C4—C16	112.6 (5)	C13'—C14'—C15'	120.7 (6)
C4'—C5'—C6'	112.5 (5)	C13—C14—C15	121.1 (6)
C4—C5—C6	112.0 (5)	C10'—C15'—C14'	121.5 (7)
C1'—C6'—C5'	112.9 (5)	C10—C15—C14	120.5 (5)

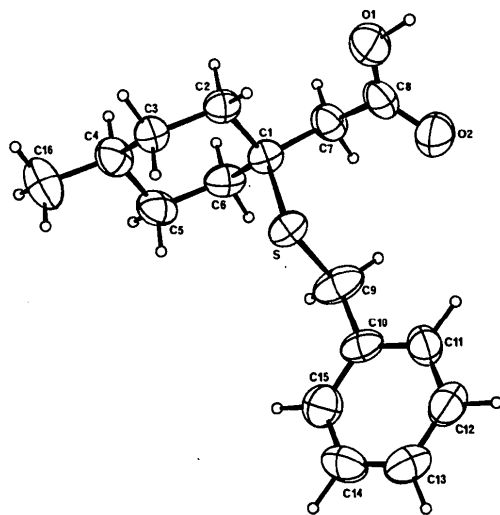


Fig. 1. ORTEP (Johnson, 1976) drawing of (I) with non-H atoms depicted at the 50% probability level; H atoms as spheres of arbitrary size.

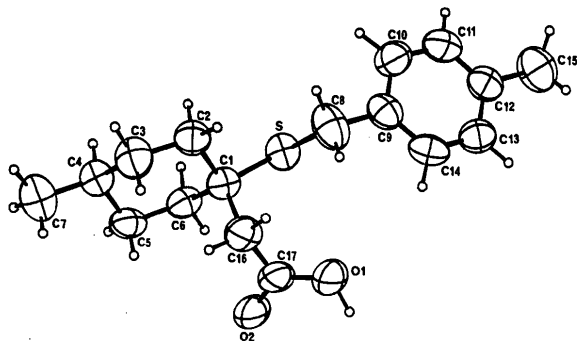


Fig. 2. ORTEP drawing of (II) with non-H atoms depicted at the 50% probability level; H atoms as spheres of arbitrary size.

the four-atom plane through the carboxyl group and the cyclohexane plane of 55.8 (2) and 58.9 (3)°, respectively. The analogous angle in (I) is 38.4 (2)°.

The nearly perpendicular orientation of the phenyl ring relative to the four-atom cyclohexane plane is virtually identical in both (II) and (II'); the respective dihedral angles are 84.2 (2) and 83.0 (2)°. The analogous angle is 110.0 (1)° for (I). If one considers that the shapes of these three molecules may be defined by three 'wedges' meeting at a common vertex (C1) and represented by a plane through each of the cyclohexane and phenyl rings and a plane through the carboxyl group, the three molecules are nearly identical in terms of the relative orientation of these planes. Owing to the geometrical isomerism, of course, the electronic distribution within two of these 'wedges' will be reversed.

There is an intermolecular hydrogen bond between carboxylic acid groups related by the crystallographic inversion center in the structure of (I). The associated metrical parameters are $O1 \cdots O2 = 2.631(3)$, $HO1 \cdots O2 = 1.84(3)$ Å with an angle at hydrogen of 172 (3)°. In (II) the intermolecular hydrogen bonding also involves carboxylic dimers formed between head-to-tail arranged independent molecules. The associated geometrical parameters are $O1 \cdots O2' = 2.640(6)$, $HO1 \cdots O2' = 1.54$ Å with an angle at H of 166° and $O1' \cdots O2 = 2.634(6)$, $HO1' \cdots O2 = 1.53$ Å with an angle at H of 159°.

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The Structures of Three Strained Cage Molecules

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Abstract. (1) Ethyl {2-hydroxy-9-methyl-6-oxopentacyclo[5.5.0.0^{4,11}.0^{5,9}.0^{8,12}]dodec-2-en-3-yl}carboxylate, $C_{16}H_{18}O_4$, $M_r = 274.32$, monoclinic, $P2_1/n$, $a =$

12.564 (1), $b = 6.825$ (1), $c = 16.088$ (2) Å, $\beta = 101.38$ (1)°, $V = 1352.4$ (2) Å³, $Z = 4$, $D_x = 1.347$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.90$ cm⁻¹, $F(000) = 584$, $T = 294$ K, $R = 0.0407$ for 1413 reflections. (2) Ethyl {2-hydroxy-1,7-dimethyl-6-oxopentacyclo[5.5.0.0^{4,11}.0^{5,9}.0^{8,12}]dodec-2-en-3-yl}carboxylate, $C_{17}H_{20}O_4$, $M_r = 288.35$, monoclinic, $P2_1/n$, $a =$

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