

This work was supported by the Polish Academy of Sciences (problem PAN-MR. 1.9).

### References

- DARRIET, H., DARRIET, J., CASSAIGNE, A. & NEUZIL, E. (1975). *Acta Cryst.* **B31**, 469–471.
- DERISSEN, J. L., ENDEMAN, H. J. & PEERDEMAN, A. F. (1968). *Acta Cryst.* **B24**, 1349–1354.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- HILDERBRAND, R., CURLEY-JOSEPH, J., LUBANSKY, H. J. & HENDERSON, T. O. (1982). *Top. Phosphorus Chem.* pp. 297–338.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- KOWALIK, J., SAWKA-DOBROWOLSKA, W. & GŁOWIAK, T. (1984). *J. Chem. Soc. Chem. Commun.* pp. 446–447.
- MARSH, R. E. & DONOHUE, J. (1967). *Adv. Protein Chem.* **22**, 235–256.
- OKAYA, Y. (1966). *Acta Cryst.* **20**, 712–715.
- RAO, S. T. (1973). *Acta Cryst.* **B29**, 1718–1720.
- ROBERTS, P. J., FOSTER, G. A., SHARIF, N. A. & COLLINS, J. F. (1982). *Brain Res.* **238**, 475–479.
- SAWKA-DOBROWOLSKA, W., GŁOWIAK, T., SIATECKI, Z. & KOWALIK, J. (1984). To be published.
- SIATECKI, Z. & KOZŁOWSKI, H. (1980). *Org. Magn. Reson.* **14**(5), 431–433.
- SIATECKI, Z. & KOZŁOWSKI, H. (1981). *Org. Magn. Reson.* **17**(3), 172–174.
- SOROKA, M. & MASTALERZ, P. (1976). *Rocz. Chem.* **50**, 661–666.
- Syntax (1976). *XTL/XTLE Structure Determination System*. Syntax Analytical Instruments, Cupertino, California.

*Acta Cryst.* (1985). **C41**, 456–458

## Methyl 3-Phenyl-4a,7,8,8a-tetrahydropyrido[4,3-e][1,4,2]dioxazine-7-carboxylate, C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub>

BY RICHARD G. BALL

*Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2*

AND EDWARD E. KNAUS AND SUSHIL K. DUBEY

*Department of Pharmacy, University of Alberta, Edmonton, Alberta, Canada T6G 2N8*

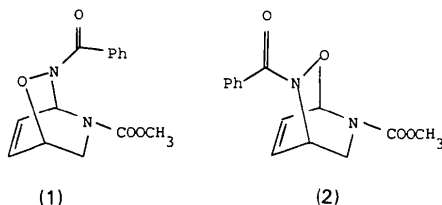
(Received 5 July 1984; accepted 24 October 1984)

**Abstract.**  $M_r = 274.28$ , monoclinic,  $P2_1/c$ ,  $a = 14.304$  (5),  $b = 10.297$  (2),  $c = 9.092$  (3) Å,  $\beta = 102.09$  (3)°,  $V = 1309$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.39$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu(\text{Mo } K\alpha) = 0.097$  mm<sup>-1</sup>,  $F(000) = 576$ ,  $T = 294$  K,  $R = 0.061$  for 769 observed reflections. The title compound was prepared by the rearrangement of the product from the reaction of nitrosocarbonylbenzene with methyl 1,2-dihydro-1-pyridinecarboxylate. The pyrido and dioxazine rings are fused in an *endo* conformation.

**Introduction.** The title compound is a rearrangement product arising from one of two possible regioisomers, (1) and (2), formed by the ( $\pi_2 + \pi_4$ ) cycloaddition reaction of nitrosocarbonylbenzene with methyl 1,2-dihydro-1-pyridinecarboxylate. The crystal structure of this rearrangement product was investigated to determine from which regioisomer it was derived.

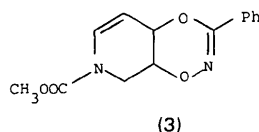
**Experimental.** A solution of tetraethylammonium periodate (5 mmol) in 20 mL dry methylene chloride was added dropwise with stirring to a solution of methyl 1,2-dihydro-1-pyridinecarboxylate (5 mmol) and *N*-benzoylhydroxylamine (5 mmol) in 100 mL dry methylene chloride under nitrogen at 195 K. The reaction mixture was allowed to warm to 298 K followed by continued stirring for an additional 6 h. The solvent was removed *in vacuo* and the residue was chromatographed on a silica-gel column using ether as the eluant to yield the ( $\pi_2 + \pi_4$ ) adduct as a viscous oil. The viscous oil was allowed to stand at room temperature for 14 d during which time it rearranged completely. Trituration of this product with hexane and then ether afforded a white solid, m.p. 401–403 K (methanol).

Crystal 0.07 × 0.09 × 0.31 mm. CAD-4 diffractometer. Lattice parameters determined using 17 reflections with  $9 < 2\theta < 20^\circ$ . Lp correction applied. No absorption correction. Intensity measurements in range  $0 < 2\theta < 54^\circ$  (index limits:  $h \pm 18$ ;  $k \pm 13$ ;  $l \pm 11$ ). Intensity standards:  $\bar{2}12$  11864 (117);  $02\bar{1}$  21098 (403). 3206 reflections measured, 2846 unique, 2077 unobserved [ $I < 3\sigma(I)$ ]. *R* factor for merging equivalent reflections 0.027. Structure solved by direct methods using *MULTAN*11/82 (Main, 1982). Full-



matrix least-squares refinement using  $F$  magnitudes. All H atoms located in a difference Fourier map and used to calculate idealized coordinates (C—H 0.95 Å). The H atoms on C(14) are disordered between two orientations and all six sites were included with the H atoms assigned occupancies of 0.5. H-atom positional parameters were constrained to 'ride' with the appropriate C atom and the thermal parameters were kept fixed at arbitrary values. Positional and isotropic thermal parameters for all non-H atoms were refined.  $R = 0.061$ ,  $wR = 0.072$ ,  $S = 1.76$ . Weights of  $1/\sigma^2(F)$  with  $\sigma(F)$  defined by Stout & Jensen (1968, equation H.14) with instability factor of 0.04.  $(\Delta/\sigma)_{\max} = 0.1$ . Maximum peak height in final difference Fourier map  $0.28(6) e \text{ \AA}^{-3}$ . No secondary-extinction correction. Atomic scattering factors,  $f'$  and  $f''$  values from *International Tables for X-ray Crystallography* (1974). Computer programs used include the Enraf-Nonius (1983) *SDP* package and *ORTEP* (Johnson, 1976).

**Discussion.** The crystal structure of the rearrangement product proves that it is (3) with the stereochemistry shown in Fig. 1.



Thus the original regioisomer must be (1) which then rearranges to (3) by a [3,3] sigmatropic shift.

The atomic positional and isotropic thermal parameters are given in Table 1.\* The bond distances

\* Lists of structure factors and H-atom positional and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39866 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

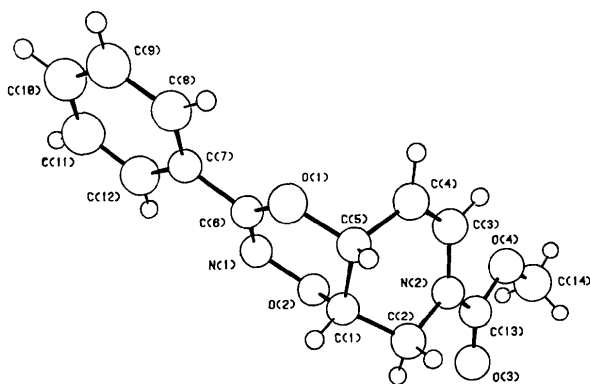


Fig. 1. Perspective view of the molecule showing the atom-numbering scheme for the non-H atoms. H-atom labels are derived from the C atom to which they are attached. Atoms are represented by thermal ellipsoids at the 50% probability level except for H atoms which are drawn at an arbitrary size.

and angles within the molecule, Table 2, are all normal values and there are no short intermolecular distances, indicating only normal van der Waals interactions between molecules. As expected the phenyl ring is essentially coplanar with the plane defined by N(1), C(6) and O(1) in order to allow for conjugation with the double bond between N(1) and C(6). Similarly, the methoxycarbonyl group is approximately coplanar with N(2), C(3) and C(4) to permit delocalization of the double bond between C(3) and C(4).

Table 1. *Positional parameters* ( $\times 10^4$ ) and *isotropic thermal parameters* ( $\times 10^2$ ), with *e.s.d.'s* in parentheses

The isotropic temperature factor is of the form  $\exp(-8\pi^2 U \sin^2 \theta / \lambda^2)$ .

	$x$	$y$	$z$	$U(\text{\AA}^2)$
O(1)	3551 (3)	4200 (5)	1504 (5)	5.4 (1)
O(2)	2316 (3)	2430 (4)	2331 (4)	4.4 (1)
O(3)	-571 (3)	2473 (5)	1383 (5)	5.9 (1)
O(4)	-432 (3)	4424 (5)	2513 (5)	6.1 (1)
N(1)	3290 (3)	2498 (5)	3095 (5)	4.4 (1)
N(2)	656 (3)	3831 (5)	1219 (6)	4.6 (1)
C(1)	2128 (4)	2886 (6)	799 (7)	4.2 (2)
C(2)	1063 (4)	2907 (7)	305 (7)	5.0 (2)
C(3)	1155 (5)	4991 (7)	1619 (8)	5.1 (2)
C(4)	2003 (4)	5201 (7)	1367 (7)	4.9 (2)
C(5)	2559 (4)	4208 (7)	721 (7)	4.2 (2)
C(6)	3799 (4)	3353 (6)	2656 (7)	4.1 (2)
C(7)	4816 (4)	3488 (6)	3415 (7)	4.2 (2)
C(8)	5378 (5)	4483 (7)	3084 (7)	5.5 (2)
C(9)	6329 (5)	4575 (8)	3804 (8)	6.4 (2)
C(10)	6721 (5)	3708 (8)	4872 (8)	6.3 (2)
C(11)	6169 (5)	2713 (8)	5243 (9)	7.3 (2)
C(12)	5214 (5)	2592 (8)	4503 (8)	6.3 (2)
C(13)	-152 (4)	3482 (7)	1694 (7)	4.9 (2)
C(14)	-1294 (5)	4143 (8)	3065 (9)	7.5 (3)

Table 2. *Bond distances* (Å) and *angles* ( $^\circ$ ) with *e.s.d.'s* in parentheses

O(1)—C(5)	1.449 (5)	C(1)—C(2)	1.495 (6)
O(1)—C(6)	1.352 (5)	C(1)—C(5)	1.501 (7)
O(2)—N(1)	1.423 (4)	C(3)—C(4)	1.298 (7)
O(2)—C(1)	1.442 (5)	C(4)—C(5)	1.489 (7)
O(3)—C(13)	1.204 (6)	C(6)—C(7)	1.480 (6)
O(4)—C(13)	1.334 (6)	C(7)—C(8)	1.374 (7)
O(4)—C(14)	1.455 (6)	C(7)—C(12)	1.385 (7)
N(1)—C(6)	1.260 (6)	C(8)—C(9)	1.383 (6)
N(2)—C(2)	1.462 (6)	C(9)—C(10)	1.351 (7)
N(2)—C(3)	1.400 (6)	C(10)—C(11)	1.379 (8)
N(2)—C(13)	1.364 (6)	C(11)—C(12)	1.397 (7)
C(5)—O(1)—C(6)	117.1 (4)	C(1)—C(5)—C(4)	110.2 (4)
N(1)—O(2)—C(1)	114.9 (3)	O(1)—C(6)—N(1)	128.3 (5)
C(13)—O(4)—C(14)	115.0 (5)	O(1)—C(6)—C(7)	112.0 (5)
O(2)—N(1)—C(6)	116.9 (4)	N(1)—C(6)—C(7)	119.7 (5)
C(2)—N(2)—C(3)	117.4 (4)	C(6)—C(7)—C(8)	122.1 (5)
C(2)—N(2)—C(13)	118.3 (4)	C(6)—C(7)—C(12)	119.1 (5)
C(3)—N(2)—C(13)	124.2 (5)	C(8)—C(7)—C(12)	118.8 (5)
O(2)—C(1)—C(2)	105.4 (4)	C(7)—C(8)—C(9)	120.7 (5)
O(2)—C(1)—C(5)	110.2 (4)	C(8)—C(9)—C(10)	120.9 (6)
C(2)—C(1)—C(5)	112.0 (4)	C(9)—C(10)—C(11)	119.6 (6)
N(2)—C(2)—C(1)	109.9 (4)	C(10)—C(11)—C(12)	120.1 (6)
N(2)—C(3)—C(4)	122.7 (5)	C(7)—C(12)—C(11)	119.9 (6)
C(3)—C(4)—C(5)	123.4 (5)	O(3)—C(13)—O(4)	124.4 (5)
O(1)—C(5)—C(1)	109.9 (4)	O(3)—C(13)—N(2)	124.5 (5)
O(1)—C(5)—C(4)	111.0 (4)	O(4)—C(13)—N(2)	111.0 (5)

## References

- Enraf-Nonius (1983). *Structure Determination Package*. Enraf-Nonius, Delft.
- International Tables for X-ray Crystallography* (1974). Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- MAIN, P. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England.
- STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*. New York: Macmillan.

*Acta Cryst.* (1985). **C41**, 458–460

**15,30-Dihydroxy-12,27-dimethyl-5,20-dioxa-2,8,17,23-tetrathia[9.9]metacyclophane\* ( $\beta$  Form), C<sub>26</sub>H<sub>36</sub>O<sub>4</sub>S<sub>4</sub>, and 15-Hydroxy-12-methyl-5-oxa-2,8-dithia[9]metacyclophane, C<sub>13</sub>H<sub>18</sub>O<sub>2</sub>S<sub>2</sub>**

BY MARIO CANNAS, GIAIME MARONGIU AND GABRIELE NAVARRA

*Dipartimento di Scienze Chimiche dell'Università, Via Ospedale 72, 09100 Cagliari, Italy*

(Received 14 June 1984; accepted 8 November 1984)

**Abstract.** C<sub>26</sub>H<sub>36</sub>O<sub>4</sub>S<sub>4</sub>,  $M_r = 540.83$ , triclinic,  $P\bar{1}$ ,  $a = 14.85$  (2),  $b = 9.18$  (2),  $c = 5.17$  (1) Å,  $\alpha = 103.4$  (3),  $\beta = 98.7$  (3),  $\gamma = 90.3$  (3)°,  $V = 677$  (2) Å<sup>3</sup>,  $Z = 1$ ,  $D_m = 1.32$ ,  $D_x = 1.33$  g cm<sup>-3</sup>, Cu  $K\alpha$ ,  $\lambda = 1.5418$  Å,  $\mu = 33.2$  cm<sup>-1</sup>,  $F(000) = 288$ ,  $T = 293$  K,  $R = 0.079$  for 1427 observed reflections. C<sub>13</sub>H<sub>18</sub>O<sub>2</sub>S<sub>2</sub>,  $M_r = 270.42$ , monoclinic,  $P2_1/c$ ,  $a = 12.61$  (2),  $b = 7.72$  (1),  $c = 14.14$  (2) Å,  $\beta = 102.8$  (3)°,  $V = 1342$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.33$ ,  $D_x = 1.34$  g cm<sup>-3</sup>, Cu  $K\alpha$ ,  $\lambda = 1.5418$  Å,  $\mu = 33.5$  cm<sup>-1</sup>,  $F(000) = 576$ ,  $T = 293$  K,  $R = 0.083$  for 1721 observed reflections. The latter molecule is a 12-membered metacyclophane macrocycle derived by introducing 5-oxa-2,8-dithianonane on the 2,6 positions of 4-methylphenol; the former, formally the dimer of the latter, is a centrosymmetric 24-membered crown metacyclophane macrocycle. In both compounds the molecular conformation is stabilized by transannular hydrogen bonds involving the hydroxyl groups.

**Introduction.** Polycondensation in benzyl alcohol of 2,6-bis[(dimethylamino)methyl]-4-methylphenol with 2,2'-oxydiethanedithiol gives both linear polymers and macrocycles (Costa Bizzarri, Della Casa, Ferruti, Ghedini, Pilati & Scapini, 1984). The latter were crystallized from toluene and from methanol giving rise to orthorhombic and triclinic crystals, respectively, both melting about 420 K. Sublimation of the crude product and successive crystallization from toluene gives monoclinic crystals with m.p. 380 K. NMR, IR and mass spectra were not conclusive in the elucidation of the molecular structures and single-crystal X-ray

analyses were therefore undertaken. In a previous paper (Cannas, Marongiu & Pintori, 1984) it was shown that the molecules present in the orthorhombic crystals are 24-membered macrocycles; herewith the structure determinations of the other two crystalline forms are reported.

**Experimental.** C<sub>26</sub>H<sub>36</sub>O<sub>4</sub>S<sub>4</sub>. Colourless needle-shaped twinned crystal, twin axis [001]; approximate dimensions 0.07 × 0.10 × 2.0 mm mounted along  $c$ ; automatic Siemens AED diffractometer, Ni-filtered Cu  $K\alpha$  radiation; accurate cell dimensions from least-squares fitting of 15 reflections  $27 \leq \theta \leq 38^\circ$ ;  $\theta$ - $2\theta$  scan; three standard reflections (142, 132, 722) recorded every 200 reflections showed linear isotropic decrease of 25%; 1675 unique reflections  $2\theta \leq 110^\circ$  ( $-15 \leq h \leq 15$ ,  $-9 \leq k \leq 10$ ,  $0 \leq l \leq 5$ ); 1427 reflections with  $I \geq 2.5\sigma(I)$  used in structure determination and refinement; intensities corrected for decomposition, Lorentz and polarization, not for absorption; structure solved by direct methods (*MULTAN78*; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined on  $F$  by block-diagonal least squares (Immirzi, 1967, 1973); separate scale factors for  $hk0$  and  $hk1$  reflections applied to take into account twinning effects on intensities; difference Fourier synthesis in final stages of refinement clearly indicated positions of all H atoms except those of methyl group; residual electron density within 0.31 e Å<sup>-3</sup>. H contribution included and held fixed in final least-squares cycles, S atoms refined anisotropically;  $R = 0.079$ ,  $wR = 0.085$ ,  $S = 0.70$ ;  $|A/\sigma|_{\max} = 0.8$ ,  $|A/\sigma|_{\text{av}} = 0.25$ ,  $w = 1/(5.2 + F_o + 0.0185F_o^2)$ .

C<sub>13</sub>H<sub>18</sub>O<sub>2</sub>S<sub>2</sub>. Crystal fragment 0.07 × 0.24 × 0.40 mm cut from larger colourless crystal, mounted

\* In the modified nomenclature cyclophane has been superseded by benzenophane.