Elbasyouny, A., Brügge, H. J., von Deuten, K., Dickel, M., Knöchel, A., Koch, K. U., Kopf, J., Melzer, D. & Rudolph, G. (1983). *J. Am. Chem. Soc.* **105**, 6568–6577.
Gabe, E. J., Le Page, Y., Charland, J. P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
Goldberg, I. (1975). *Acta Cryst.* **B31**, 754–762.
Goldberg, I. (1984). *Inclusion Compounds*, Vol. 2, edited by J. L. Atwood, J. E. D. Davies & D. D. MacNicol, ch. 9, pp. 261–335. London: Academic Press.
Grant, G. F. & Gabe, E. J. (1978). *J. Appl. Cryst.* **11**, 114–120.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Kaufmann, R., Knöchel, A., Kopf, J., Oehler, J. & Rudolph, G. (1977). *Chem. Ber.* **110**, 2249–2253.
Pauling, L. (1960). *The Nature of the Chemical Bond*. Ithaca, New York: Cornell Univ. Press.
Rogers, R. D. & Green, L. M. (1986). *J. Incl. Phenom.* **4**, 77–84.
Weber, G. (1983). *J. Mol. Struct.* **93**, 333–336.
Weller, F., Borgholte, H., Stenger, H., Vogler, St. & Dehnicke, K. (1989). *Z. Naturforsch. Teil B*, **44**, 1524–1530.

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Structure of (*E*)-5-(Methoxymethylene)-2,4-imidazolidinedione

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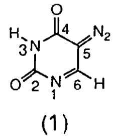
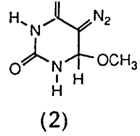
Abstract. $C_5H_6N_2O_3$, $M_r = 142.11$, monoclinic, $P2_1/n$, $a = 3.862\,(1)$, $b = 16.329\,(2)$, $c = 10.088\,(1)$ Å, $\beta = 98.77\,(2)°$, $V = 628.7\,(2)$ Å^3, $Z = 4$, $D_x = 1.50$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0.71069 Å, $\mu = 1.18$ cm^{-1}, $F(000) = 296$, $T = 296$ K, $R = 0.035$ for 1124 independent reflections with $I > 3\sigma(I)$. The structure is a hydantoin derivative with a methoxymethylene group substituted at the 5-position. Excluding the H atoms, the molecule is planar to within 0.032 Å. All of the N and O atoms are involved in an intermolecular hydrogen-bonding network *via* N—H···O and C—H···O interactions. The packing arrangement is a linear ribbon motif with the ribbons stacked to form the short *a* axis.

Introduction. 5-Diazouracil (1) and its derivatives have been of enormous medicinal interest (Previc & Richardson, 1969). Reaction of (1) with methanol gives 5-diazo-6-methoxydihydrouracil (2) (Thurber & Townsend, 1972). The structure of (2) has been confirmed by X-ray crystallography (Abraham, Cochran & Rosenstein, 1971). Morpholine, a secondary amine, also adds to the 1,6-double bond in (1) to give 5-diazo-6-morpholinodihydrouracil (3) (Mathur & Shechter, 1990). Thermolysis of (3) in the presence of catalytic amounts of rhodium acetate in isobutyronitrile at 378 K gives 5-morpholinouracil (4) (Mathur & Shechter, 1990). Similar treatment of (2), however, yields a compound whose spectral properties do not match the expected 5-methoxyuracil (5) (Mathur & Shechter, 1991). An X-ray analysis of this solid reveals the product to be (*E*)-5-(methoxymethylene)-2,4-imidazolidinedione (6) and its structure is reported herein.



(1)



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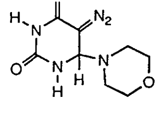

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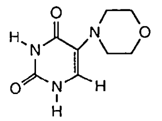

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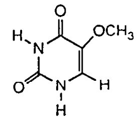

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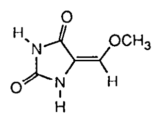

(6)

Experimental. The synthesis of the title compound (6) is reported elsewhere (Mathur & Shechter, 1991). Only the *E* isomer was isolated. Formation of only one isomer in the synthesis of other methylenehydantoins has been previously reported (Tan, Ang & Fong, 1986). The compound crystallized from water as clear orange rectangular rods. The crystal used for data collection was cut from a long rod and was 0.23 × 0.46 × 0.50 mm in size.

Examination of the diffraction pattern with a Rigaku AFC-5S diffractometer indicated a monoclinic crystal system with systematic absences $0k0$, $k = 2n + 1$ and $h0l$, $h + l = 2n + 1$, which uniquely determine the space group as $P2_1/n$. At room temperature the unit-cell constants are based on a symmetry-restricted least-squares fit of the setting angles for 25 reflections in the 2θ range 28 to 30° with graphite-monochromated Mo $K\alpha$ radiation.

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Table 1. *Final positional and thermal parameters for* (6)

The form of the equivalent isotropic thermal parameter is $B_{eq} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$.

	x	y	z	B_{eq} or B(Å^2)
O(1)	0.7522 (3)	0.17370 (7)	0.5638 (1)	3.50 (5)
O(2)	−0.0142 (3)	0.45675 (7)	0.3298 (1)	3.81 (5)
O(4)	0.5273 (3)	0.32052 (7)	0.7020 (1)	3.72 (5)
N(1)	0.2737 (3)	0.33250 (8)	0.3561 (1)	2.86 (5)
N(3)	0.2434 (3)	0.40553 (8)	0.5366 (1)	2.90 (5)
C(2)	0.1499 (4)	0.40345 (9)	0.3980 (1)	2.72 (5)
C(4)	0.4181 (4)	0.33586 (9)	0.5846 (1)	2.57 (5)
C(5)	0.4422 (4)	0.28625 (8)	0.4649 (1)	2.42 (5)
C(6)	0.5948 (4)	0.2141 (1)	0.4546 (1)	2.73 (6)
C(7)	0.8900 (4)	0.0947 (1)	0.5383 (2)	3.94 (7)
H(1)	0.225 (5)	0.315 (1)	0.279 (2)	4.0 (4)†
H(3)	0.191 (5)	0.448 (1)	0.584 (2)	4.6 (4)†
H(6)	0.602 (4)	0.188 (1)	0.370 (2)	3.2 (3)†

† Atoms refined isotropically.

Table 2. *Bond lengths* (Å) *and angles* (°) *for* (6)

O(1)—C(6)	1.347 (2)	N(1)—C(5)	1.407 (2)
O(1)—C(7)	1.433 (2)	N(3)—C(2)	1.390 (2)
O(2)—C(2)	1.224 (2)	N(3)—C(4)	1.373 (2)
O(4)—C(4)	1.221 (2)	C(4)—C(5)	1.469 (2)
N(1)—C(2)	1.346 (2)	C(5)—C(6)	1.329 (2)
N(1)—H(1)	0.82 (2)	N(3)—H(3)	0.89 (2)
C(6)—H(6)	0.96 (2)		

C(6)—O(1)—C(7)	115.3 (1)	O(4)—C(4)—C(5)	129.0 (1)
C(2)—N(1)—C(5)	111.2 (1)	N(3)—C(4)—C(5)	104.9 (1)
C(2)—N(3)—C(4)	111.9 (1)	N(1)—C(5)—C(4)	105.4 (1)
O(2)—C(2)—N(1)	127.8 (1)	N(1)—C(5)—C(6)	125.0 (1)
O(2)—C(2)—N(3)	125.5 (1)	C(4)—C(5)—C(6)	129.6 (1)
N(1)—C(2)—N(3)	106.7 (1)	O(1)—C(6)—C(5)	121.4 (1)
O(4)—C(4)—N(3)	126.2 (1)		

Intensity data were measured by the ω–2θ scan method for the $+h$, $+k$, $\pm l$ quadrant (h 0 to 5, k 0 to 21, l −13 to 12), with $4 \leq 2\theta \leq 55°$. Scan widths were $(1.55 + 0.35\tan\theta)°$ in ω and the scan speed was 4° min^{-1} in ω with a maximum of three rescans per reflection allowed. Six standard reflections (101, 12$\bar{1}$, 03$\bar{1}$, 19$\bar{4}$, 136 and 1,11,0) were measured after every 150 reflections and indicated that the crystal was stable during data collection. Data reduction, which included corrections only for Lorentz and polarization effects, and all subsequent calculations were performed with the *TEXSAN* package of crystallographic programs (Molecular Structure Corporation, 1987). A total of 1700 reflections was measured (excluding standards). The symmetry-equivalent reflections were averaged to give 1431 unique reflections (excluding systematic absences) with an R_{int} value of 0.009 (based on F^2).

The structure was solved using the direct-methods program *MITHRIL* (Gilmore, 1983). All the non-H atoms were located on an electron density map. Isotropic refinement of this model converged at an R value of 0.130. After a cycle of anisotropic refinement, all the H atoms were located on a difference electron density map. The methyl-group H atoms were idealized to sp^3 geometry and included in the model as fixed contributions with the assumptions: C—H = 0.98 Å and $B(\text{H}) = 1.2B_{eq}(\text{C})$. The other three H atoms, H(1), H(3) and H(6), were refined isotropically. At this point a difference electron density map revealed a second orientation for the methyl-group H atoms. These H atoms were also idealized to sp^3 geometry and included in the model as fixed contributions. Occupancy factors for both sets of methyl H atoms were fixed at values based on relative peak heights from the difference electron density maps. All full-matrix least-squares refinements were based on F so that the function minimized in least squares was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. The final refinement cycle for the 1124 intensities with $F_o^2 > 3\sigma(F_o^2)$ and the 103 variables resulted in agreement indices of $R(F) = 0.035$, $wR(F) = 0.046$ and S (error in observation of unit weight) = 1.97. The final difference electron density map contained maximum and minimum peak heights of 0.16 and −0.19 e Å^{-3}. The maximum shift to e.s.d. ratio in the last refinement cycle was 0.03. Scattering factors for the non-H atoms were obtained from the *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 71, 148) and anomalous-scattering components were included for these atoms. The H-atom scattering factors were taken from Stewart, Davidson & Simpson (1965). Final positional parameters with equivalent isotropic temperature factors are listed in Table 1.*

Discussion. Bond distances and angles for (6) are displayed in Table 2. The *ORTEP*II drawing (Johnson, 1976) in Fig. 1 shows the labeling scheme. A stereoview of the unit-cell packing diagram appears in Fig. 2. This structure consists of the 2,4-imidazolidinedione ring (commonly known as hydantoin) with a methoxymethylene group substituted at the 5-position. A search of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) reveals only five other structures of this same type, *i.e.*, with a methylene linkage present at the 5-position and not a part of any other ring system. These five structures are all 5-(arylmethylene)hydantoin derivatives: the Z isomer of 5-[(4-methoxyphenyl)methylene]imidazolidine-2,4-dione (Drew, Mok, Ang & Tan, 1987*a*), the Z isomer of 5-benzylidene-1-methyl-2,4-imidazolidinedione (Drew, Mok, Ang & Tan, 1987*b*), the E isomer of 5-benzylidene-1-methyl-2,4-imidazolidinedione (Drew, Mok, Ang & Tan, 1987*c*), and the E and Z isomers of 1-methyl-5-

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* Lists of final anisotropic thermal parameters, calculated H-atom positions, bond lengths and angles involving H atoms, least-squares planes, and observed and calculated structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54535 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

[(2,4,6-trimethylphenyl)methylene]imidazolidine-2,4-dione (Drew, Mok, Ang & Tan, 1987*d*). The structure determined here is that of the *E* isomer. The five-membered ring in (6) is essentially planar and the other five non-H atoms in this structure are at most 0.032 Å from the least-squares plane through this ring. The metrical parameters at the C(5) atom fall within the ranges observed for the five 5-(arylmethylene)hydantoin structures. The N(1)—C(5) and C(4)—C(5) bond lengths and the N(1)—C(5)—C(4) angle are 1.407 (2), 1.469 (2) Å and 105.4 (1)°, respectively, while the previously reported ranges are 1.373 to 1.404 Å for N(1)—C(5), 1.464 to 1.492 Å for C(4)—C(5) and 104.2 to 105.8° for N(1)—C(5)—C(4). The other two angles at atom C(5) are significantly different from each other: N(1)—C(5)—C(6) is 125.0 (1) and C(4)—C(5)—C(6) is 129.6 (1)°. This distortion is in the direction expected for an *E* isomer.

The short *a* axis of 3.862 Å and the packing arrangement shown in Fig. 2 are features found in the *β*-structural type packing motifs observed for both planar chloroaromatic and oxygenated aromatic compounds (Sarma & Desiraju, 1986). The packing arrangements adopted by these compounds are categorized as planar sheets, linear ribbons or corrugated sheets. This hydantoin structure packs in a linear ribbon motif which is stabilized by hydrogen-bonding interactions. Because of the planarity of the molecule the ribbons are able to stack to form the short *a* axis. The metrical parameters for the infinite intermolecular hydrogen-bonding network are listed in Table 3. Within a ribbon a pair of N—H···O bonds links molecules related by an inversion center: each N(3) and O(2) atom of one molecule is involved in a hydrogen bond with an O(2) and N(3) atom, respectively, in an adjacent molecule with N(3)···O(2) = 2.832 (2) Å. A three-center hydrogen bond between the N(1) atom and the O(1) and O(4) atoms in a glide-plane-related molecule links two molecules which are in different ribbons and different stacks: N(1)···O(1) = 2.939 (2) and N(1)···O(4) = 3.019 (2) Å. There are also two C—H···O interactions involving atoms C(6) and O(4) at 3.148 (2) and 3.301 (2) Å. The O(4) atoms are located in molecules which are within the same stack and related to each other *via* a translation, while the molecule containing C(6) is in an adjacent stack. The role of C—H···O interactions in stabilizing oxygenated aromatic compounds in the 4 Å short-axis *β*-packing mode has been reviewed (Sarma & Desiraju, 1986, 1987). These interactions appear to play a part in stabilizing the packing of this hydantoin structure.

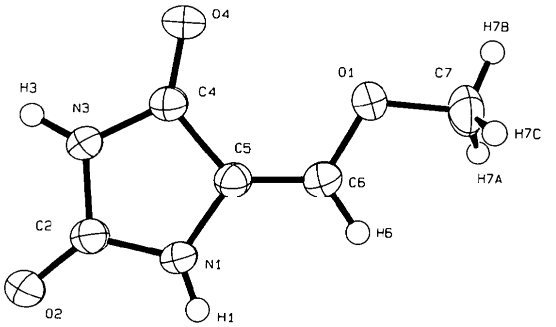

Fig. 1. *ORTEP*II drawing with the labeling scheme for (6). The non-H atoms are represented by 50% probability thermal ellipsoids, while the H atoms are drawn with an artificial radius. Only one orientation for the methyl-group H atoms is shown.

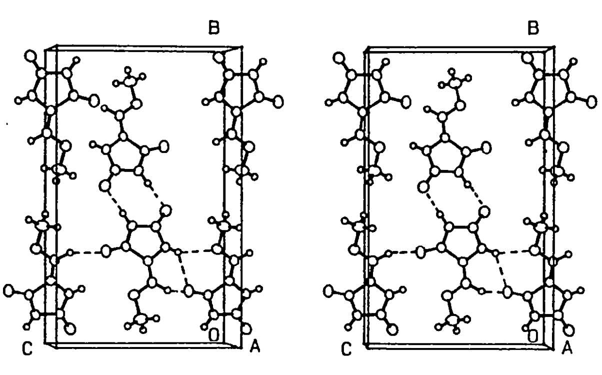

Fig. 2. Stereodrawing of the unit cell. Hydrogen bonds have been designated with dashed lines.

Table 3. *Hydrogen-bond parameters for* (6) (Å, °)

D···*A*		H···*A*		*D*—H···*A*	
N(3)···O(2^{i})	2.832 (2)	H(3)···O(2^{i})	1.95 (2)	N(3)—H(3)···O(2^{i})	172 (2)
N(1)···O(1^{ii})	2.939 (2)	H(1)···O(1^{ii})	2.20 (2)	N(1)—H(1)···O(1^{ii})	150 (2)
N(1)···O(4^{ii})	3.019 (2)	H(1)···O(4^{ii})	2.44 (2)	N(1)—H(1)···O(4^{ii})	129 (2)
C(6)···O(4^{ii})	3.148 (2)	H(6)···O(4^{ii})	2.58 (2)	C(6)—H(6)···O(4^{ii})	118 (1)
C(6)···O(4^{iii})	3.301 (2)	H(6)···O(4^{iii})	2.54 (2)	C(6)—H(6)···O(4^{iii})	137 (1)

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$; (iii) $\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$.

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References

Abraham, D. J., Cochran, T. G. & Rosenstein, R. D. (1971). *J. Am. Chem. Soc.* **93**, 6279–6281.

Allen, F. H., Kennard, O. & Taylor, R. (1983). *Acc. Chem. Res.* **16**, 146–153.

Drew, M. G. B., Mok, K. F., Ang, K. P. & Tan, S. F. (1987*a*). *Acta Cryst.* C**43**, 743–745.

Drew, M. G. B., Mok, K. F., Ang, K. P. & Tan, S. F. (1987*b*). *Acta Cryst.* C**43**, 745–748.

Drew, M. G. B., Mok, K. F., Ang, K. P. & Tan, S. F. (1987*c*). *Acta Cryst.* C**43**, 1177–1179.

Drew, M. G. B., Mok, K. F., Ang, K. P. & Tan, S. F. (1987*d*). *Acta Cryst.* C**43**, 969–972.

Gilmore, C. J. (1983). *MITHRIL. A Computer Program for the Automatic Solution of Crystal Structures from X-ray Data.* Univ. of Glasgow, Scotland.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Mathur, N. C. & Shechter, H. (1990). *Tetrahedron Lett.* **31**, 6965–6968.
Mathur, N. C. & Shechter, H. (1991). *Tetrahedron Lett.* **32**, 3799–3802.
Molecular Structure Corporation (1987). *TEXSAN. TEXRAY Structure Analysis Package.* Version 2.1. MSC, 3200A Research Forest Drive, The Woodlands, TX 77381, USA.
Previc, E. & Richardson, S. (1969). *J. Bacteriol.* **97**, 416–425.
Sarma, J. A. R. P. & Desiraju, G. R. (1986). *Acc. Chem. Res.* **19**, 222–228.
Sarma, J. A. R. P. & Desiraju, G. R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. 1195–1202.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
Tan, S.-F., Ang, K.-P. & Fong, Y.-F. (1986). *J. Chem. Soc. Perkin Trans.* 2, pp.1941–1944.
Thurber, T. C. & Townsend, L. B. (1972). *J. Heterocycl. Chem.* **9**, 629–636.

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Structures of a Cyclic Diimidodisiloxane and its Parent Dianhydride

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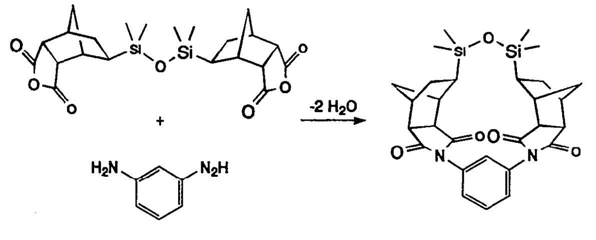
Abstract. (1): (±)-5,5′-(1,1,3,3-Tetramethyldisiloxane-1,3-diyl)bis{(1*R**,2*S**,3*S**,4*R**,5*S**)-bicyclo[2.2.1]heptene-2,3-dicarboxylic anhydride}, $C_{22}H_{30}O_7Si_2$, $M_r = 462.6$, monoclinic, *Cc*, $a = 8.519$ (6), $b = 22.21$ (1), $c = 13.36$ (2) Å, $\beta = 108.06$ (9)°, $V = 2403.4$ Å^3, $Z = 4$, $D_x = 1.28$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.9$ cm^{-1}, $F(000) = 984$, room temperature, final $R = 0.0908$ for 1942 unique observed reflections. (2): (±)-(2*R**,3*S**,3a*S**,12a*S**,13*S**,14*R**,15a*R**,16*S**,20*S**,20a*R**)-2,3,3a,13,14,15,15a,16,17,19,20,20a-Dodecahydro-17,17,19,19-tetramethyl-2,20:3,5:11,13:14,16-tetramethano-6,10-metheno-5*H*-dicyclopent[*d*,*o*][1,7,13,2,18]oxadiazadisilacyclooctadecene-4,12,23,25(1*H*,12a*H*)-tetrone, $C_{28}H_{34}N_2O_5Si_2$, $M_r = 534.8$, orthorhombic, *Pnca*, $a = 11.567$ (3), $b = 12.585$ (4), $c = 18.430$ (4) Å, $V = 2683.0$ Å^3, $Z = 4$, $D_x = 1.32$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.7$ cm^{-1}, $F(000) = 1136$, room temperature, final $R = 0.0833$ for 998 unique observed reflections. The structures of the silicone dianhydride (1) and its unstrained cyclocondensation product with *m*-phenylenediamine (2) have been determined. The bond lengths and angles of the two compounds are very similar except for the Si—O—Si bond angle.

Introduction. This laboratory has been active in the synthesis of functionalized disiloxanes and the preparation of polyimidosiloxanes from them. In particular we have investigated the dianhydride 5,5′-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(bicyclo[2.2.1]heptene-2,3-dicarboxylic anhydride) (1) and the polymer and cyclooligomers which result from its condensation with *m*-phenylenediamine, as shown in the scheme below. In the preparation of the polyimide we have been able to isolate the cyclic monomer (2) in high yield. The monomer was also isolated from a polymerization mixture where the molecular weight was built by siloxane equilibrations (Buese, 1990). In that process, the enthalpy of polymerization is zero. Hence, the cyclic monomer (2) is free of strain. Crystals of (1) and (2) were isolated and determined to be the D,L isomers rather than the *meso* isomers. The first difference in the composition of atoms between these two disiloxanes occurs five bonds from the Si atoms. The configuration of substituents about each atom up to that point is identical. This paper describes the structure of the two disiloxanes, (1) and (2). It will be shown that the common segments of these two unstrained structures are significantly different only in conformation and in the Si—O—Si bond angle.



Experimental. The synthesis of (1) has been reported by Ryang (1983). The white solid had a melting

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