

We thank the National Institutes of Health for an instrumentation grant (grant 1510 RRO 1486 01A1) and the 3M Corporation, St. Paul, MN, for support through a grant to Rutgers University.

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Acta Cryst. (1990). **C46**, 640–643

Methyl *trans*-2-(Diphenylmethyl)-5-(hydroxymethyl)-3-isoxazolidinylacetate and *cis*-5-(Ethoxymethyl)-2-phenyl-3-isoxazolidinyl Phenyl Ketone

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(Received 2 June 1989; accepted 21 July 1989)

Abstract. C₁₉H₂₁NO₄ (1): $M_r = 327.38$, monoclinic, $P2_1/n$, $a = 10.103$ (3), $b = 20.253$ (4), $c = 9.273$ (2) Å, $\beta = 115.49$ (2)°, $V = 1713$ (1) Å³, $Z = 4$, $D_m = 1.25$ (2), $D_x = 1.27$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.52$ cm⁻¹, $F(000) = 696.0$. Final conventional $R = 0.046$ for 2742 unique observed reflections. C₁₉H₂₁NO₃ (2): $M_r = 311.37$, orthorhombic, $Pbca$, $a = 18.213$ (3), $b = 20.451$ (4), $c = 8.904$ (2) Å, $V = 3317$ (3) Å³, $Z = 8$, $D_m = 1.24$ (2), $D_x = 1.25$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.48$ cm⁻¹, $F(000) = 1328.0$. Final conventional $R = 0.066$ for 1836 unique observed reflections. The stereochemistry of both compounds was established unequivocally. The conformation of the isoxazolidine ring of (1) has approximate C_2 symmetry through C(5), while that

of (2) has C_s symmetry, N(2) being the out-of-plane atom. Two substituents at N(2) and C(3) of both compounds have a *trans*-diaxial orientation in the crystal structure.

Introduction. The investigation of regio- and stereo-selectivities in the 1,3-dipolar cycloaddition of nitrones is one of the most stimulating problems from both theoretical and synthetic points of view (Padwa, 1984). In order to clarify the selectivities, it is essential to elucidate the stereochemistry of the isoxazolidine ring. However, it is sometimes difficult to assign the stereochemistry by ordinary ¹H NMR techniques because the isoxazolidine ring may exist in many different conformers.

Table 1. Final atomic coordinates of the non-H atoms ($\times 10^4$) and equivalent isotropic temperature factors with e.s.d.'s in parentheses

	x	y	z	B_{eq}^* (\AA^2)
(1)				
O(1)	2216 (2)	657 (1)	2501 (2)	4.3 (1)
N(2)	1467 (2)	1089 (1)	3112 (3)	3.8 (1)
C(3)	2583 (3)	1198 (1)	4822 (3)	4.0 (1)
C(4)	4042 (3)	1222 (2)	4798 (4)	4.3 (1)
C(5)	3787 (3)	770 (2)	3389 (4)	4.2 (1)
C(6)	2521 (3)	631 (2)	5840 (4)	4.8 (1)
O(7)	3355 (3)	184 (1)	6298 (4)	10.7 (2)
O(8)	1456 (3)	693 (1)	6199 (3)	7.2 (1)
C(9)	1313 (5)	180 (2)	7210 (5)	9.1 (2)
C(10)	4295 (4)	1044 (2)	2220 (4)	6.0 (2)
O(11A)	5746 (4)	1116 (2)	2892 (5)	5.8 (2)
O(11B)	4334 (8)	606 (3)	1197 (7)	8.1 (3)
C(12)	1099 (3)	1710 (1)	2153 (3)	3.5 (1)
C(13)	217 (3)	1576 (1)	331 (3)	3.5 (1)
C(14)	302 (3)	2022 (2)	-742 (4)	4.3 (1)
C(15)	-530 (4)	1947 (2)	-2408 (4)	5.3 (2)
C(16)	-1460 (4)	1421 (2)	-3036 (4)	5.4 (2)
C(17)	-1550 (4)	967 (2)	-1978 (4)	5.0 (1)
C(18)	-715 (3)	1043 (2)	-307 (4)	4.3 (1)
C(19)	258 (3)	2151 (1)	2735 (3)	3.5 (1)
C(20)	803 (4)	2759 (2)	3411 (4)	4.5 (1)
C(21)	1 (4)	3173 (2)	3889 (4)	5.4 (2)
C(22)	-1345 (4)	2973 (2)	3676 (4)	5.6 (2)
C(23)	-1887 (4)	2366 (2)	3026 (4)	5.7 (2)
C(24)	-1092 (3)	1954 (2)	2557 (4)	4.8 (1)
(2)				
O(1)	7052 (2)	4351 (2)	-400 (4)	4.0 (2)
N(2)	7533 (3)	4814 (2)	294 (5)	3.5 (2)
C(3)	7092 (3)	5058 (3)	1562 (6)	3.5 (3)
C(4)	6680 (4)	4466 (3)	2139 (7)	4.1 (3)
C(5)	6662 (3)	4010 (3)	787 (7)	4.0 (3)
C(6)	6593 (3)	5590 (3)	913 (6)	3.9 (3)
O(7)	5935 (2)	5513 (2)	861 (6)	5.8 (2)
C(8)	6945 (3)	6187 (3)	283 (6)	3.7 (3)
C(9)	6610 (4)	6497 (3)	-931 (7)	4.7 (3)
C(10)	6931 (4)	7048 (3)	-1546 (8)	5.5 (4)
C(11)	7572 (4)	7296 (3)	-962 (8)	5.1 (3)
C(12)	7893 (4)	7001 (3)	236 (8)	5.1 (3)
C(13)	7590 (4)	6443 (3)	847 (7)	4.4 (3)
C(14)	5916 (4)	3857 (3)	202 (8)	5.1 (4)
O(15)	5971 (3)	3390 (2)	-941 (6)	7.7 (3)
C(16)	5278 (5)	3254 (4)	1501 (12)	12.5 (6)
C(17)	5263 (5)	2581 (4)	-2271 (11)	11.4 (6)
C(18)	8240 (3)	4545 (3)	587 (6)	3.5 (3)
C(19)	8739 (3)	4897 (3)	1443 (7)	4.6 (3)
C(20)	9451 (4)	4675 (4)	1606 (9)	5.5 (4)
C(21)	9668 (4)	4102 (4)	935 (9)	5.7 (4)
C(22)	9176 (4)	3750 (4)	114 (8)	5.7 (4)
C(23)	8463 (4)	3965 (3)	-74 (7)	4.6 (3)

* B_{eq} is the arithmetic mean of the principal axes of the thermal ellipsoid.

In the course of our work on 1,3-dipolar cycloaddition, we obtained several isoxazolidine derivatives, some of which were obtained in crystalline form. The reaction of *N*-diphenylmethyl- α -methoxy-carbonylmethanimine *N*-oxide with acryl aldehyde gave a mixture of two epimeric adducts in the ratio 82:18. The aldehyde group was easily reduced by sodium borohydride at low temperature to give crystalline alcohols [(1) and (1a)], from which the major isomer (1) was separated by recrystallization. The stereochemistry of (1) has previously been assumed to be 3,5-*trans* by converting it to allo-hydroxyproline (Hara, Inouye & Kakisawa, 1981).

The reaction of *N*-phenyl- α -benzoylmethanimine *N*-oxide with 3-ethoxypropene gave a mixture of regioisomers (2) and (2a) [(2):(2a) = 91:9]. The stereochemistry of the major isomer (2) remained

Table 2. Selected bond distances (\AA), bond angles ($^\circ$) and torsion angles ($^\circ$) around the isoxazolidine ring with e.s.d.'s in parentheses

	(1)	(2)
O(1)—N(2)	1.424 (3)	1.431 (5)
N(2)—C(3)	1.515 (3)	1.472 (7)
C(3)—C(4)	1.484 (4)	1.514 (8)
C(4)—C(5)	1.525 (4)	1.524 (8)
C(5)—O(1)	1.458 (3)	1.451 (7)
N(2)—C(subst)	1.493 (3)	1.425 (7)
C(3)—C(subst)	1.506 (4)	1.530 (8)
C(5)—C(subst)	1.491 (4)	1.489 (8)
C(3)—H(3)	0.95 (3)	1.00 (5)
C(4)—H(4A)	1.00 (2)	0.98 (6)
C(4)—H(4B)	0.98 (3)	1.00 (6)
C(5)—H(5)	1.03 (3)	0.94 (5)
(1)		(2)
N(2)—O(1)—C(5)	108.3 (2)	107.6 (4)
O(1)—N(2)—C(3)	102.8 (2)	102.9 (4)
O(1)—N(2)—C(subst)	108.6 (2)	112.1 (4)
C(3)—N(2)—C(subst)	112.5 (2)	118.9 (4)
N(2)—C(3)—C(4)	106.6 (2)	105.0 (4)
N(2)—C(3)—C(subst)	109.4 (2)	105.9 (4)
C(4)—C(3)—C(subst)	110.1 (2)	113.7 (5)
C(3)—C(4)—C(5)	101.0 (2)	103.4 (5)
O(1)—C(5)—C(4)	108.6 (2)	105.7 (4)
O(1)—C(5)—C(subst)	106.2 (2)	107.0 (5)
C(4)—C(5)—C(subst)	114.5 (3)	115.1 (5)

Torsion angles and the observed J (Hz); e.s.d.'s in angles are 2–5 $^\circ$

	(1)	J	(2)	J
H(3)—C(3)—C(4)—H(4A)	31.5	8.5	18.9	8.5
H(3)—C(3)—C(4)—H(4B)	90.5	4.2	99.6	4.2
H(4A)—C(4)—C(5)—H(5)	140.0	7.9	5.7	8.3
H(4B)—C(4)—C(5)—H(5)	16.4	7.6	127.8	7.2

uncertain (Niwayama, Dan, Inouye & Kakisawa, 1985).

We present here a single-crystal X-ray analysis of two isoxazolidine derivatives (1) and (2) in order to elucidate the ambiguous stereochemistry of those adducts.

Experimental. Isoxazolidine (1): colorless prisms from benzene; D_m by flotation in aqueous KI; systematic absences (from Weissenberg photographs) $h00$ for $h = 2n$, $0k0$ for $k = 2n$, $00l$ for $l = 2n$ and $(h0l)$ for $h + l = 2n$; crystal $0.38 \times 0.27 \times 0.28$ mm; Rigaku AFC-5 automated four-circle diffractometer; graphite-monochromated Mo $K\alpha$ radiation, 50 kV and 160 mA; unit-cell dimensions by least-squares refinement from 25 reflections with $19 < 2\theta < 21^\circ$; 2θ - ω scan, scan rate 2° min^{-1} , $\Delta\omega = (1.0 + 0.5 \tan\theta)^\circ$; three standard reflections measured every 50 reflections with $\pm 1\%$ fluctuation; 3039 unique reflections, $2\theta_{\text{max}} = 50^\circ$ ($-12 \leq h \leq 10$, $0 \leq k \leq 24$, $0 \leq l \leq 11$); 2742 reflections with $|F_o| > 3\sigma(F_o)$ used for structure determination; intensities corrected for Lorentz and polarization, not for absorption; structure solved by direct methods (SHELX76; Sheldrick, 1976); first E map ($E \geq 1.5$) revealed positions of all non-H atoms; disorder at the hydroxymethyl group [C(10)—O(11)], site occupancy 0.6:0.4; all H atoms except those around disordered part and of methyl group located from difference

Fourier synthesis; H atoms on methyl group given fixed geometries C—H 1.04 Å and U 0.1 Å²; final refinement on F with anisotropic temperature factors for all non-H atoms and with isotropic H atoms (except H atoms mentioned above), $R = 0.046$, $wR = 0.046$, $w = 1/\sigma^2(F_o)$ from counting statistics, $S = 0.77$; $(\Delta/\sigma)_{\max} < 0.2$; $|\Delta\rho|_{\max}$ in final difference Fourier map = 0.19 e Å⁻³.

Isoxazolidine (2): colorless prisms from hexane-benzene; D_m by flotation in aqueous KI; systematic absences (from Weissenberg photographs) $hk0$ for $h = 2n$, $0kl$ for $k = 2n$ and $h0l$ for $l = 2n$; crystal 0.30 × 0.25 × 0.08 mm; collection of the reflection data and structural analyses similar to (1); three standard

reflections measured every 56 reflections with ±3% fluctuation; 2176 unique reflections, $2\theta_{\max} = 45^\circ$ ($0 \leq h \leq 19$, $0 \leq k \leq 22$, $0 \leq l \leq 9$); 1838 reflections with $|F_o| > 3\sigma(F_o)$ used for structure determination; two large reflections apparently seriously affected by extinction (200,020) omitted from final refinement; first E map ($E \geq 1.5$) revealed positions of 20 non-H atoms; successive difference Fourier syntheses determined positions of all non-H atoms; all H atoms located from difference Fourier synthesis; H atoms on methyl group given fixed geometries C—H 1.04 Å and U 0.1 Å²; bond length C(16)—C(17) constrained to 1.54 Å with $\sigma = 0.002$; final refinement on F with anisotropic temperature factors for all non-H atoms and with isotropic H atoms (except H atoms mentioned above), $R = 0.066$, $wR = 0.066$, $S = 2.17$; $(\Delta/\sigma)_{\max} < 0.2$; $|\Delta\rho|_{\max}$ in final difference Fourier map = 0.13 e Å⁻³. All numerical calculations carried out on a Facom M-382 computer in the Science Information Processing Center of the University of Tsukuba; scattering factors from *International Tables for X-ray Crystallography* (1974).

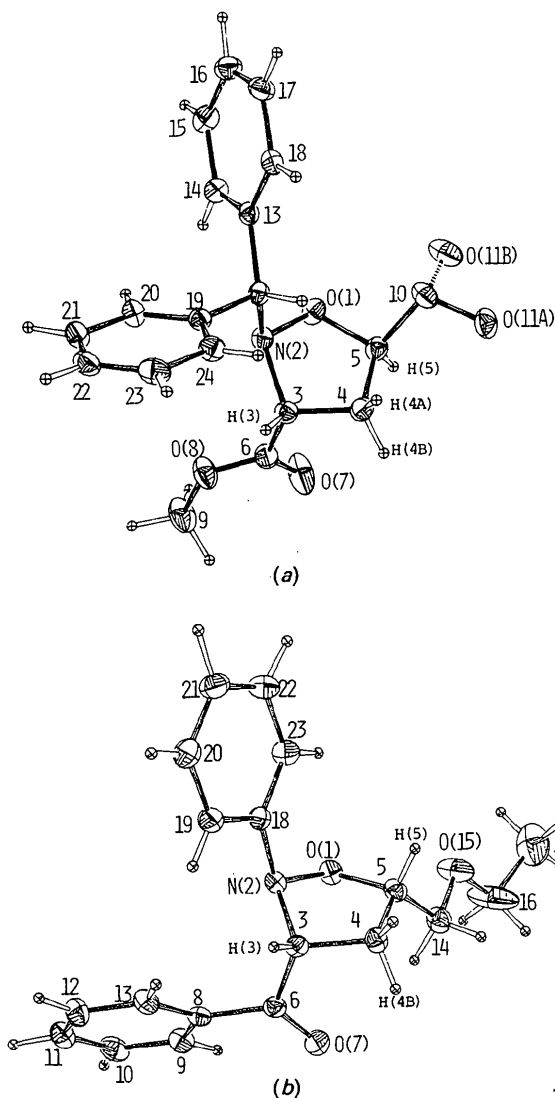


Fig. 1. ORTEP (Johnson, 1976) drawings of the molecules with thermal ellipsoids at the 50% probability level and numbering schemes. H atoms are represented by circles of radius 0.1 Å. (a) (1), the disordered part is shown by the dotted line. (b) (2).

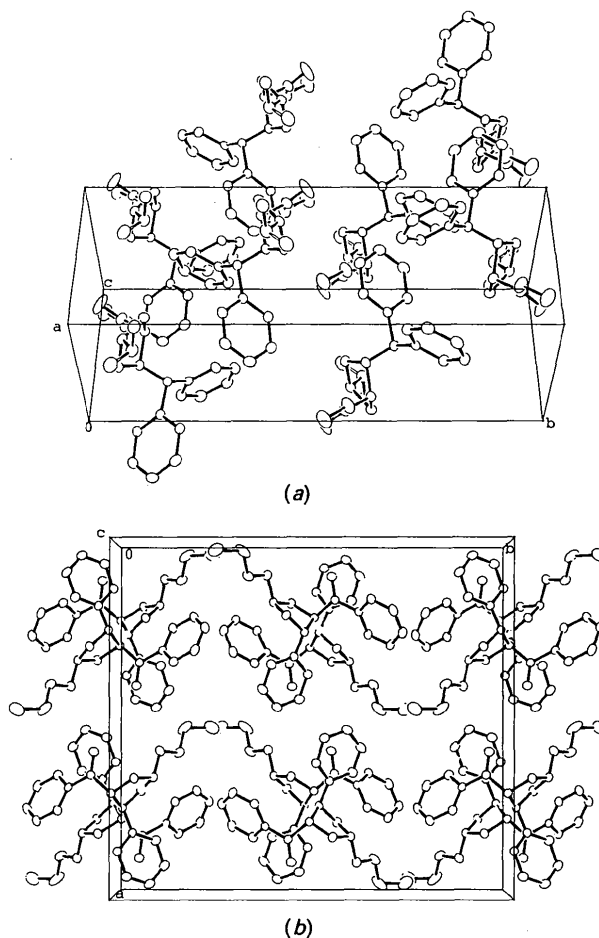


Fig. 2. The crystal packings. (a) (1); (b) (2).

Discussion. The final atomic parameters are listed in Table 1.* Molecular structures of (1) and (2) are shown in Fig. 1 with numbering schemes. The stereochemistry of (1) is shown to be 3,5-*trans* as previously thought and that of (2) as 3,5-*cis* unequivocally. The geometries of the isoxazolidine rings in both compounds are similar but a slight difference is observed in some of the bond lengths and angles as shown in Table 2. The conformation of the isoxazolidine ring in the crystal has approximate C_2 symmetry through C(5) in (1) [deviation from O(1)—C(5)—C(4) plane: N(2) -0.21 Å and C(3) $+0.34$ Å], and C_s symmetry [with N(2) the out-of-plane atom] in (2) [N(2) -0.56 Å]. In both compounds, the configuration of the substituents at the N(2) and C(3) positions is *trans*-diaxial due to the steric repulsion of the two substituents. The torsion angles between the protons on the ring are shown in Table 2 together with the coupling constants observed in $CDCl_3$. The angles and the coupling constants are not necessarily correlated; this is apparently due either to the pseudorotation or to equilibrium among several conformers in solution.

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, and bond lengths have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52448 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The crystal packings are shown in Fig. 2. In (1), both the disordered hydroxyl groups [C(10)—O(11A) and C(10)—O(11B)] are bonded to the carbonyl O atom [O(7)] of the ester group [O(11A)(x, y, z) \cdots O(7) ($1-x, -y, 1-z$) = 2.781 (5) Å, C(10)—O(11A) \cdots O(7) = 100.9 (3) $^\circ$; O(11B)(x, y, z) \cdots O(7) ($1-x, -y, 1-z$) = 2.956 (8) Å, C(10)—O(11A) \cdots O(7) = 93.3 (4) $^\circ$]. Other interatomic contacts are within van der Waals distances; the shortest distance is 3.302 (5) Å for O(1)(x, y, z) \cdots C(17)($-x, -y, -z$). On the other hand, only van der Waals contacts are recognized in (2). The shortest distance is 3.348 (7) Å for C(3)(x, y, z) \cdots O(1)($1.5-x, 1-y, 0.5+z$). The somewhat large thermal vibrations observed at C(16) and C(17) in (2) may be due to the presence of some disorder around the ethoxymethyl group.

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Acta Cryst. (1990). **C46**, 643–645

X-ray Structure of the Monoclinic Form of 1,8,15,22-Tetrathia[1.1.1]-metacyclophane

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(Received 11 May 1989; accepted 27 June 1989)

Abstract. 2,8,14,20-Tetrathiapentacyclo[19.3.1.1^{3,7}.-19¹³.1^{15,19}]octacosane-1(25),3,5,7(28),9,11,13(27),15,17,-19(26),21,23-dodecaene, $C_{24}H_{16}S_4$, $M_r = 432.6$, monoclinic, $P2_1/n$, $a = 15.418$ (2), $b = 7.776$ (1), $c = 17.048$ (1) Å, $\beta = 93.24$ (1) $^\circ$, $V = 2040.5$ (3) Å³, $Z = 4$, $D_x = 1.408$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.46$ mm⁻¹, $F(000) = 896$, $T = 293$ K, $R = 0.052$ for 1848 observed reflections. The molecule has distorted *mm2* symmetry and a nonplanar conformation, close to that observed in the triclinic form. Two of the

four benzene rings have rather short contacts of ~ 3.50 Å with the corresponding and almost parallel rings of the neighbouring molecules, suggesting a weak intermolecular stacking interaction.

Introduction. The conformational flexibility of phenylenesulfides resulting in the existence of different conformers in crystals is of significant importance for their possible application as complexones (Ovchinnikov, Zamaev, Shklover, Palyulin,