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Article

Derivatives of *N,N'*-bis[2-hydroxy-1,1-bis(hydroxymethyl)ethyl]ethanediamide

***John N. Low*[a], *Bruce F. Milne*[a], *Jennifer-Nicola Ross*[a] *and James L. Wardell**[b]**

[a] *Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland*

[b] *Departamento de Química Inorgânica, Instituto de Química, Universidade Federal do Rio de Janeiro, CP 68563, 21945-970, Rio de Janeiro - RJ, Brazil*

O composto $[(HOCH_2)_3CNHC(O)]_2$ (**1**), formado a partir da reação de $(HOCH_2)_3CNH_2$ com EtOC(O)C(O)OEt, reage com aldeídos aromáticos ArCHO, gerando como produtos bis-alquilideno simétricos, *N,N'-bis*(2-Ar-5-$ROCH_2$-1,3-dioxan-5-a)etanodiamides **3** (Ar = Ph, *p*-MeC_6H_4 or *p*-$MeOC_6H_4$, R = H). Uma reação similar com Me_2CO produziu *N'-bis*(2,2-dimethil-5-hidroximetil-1,3-dioxan-5-a)etanodiamida (**2**). Enquanto três estereoisômeros (*Z,Z*)-, (*Z,E*)- e (*E,E*)-**3** (Ar = Ph, R = H) foram formados a partir da reação de **1** com PhCHO, somente (*Z,Z*)-**3** (Ar = *p*-MeC_6H_4 ou *p*-$MeOC_6H_4$, R = H) foi isolado quando **1** reagiu com ArCHO (Ar = *p*-MeC_6H_4 ou *p*-$MeOC_6H_4$). As conformações *Z* têm os grupos: aril- equatorial, $HOCH_2$- equatorial e amido-axial, no sólido e em solução, enquanto as conformações *E* têm os grupos aril- equatorial, amido- equatorial e $HOCH_2$- axial. Uma mistura na proporção 1:1 de (*Z,Z*)-: (*E,E*)-**3** (Ar = Ph, R = H) co-cristaliza. As energias de conformação de (*Z,Z*)- e (*E,E*)-**3** (Ar = Ph, R = H) e **1** foram determinadas por cálculos de mecânica molecular. O estereoisômero (*Z,Z*)-**3** (Ar = Ph, R = H) é mais reativo do que o (*E,E*) em reações de alquilação: somente o estereoisômero (*Z,Z*)-**3** (Ar = Ph, R = Ph_3SnCH_2) foi isolado da reação de uma mistura de (*Z,Z*)- e (*E,E*)-**3** (Ar = Ph, R = H) com Ph_3SnCH_2I. Quando uma mistura 1:1 de (*Z,Z*)- e (*E,E*)-3 (Ar = Ph, R = H) foi reagida com um excesso de brometo alílico, uma mistura na proporção de 4:3 de (*Z,Z*)- e (*E,E*)-**3** (Ar = Ph, R = $H_2C{=}CHCH_2$) foi isolada. Reação de oxomercuração de (*Z,Z*)- e (*E,E*)-**3** (Ar = Ph, R = $H_2C{=}CHCH_2$) com $Hg(OAc)_2$ em metanol, seguida por uma troca aniônica utilizando NaCl, produziu um único estereoisômero, {*N*-(*Z*)-[[(R^2)-5-(3-cloromercuria-2-metoxipropil)oximetil]-2-fenil-1,3-dioxan-5-il]}{*N*'-(*Z*)-[[(S^2)-5-(3-cloromercúria-2-metoxipropil)oximetil]-2-fenil-1,3-dioxan-5-il]}etanodiamida (**4**) que foi caracterizado por cristalografia de raio X.

Compound, $[(HOCH_2)_3CNHC(O)]_2$ (**1**), obtained from $(HOCH_2)_3CNH_2$ and EtOC(O)C(O)OEt, reacts with aryl aldehydes, ArCHO, to give the symmetric bis-alkylidene derivatives, *N,N'*-bis(2-Ar-5-$ROCH_2$-1,3-dioxan-5-yl)ethanediamides **3** (Ar = Ph, *p*-MeC_6H_4 or *p*-$MeOC_6H_4$, R = H). A similar reaction with Me_2CO produced *N'*-bis(2,2-dimethyl-5-hydroxymethyl-1,3-dioxan-5-yl)ethanediamide (**2**). While three stereoisomers, (*Z,Z*)-, (*Z,E*)- and (*E,E*)-**3** (Ar = Ph, R = H), were formed from **1** and PhCHO, only (*Z,Z*)-**3** (Ar = *p*-MeC_6H_4 or *p*-$MeOC_6H_4$, R = H) was isolated from ArCHO (Ar = *p*-MeC_6H_4 or *p*-$MeOC_6H_4$) [the *Z* conformations in the solid state and in solution have *equatorial*-aryl, *equatorial*-$HOCH_2$ and *axial*-amido groups: *E* forms have *equatorial*-aryl, *equatorial*-amido and *axial*-$HOCH_2$ groups]. A 1:1 mixture of (*Z,Z*)-:(*E,E*)-**3** (Ar = Ph, R = H) co-crystallises. Molecular mechanics calculations have been carried out on the conformation energies of (*Z,Z*)-and (*E,E*)-**3 (**Ar = Ph, R = H) and **1** and support the crystallographic and spectral findings. The stereoisomer, (*Z,Z*)-**3** (Ar = Ph, R = H), is more reactive in alkylation reactions than the (*E,E*)-form: only (*Z,Z*)-**3** (Ar = Ph, R = Ph_3SnCH_2) was isolated from the reaction of a mixture of (*Z,Z*)- and (*E,E*)-**3** (Ar = Ph, R = H) with Ph_3SnCH_2I. From the reaction of excess allyl bromide with a 1:1 mixture of (*Z,Z*)- and (*E,E*)-**3** (Ar = Ph, R = H), a 4:3 mixture of (*Z,Z*)- and (*E,E*)-**3** (Ar = Ph, R = $H_2C{=}CHCH_2$) was isolated. Oxymercuriation of (*Z,Z*)-**3** (Ar = Ph, R = $H_2C{=}CHCH_2$) with $Hg(OAc)_2$ in MeOH, followed by anion exchange using NaCl, produced the single stereoisomer, {*N*-(*Z*)-[[(R^2)-5-(3-chloromercuri-2-methoxypropyl)oxymethyl]-2-phenyl-1,3-dioxan-5-yl]}{*N*'-(*Z*)-[[(S^2)-5-(3-chloromercuri-2-methoxypropyl)oxymethyl]-2-phenyl-1,3-dioxan-5-yl]}ethanediamide (**4**), characterised by X-ray crystallography.

Keywords: alkylidene formation, stannylation, oxymercuriation, X-ray crystallography, molecular mechanics

* e-mail: j.wardell@abdn.ac.uk

Introduction

Despite being known for at least half a century,[1] and being readily prepared from common precursors, the symmetric diamido-hexol, *N,N*'-bis[2-hydroxy-1,1-bis(hydroxymethyl)ethyl]ethanediamide, $[(HOCH_2)_3CNHC(O)]_2$ (**1**), has attracted only occasional attention. However, its versatility as a precursor has still been well indicated, *e.g.*, its hexa-*O*-derivatives have been mentioned in patents as potential explosives,[2] as sustained release [nitrogen] fertilizers,[3] in preparations of ink-jets dyes[4] and as antioxidants.[5] Unsubstituted **1** has also been used as a precursor of sucrose mimics[6] and as a ligand in lanthanide complexes in a study of the catalysed hydrolysis of phosphate esters.[7]

The versatility of **1** as a precursor would be greatly enhanced if reactions at the hydroxyl groups were controlled. Such a control effectively requires selective protection of the OH groups. A study of the protection of the OH groups in **1** has been carried out and the findings on the use of alkylidene groups are reported here.

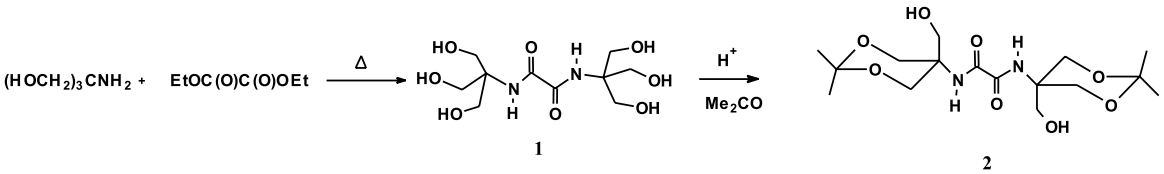
Results and Discussion.

Compound **1** was readily obtained by a published route[6] from $(HOCH_2)_3CNH_2$ and EtO_2CCO_2Et.

*O-Alkylidene derivatives of **1***

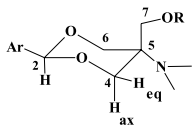
The reaction of a 1:1 mole ratio of **1** with Me_2CO in the presence of a catalytic amount of H_2SO_4 was sluggish and unselective, with both mono-and bis-isopropylidene derivatives being formed. Reaction with excess Me_2CO gave the bis-isopropylidene derivative, *N,N*'-bis(2,2-dimethyl-5-hydroxymethyl-1,3-dioxan-5-yl)ethanediamide (**2**), Scheme 1. Reaction of **1** with excess ArCHO similarly produced *N,N*' -bis-(5-$HOCH_2$-2-Ar-1,3-dioxan-5-yl)ethanediamide **3** (R = H). The chemical shifts for the NH, CH_2OH and 1,3-dioxanyl CH_2 ring protons in **2** are similar to those in (*Z,Z*)-**3** (R = H) and are quite distinct from those in (*E,E*)-**3** (R = H), see Tables 1 and 2 and the later discussion. Thus as in (*Z,Z*)- **3** (R = H)**,** the conformation of the chair shaped 1,3-dioxanyl rings in **2** in solution has the NH(CO) units in axial sites and the CH_2OH (and aryl) groups in equatorial positions. As shown by the NMR spectra, the 1,3-dioxanyl rings are conformationally rigid at ambient temperature with no chair ⇔ chair conversions detected for either the (*Z*) or (*E*)-forms: furthermore no (*Z*)- ⇔ (*E*)- conversions occur.

Three solid stereoisomeric benzylidene products, (*Z,Z*)-, (*Z,E*)- and (*E,E*)-**3** (Ar = Ph, R = H), were isolated from the reaction of **1** with excess PhCHO, see Figure 1. The mole ratios of the initial products, (*Z,Z*)-, (*Z,E*)- and (*E,E*)-**3 (**Ar = Ph, R = H), as determined by ^{1}H NMR spectroscopy, were 1.8: 1.3: 1, *i.e.*, an overall (*Z*): (*E*) ratio of *ca*. 3:2. Recrystallisation of the initial reaction products from aqueous acetone gave as the first crop of crystals, a 1:1 mixture of (*Z,Z*)- and (*E,E*)-**3** (Ar = Ph, R = H), as indicated by NMR spectroscopy and confirmed by X-ray crystallography.[8] Of interest, while co-crystallisation of enantiomers is often reported, reports of the co-crystallisations of other types of isomers, such as the stereoisomers here, are seldom made. This co-crystallized stereoisomeric mixture possessed a wide melting range, 185-224°C. Successive recrystallisations, from ethyl acetate, of the material left in the mother liquor, led to the isolation of crystalline (*Z, Z*)-**3** (Ar = Ph, R = H), m.p. 238-241°C, and subsequently (*Z,E*)-**3** (Ar = Ph, R = H), m.p. 194-197°C. As well as the crystal structure of the 1:1 stereoisomeric mixture, that of the (*Z,Z*)-stereoisomer has also been reported.[8] Suitable crystals of the (*Z,E*)-**3** (Ar = Ph, R = H) isomer could not be grown for crystallography but its stereochemistry was readily resolved from the ^{1}H and ^{13}C NMR spectra. The (*Z,Z*)-**3** (Ar = Ph, R = H) molecules in the solid state are *Z*-shaped, whereas the (*E,E*)-isomers are maximally extended, as shown in Figure 1. A "*L*"-shape is proposed for the (*Z,E*)-stereoisomer. The (*Z,Z*)-**3** (Ar = Ph, R = H) molecular shapes are essentially identical in the 1:1 stereoisomeric mixture and in the pure single stereoisomer sample. The 1,3-dioxanyl rings adopt chair conformations in all molecules, with the phenyl substituents, at C-2, always in equatorial sites. In (*E*)- and (*Z*)-5-hydroxymethyl-2-phenyl-1,3-dioxane rings, the hydroxymethyl groups at C-5 are in axial and equatorial sites, respectively. There are inversion symmetry related pairs of intramolecular N-H—O hydrogen bonds between amide N-H and adjacent carbonyl

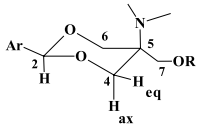


Scheme 1.

Table 1. ^{1}H NMR data for **2** and **3** in DMSO-d_6



E form



Z form

Compound	H-2 (s)	H-4(H-6) (d) ax eq; [J(H_{ax}-H_{eq})]	NH (s)	H-7 [J(H,OH)]	OH [J(H,OH)]	Phenyl [J(H-H)]	Others
2	-	3.75 4.13 [11.7]	7.93	3.68 [5.8]	5.04(t) [5.8]	-	1.31 & 1.34 (Me)
(Z,Z)-**3** (Ar = Ph, R = H)	5.55	3.96 4.47 [11.6]	8.02	3.64 [5.7]	5.03(t) [5.7]	7.34-7.43(m)	
(Z,E)-**3** (Ar = Ph, R = H)	5.54	3.96 4.46 [11.6]	7.99	3.63 [5.75]	5.00(t) [5.7]	7.34-7.43(m)	
	5.56	4.22 [0]	8.11	3.93 [5.75]	5.21(t) [5.8]		
(E,E)-**3** (Ar = Ph, R = H)	5.57	4.23 4.24 [10.9]	8.10	3.96 [5.8]	5.20(t) [5.8]	7.34-7.43(m)	
(Z,Z)-**3** (Ar = *p*-$MeOC_6H_4$ R = H)	5.50	3.81 4.45 [11.6]	8.02	3.65 [2.8]	5.02(t) [2.8]	6.91(d)& 7.34(d) [8.7]	3.74 (OMe)
(Z,Z)-**3** (Ar = *p*-MeC_6H_4 R = H)	5.51	3.96 4.46 [11.6]	8.02	3.65 [-]	4.25-4.75(br) [-]	7.15(d)& 7.24(d) [8.0]	2.28 (Me)
(Z,Z)-**3** (Ar = Ph, R = $MeSO_2$)	5.62-5.67	4.01-4.23	8.23	4.50 [-]	-	7.35-7.57 (m)	2.38 (Me)
(E,E)-**3** (Ar = Ph, R = $MeSO_2$)	5.62-5.67	4.41-4.59	8.44	4.83 [-]	-	7.35-7.57 (m)	2.50 (Me)
(Z,Z)-**3** (Ar = Ph, R = H_2C=$CHCH_2$)	5.59	3.99 4.53 [11.5]	8.18	3.65 (s)	-	7.34-7.39(m)	3.94 5.77-5.90, 5.26, 5.16
(E,E)-**3** (Ar = Ph, R = H_2C=$CHCH_2$)	5.57	4.10 4.35 [11.2]	8.27	3.93-4.08 (m)	-	7.34-7.46(m)	3.93 5.78-5.98, 5.13-5.34
(Z,Z)-**3** (Ar = Ph, R = Ph_3SnCH_2)[a]	5.28	3.88 4.30 [11.8]	7.87	4.31	-	7.37-7.50 7.59-7.64	3.82 ($SnCH_2$)

[a] in $CDCl_3$

Table 2. ^{13}C NMR and ^{119}Sn NMR data for **2** and **3** in DMSO-d_6

Compound	C-2	C-4 (C-6)	C5	C(O)	C-7	Others, δ^{13}C, unless stated
2	99.3	62.6	57.7	161.2	61.5	24.6 & 25.7 (Me)
(*Z,Z*)-**3** (Ar = Ph, R = H)	102.1	70.6	56.4	161.3	61.0	127.7, 129.7, 130.4 & 139.7 (Ph)
(*E,E*)-**3** (Ar = Ph, R = H)	102.4	69.4	54.5	161.3	61.3	128.0, 129.7, 130.4 & 139.6 (Ph)
(*Z,E*)-**3** (Ar = Ph, R = H)	102.1 102.4	70.6 69.4	56.4 54.5	161.1 161.5	61.0 61.3	127.7, 127.8,129.6, 130.5 & 139.6, 139.7 (Ph)
(*Z,Z*)-**3** (Ar = *p*-$MeOC_6H_4$ R = H)	102.1	70.6	56.3	161.3	61.0	56.7 (OMe), 115.0, 129.1, 132.1 & 161.1 (Ph)
(*Z,Z*)-**3** (Ar = Ph, R = $MeSO_2$)	102.4	69.9	54.5	161.7	53.7	38.6, 127.8, 129.6, 130.6 & 139.4 (Ph)
(*E,E*)-**3** (Ar = Ph, R = $MeSO_2$)	102.9	69.7	53.3	161.6	54.9	38.7, 127.8, 129.7, 130.6 &139.3 (Ph)
(*Z,Z*)-**3** (Ar = Ph, R = H_2C=$CHCH_2$)	102.4	69.5	55.6	161.4	70.8	73.4, 118.4 & 136.4 (allyl), 127.7, 129.6, 130.4 & 139.4 (Ph)
(*E,E*)-**3** (Ar = Ph, R = H_2C=$CHCH_2$)	102.2	69.1	53.9	161.3	70.1	73.1, 118.2 & 136.3 (allyl), 127.8, 129.8, 130.5 & 139.6 (Ph)
(*Z,Z*)-**3** (Ar = Ph, R = Ph_3SnCH_2) in $CDCl_3$	102.6	70.6	54.3	160.5	74.6[a]	64.0[b], 126.1, 128.2, 128.6 & 129.1 (PhCH) 136.7[c], 137.0[d], 137.2[e] & 137.6[f] (PhSn) δ^{119}Sn -139.8

[a] J(^{119,117}Sn-^{13}C) = 54Hz; [b] J(^{119,117}Sn-^{13}C) = 470, 452Hz; [c] J(^{119,117}Sn-^{13}C-p) = 17Hz; [d] J(^{119,117}Sn-^{13}C-m) = 44Hz; [e] J(^{119,117}Sn-^{13}C-o) = 33Hz; [f] J(^{119,117}Sn-^{13}C) = 486, 470Hz

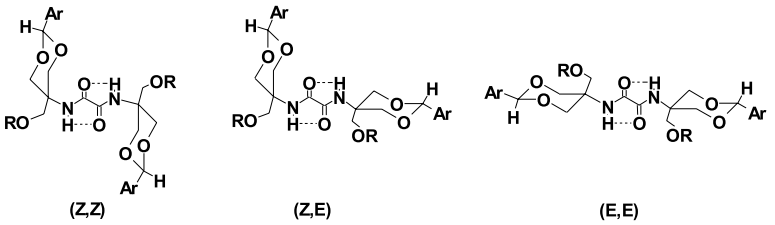


Figure 1. Stereoisomers of *N,N'*-bis(2-aryl-5-alkoxymethyl-1,3-dioxan-5-yl)ethanediamide (**3**)

oxygen centres: intermolecular O-H—O hydrogen bonding between hydroxymethyl group and carbonyl atoms link molecules.[8]

From reaction of **1** with *p*-methoxybenzaldehyde or *p*-methylbenzaldehyde, only the (*Z,Z*)-isomer of **3** (Ar = *p*-R'C_6H_4, R' = MeO or Me, R = H) was isolated. NMR spectra clearly indicated their stereochemistries to be (*Z,Z*), with no other isomer present in the isolated and toluene-washed compounds. Both the (*Z,Z)*-isomers were essentially insoluble in most common organic solvents, and only sparingly so in DMSO. They were obtained from the reaction mixtures as pure compounds merely by extensive extractions with toluene, to remove the excess aldehyde. Small quantities of the other stereoisomers could have been lost with the washings: as there was no indications in the NMR spectra for other stereoisomers in the original crude product mixtures, the maximum amounts of these would have to be less than 5%.

*Molecular mechanics calculations on **1** and **3** (Ar = Ph, R = H)*

Molecular mechanics calculations on **1** and **3** (Ar = Ph, R = H) were obtained[9] using the program Macromodel v6.5. Molecules in the gas phase were investigated using a 5000 step Monte Carlo search for conformers, followed by energy minimisation of the conformers generated. All energy minimisations were performed with the Macromodel MM2* force field: solvent effects were assessed by the GB/AS continuum solvent model.[10]

Calculations on **1** and **3** (Ar = Ph, R = H) were limited to symmetric structures, *e.g.*, only the (*Z,Z*)- and (*E,E*)- and not (*Z,E*)-forms of **3** were included in the calculations. Two favoured conformations, **1a** and **1b**, were calculated for **1**, the more stable form in the three phases considered being invariably **1a**, see Figure 2 and Table 3**.** In both conformations, one of the CH_2OH groups in each $C(CH_2OH)_3$ unit is H-bonded to the carbonyl oxygen of the adjacent amide. The distinction between **1a** and **1b** resides in the orientations of the other two CH_2OH units, see Figure 2: these two OH groups are considered to be

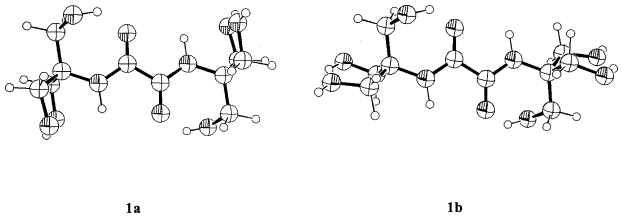


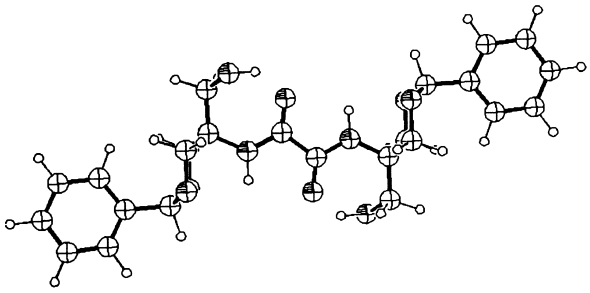
Figure 2. Symmetric conformations of **1**

Table 3. Molecular mechanics (MM2*) calculated energies for conformations of **1** and **3**

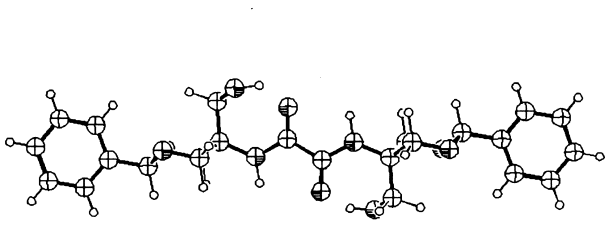
Conformation	Energy ($KJmol^{-1}$)		
	gas phase	***H_2O***	***$CHCl_3$***
1a	-113.2	-187.46	-161.98
1b	-93.04	-173.19	-145.95
[(*E,E*)-**3a**]	-357.07	-384.87	-428.95
[(*E,E*)-**3b**]	-336.26	-373.54	-409.03
[(*Z,Z*)-**3b**]	-362.32	-371.94	-404.44
[(*Z,Z*)-**3a**]	-362.32	-397.37	-438.07

those used in the formation of the 1,3-dioxanyl rings in **3** (Ar = Ph, R = H). Calculations were carried out on four conformers of **3** (Ar = Ph, R = H) - two (*Z,Z*)- and two (*E,E*)-forms in three different phases, see Figure 3. Differences in the relative energies are found between the three phases, indicating the importance of solvation and H-bonding. The relative energies calculated for the organic solvent, $CHCl_3$, are most relevant to the reactions carried out in the aryl aldehyde.

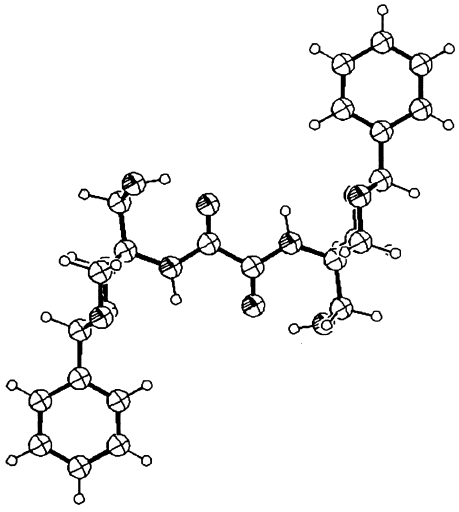
Reaction of PhCHO with the more stable **1a** conformer provides either the (*E,E*)-conformer [(*E,E*)-**3a**] (Ph axial/ CH_2OH equatorial) or the (*Z,Z*)- conformer [(*Z,Z)*-**3a**] (Ph equatorial/ CH_2OH equatorial): calculations show that [(*Z,Z)*-**3a**] is the more stable in $CHCl_3$. Reaction of PhCHO with the other conformer **1b** will provide either the (*E,E*) conformer [(*E,E*)-**3b**] (Ph equatorial/ CH_2OH axial) or the *(Z,Z)*-conformer [(*Z,Z*)-**3b**] (Ph axial/ CH_2OH axial). Calculations indicated that of these two, [(*E,E)*-**3b**] is favoured. Thus the molecular mechanics calculations point to the favoured formations of [(*Z,Z*)-**3a**] and [(*E,E*)-**3b**] with the former dominating, from the two symmetrical forms of



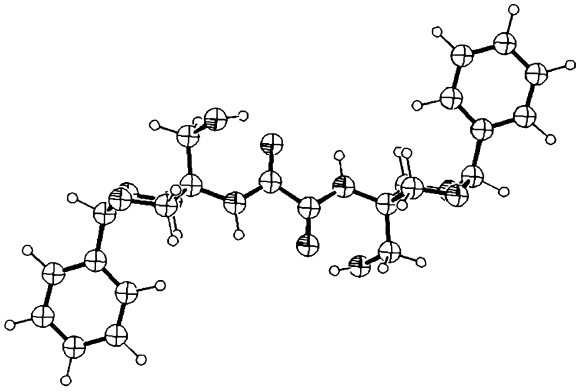
[(*E,E)*-**3a**]



[(*E,E)*-**3b**]



[(*Z,Z)*-**3a**]



[(*Z,Z*)-**3b**]

Figure 3. Symmetric conformers of **3**

1. The calculated preference for the *Z*-conformations of the 1,3-dioxanyl rings [*i.e.* with axial amido groups] and the indications that the phenyl groups are generally in equatorial sites are in agreement with the NMR and crystallographic findings.

The preference for the amido group over the CH_2OH group to occupy axial sites in **3** is similar to the situation reported for cyclohexane derivatives. In cyclohexanes, substituents, X, invariably favour equatorial sites. For example, the preferences [conformational energies][11] for NHC(O)OPh, CH_2OH and Ph to be in equatorial sites in cyclohexanes are 6.7, 7.36 and 11.7 kJ mol^{-1}, respectively, the NHC(O)Ph group being the nearest to the NHCOCONH group for which data could be found.[11] However, this equatorial preference need not apply to X-substituted 1,3-dioxanes, where polar O—X interactions have to be considered. As also pointed out by Eliel and Wilen,[11] steric compression of axial groups by lone pairs on oxygen atoms in 1,3-dioxanes is very small compared to the compression by syn-axial H-atoms in cyclohexanes. These effects can, in fact, result in a preference for axial positions, as shown, for example, by the CH_2OH group in 5-hydroxymethyl-2-isopropyl-1,3-dioxane in CCl_4 solution.[11]

Reactions of the alkylidene derivatives

The remaining free hydroxyl groups in **3** (Ar = Ph, R = H) can be successfully derivatised as illustrated by the use of methanesulfonyl chloride and allyl bromide. Reactions of the 1:1 (*Z,Z*): (*E,E*)-**3** mixture with these reagents gave 1:1 (*Z,Z*): (*E,E*)-mixtures of *N,N'*-bis(5-mesyloxymethyl-2-phenyl-1,3-dioxan-5-yl)ethanediamides **3** (Ar = Ph, R = $MeSO_2$), and *N,N'*-bis(5-allyloxymethyl-2-phenyl-1,3-dioxan-5-yl)ethanediamides **3** (Ar = Ph, R = CH_2=$CHCH_2$), respectively, as shown by the NMR spectra. Work-up can lead to preferential isolation of one of the components, *e.g.*, [(*Z,Z*)-**3** (Ar = Ph, R = H_2C=$CHCH_2$)] was isolated in a pure form on recrystallisation of the 1:1 mixture of

[(*Z,Z*):(*E,E*)-**3** (Ar = Ph, R = CH_2=$CHCH_2$)], from ethyl acetate: further work-up of the mother liquor, unfortunately, resulted in irreversible changes, which prevented the collection of [(*E,E*)-**3** (Ar = Ph, R = CH_2=$CHCH_2$)]. In general, separation of both sets of isomers could be achieved by chromatography. Attempts to obtain *N,N'*-bis(5-chloromethyl-2-phenyl-1,3-dioxan-5-yl)ethanediamides from **3** (Ar = Ph, R = H) using Ph_3P/CCl_4 or thionyl chloride were unsuccessful: no reaction occurred using Ph_3P/CCl_4, even on reflux, while extensive decomposition resulted from the use of thionyl chloride.

Organometallic derivatives

Bis-oxymercuriation of (*Z,Z*)-**3** (Ar = Ph, R = CH_2=$CHCH_2$) using $Hg(OAc)_2$ in methanol proceeded readily at room temperature.[12] NMR spectroscopy indicated that the product, isolated on crystallisation from Me_2CO/ethyl acetate, after anion exchange with NaCl, was the Marknovikov adduct, *N,N'*-bis-{(*Z*)-[5-[(3-chloromercuri-2-methoxypropyl)oxymethyl]-2-phenyl-1,3-dioxan-5-yl]}ethanediamide (**4**) Equation 1. The atom arrangements in **4** were confirmed by X-ray crystallography. Furthermore, the stereochemistries at the -CH(OMe)- centres [C(19) and C(19a) in the crystallographic numbering scheme] were revealed, see Figure 4. Unfortunately, the structure of **4** was only refined to 9.4%, due in the greater part to crystal decomposition in the X-ray beam.

The molecule of **4** possesses a centre of symmetry at the midpoint of the central (O)-C-C(O) bond with both mercury sites being equivalent. Due to the symmetry in **4**, selected geometric parameters for only one half of the molecule are listed in Table 4: parameters involving atoms in the other half of the molecule are indicated by the use of the superscipt ([a]) [symmetry operation *a*: -x, 2-y, 1-z]. The carbon atoms at which the OMe groups are attached have opposite chirality and so overall the molecule is achiral, *i.e.* we have {*N*-(*Z*)-[[(R^2)-5-(3-chloromercuri-2-methoxypropyl)oxymethyl]-2-phenyl-1,3-dioxan-5-yl]}{*N'*-(*Z*)-[[(S^2)-5-(3-chloromercuri-2-methoxypropyl)oxymethyl]-2-phenyl-1,3-dioxan-5-yl]}ethanediamide stereoisomer of **4**: the high yield of the isolated stereoisomer pointed to a

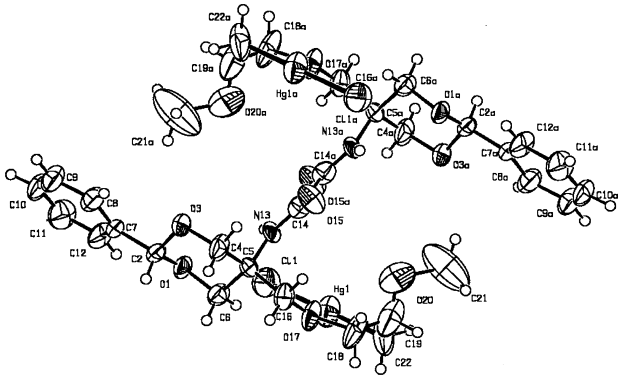
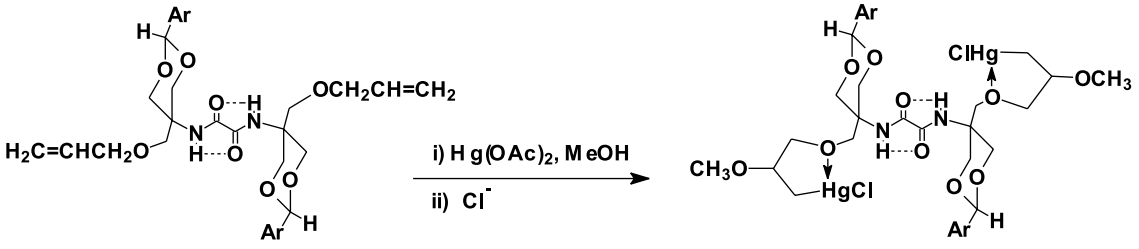


Figure 4. Atom numbering system and atom arrangements in **4.** Probability ellipsoids drawn at the 50% level



(1)

Table 4. Selected geometric parameters (Å,°) for **4**

Hg(1)-Cl(1)	2.331(6)	Hg(1)-C(22)	2.06(3)
Hg(1)-O(17)	2.882(15)	Hg(1)-O(20)	2.04(3)
O(15)-C(14)	1.29(2)	C(14)-C(14a)	1.520(5)
N(13)-C(5)	1.48(2)	N(13)-C(14)	1.22(2)
Cl(1)-Hg(1)-C(22)	179.6(7)	O(15)-C(14)-N(13)	129.2(17)
C(22)-Hg-O(17)	71.0(9)	C(22)-Hg-O(20)	43.8(8)
Cl(1)-Hg-O(17)	109.5(3)	Cl(1)-Hg-O(20)	136.2(5)
O(17)-Hg-O(20)	53.9(7)	O(15)-C(14)-C(14)	111.5(15)
N(13)-C(14)-C(14)[a]	118.9(16)	C(5)-N(13)-C(14)	125.4(14)
Hg(1)—Hg(1)[i]	3.775(2)		
O(20)-C(19)-C(22)-Hg(1)	-63(3)°	C(18)-C(19)-C(22)-Hg(1)	62(3)°

a: symmetry operation: -x, 2-y, 1-z; *i*: symmetry operation: -x, 3-y, -z

high stereoselectivity in the mercuriation reaction. Indeed other stereoisomers of **4**, *e.g.* the bis-[(*N*,*N*'-(*Z*),(*R*^{2})] or bis-[(*N*,*N*'-(*Z*),(*S*^{2})] stereoisomers, were not detected. The dioxanyl rings, as found for stereoisomers of **3** (Ar = Ph: R = H) have chair conformations, with puckering parameters,[13] amplitude (Q) = 0.570(16)^o, θ = 175.3(17)^o, ϕ = 191(25)^o.

The primary bonds to each Hg in **4** are essentially collinear, C(22)-Hg(1)-Cl(1) / [C(22)^a-Hg(1)^a-Cl(1)^a] = 179.6(7)^o, see Table 4: the primary bond lengths, Hg(1)-C(22) / [Hg(1)^a-C(22)^a] = 2.06(3)Å and Hg(1)-Cl(1) / [Hg(1)^a-Cl(1)^a] = 2.331(6)Å, are in the expected regions.[14-16] As well as forming primary bonds, mercury(II) also exhibits a strong tendency to form secondary bonds within the sum of the van der Waals radii of the relevant atoms.[14-17] There is some controversy over the value of the van der Waals radius of mercury. Values of 1.73–2.00Å have been suggested by Canty and Deacon,[18] while even higher values, 2.1-2.2Å, have been proposed by Batsanov,[19] all these being much higher than the value of 1.55Å, estimated from the critical volume of the metal.[20] As the generally accepted van der Waals radius for O is 1.50Å, the O(17)-Hg(1) /[O(17)a—Hg(1)a] intramolecular separations of 2.882(15)Å fall well within the van der Waals radii sum for Hg and O, no matter which Hg vdW value is taken. These secondary Hg-O bonds result in the formation of 5-membered Hg(1)-O(17)-C(18)-C(19)-C(22) / [Hg(1)^a-O(17)^a-C(18)^a-C(19)^a-C(22)^a] rings with envelope conformations [flap at C(19) / C(19)^a]. Other intramolecular, Hg—O separations, Hg(1)-O(20) / [Hg(1)^a-O(20)^a] = 3.32(3)Å, are within the majority of the limits set for the sum of the van der Waals radii for Hg and O. As shown in Figure 5, the gauche arrangements of Hg(1) and O(20), Hg(1) and C(18), about the C(19)-C(22) bond, are ideal for Hg—O (20) and Hg—O(17) interactions and are taken as indications of secondary bonding.

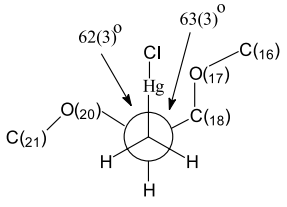


Figure 5. Arrangement at the mercury centre in **4** looking down the C(22)-C(19) bond

There are, in addition, intermolecular contacts, Hg—Hg^i [3.776(2)Å] in **4**: symmetry operation *i*: -x, 3-y, -z], which produce staggered chains of molecules almost parallel to the *b*, *c* diagonal. Intermolecular mercury—mercury interactions have been variously reported, for example,[21] Hg—Hg = 3.5620(5)Å in [Hg_3O(1,3-dimethyl-uracil-5-yl)$_3$]NO_3.2H_2O. The closest Hg separations with aromatic C atoms in **4** occur at distances of 3.75-3.79Å, *cf.* vdW radius of C = 1.65-1.70Å.[20] As found generally in organomercury chemistry, secondary bonds have little effect on the linear geometry of the primary bonds.[14-16]

As with **3** (Ar = Ph, R = H), there are intramolecular hydrogen bonds involving N(13)-H(13)—O(15) [N(13)-H(13) = 0.86Å: H(13)—O(15) = 2.28Å: N(13)—O(15) 2.67(2) Å: N(13)-H(13)—O(15) = 108^o] and analogously for N(13)^a-H(13)^a—O(15)^a.

Attempts to get Ph_3SnH addition to the alkenyl groups in (*Z*,*Z*)-**3** (Ar = Ph, R = CH_2=$CHCH_2$), in the presence of the radical initiator, AIBN, failed: complete recover of [(*Z*,*Z*)-**3** (Ar = Ph, R = CH_2=$CHCH_2$)] was made and a near quantitative formation of $Ph_3SnSnPh_3$ was indicated. Tin hydrides, such as Ph_3SnH, are known to be sensitive to organic bases, such as amines and sulfoxides, and decompose to $Ph_3SnSnPh_3$:[22] it appears that the amido derivative, (*Z*,*Z*)-**3** (Ar = Ph, R = CH_2=$CHCH_2$), is also sufficiently basic to affect this decomposition.

A bis-stannylated derivative was, however, obtained from **3** (Ar = Ph, R = H): the compound, (*Z*,*Z*)-**3** (Ar = Ph, R = Ph_3SnCH_2), d^{119}Sn = -139.8ppm, was isolated from the reaction of the 1:1 mixture of (*Z*,*Z*)-:(*E*,*E*)-**3** (Ar = Ph, R = H), with Ph_3SnCH_2I [1:2.05 mole ratio], in DMF in the presence of NaH, after chromatography, see Figure 6. The ^{119}Sn NMR spectrum of the crude reaction product, prior to chromatographic separation, exhibited several peaks: the most intense peak being at -139.8ppm, *i.e.* the precise value of the isolated product. Other peaks were also in the region expected for Ph_3SnCH_2OR* compounds [-145 to -135ppm],[23] but all these were minor peaks. It is possible

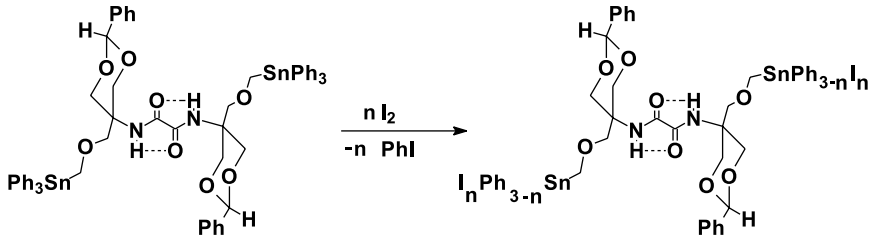


Figure 6. (*Z*,*Z*)-**3** (Ar = Ph, R = Ph_3SnCH_2) and reactions with iodine

that the stannylated derivative of (*E,E*)-**3** (Ar = Ph, R = H) would also have a δ^{119}Sn value of -139.8ppm, and that it was also present among the reaction products, but it somehow escaped isolation by chromatography. However, the latter is considered unlikely, and it is assumed that (*E,E*)-**3** (Ar = Ph, R = Ph_3SnCH_2) could not be a significant product, if formed at all. The crystal structure determination of (*Z,Z*)-**3** (Ar = Ph, R = Ph_3SnCH_2), already reported,[24] indicated the tin centres to be 4-coordinate, with slightly distorted tetrahedral geometries, as have been found for other Ph_3SnOR* compounds.[23] As also in these other Ph_3SnCH_2OR* compounds, the intramolecular Sn—O(C-5) separation is short [2.91(1)Å] and within the limits accepted for coordination [the sum of the van der Waals radii for Sn and O is *ca.* 4.1Å].[20] However, no Sn-O bonding is assumed since the C-Sn-C angles are close to those expected for a 4-coordinate and near tetrahedral arrangement. Any Sn—O interaction would create, in any case, highly strained three membered rings.

As shown by the structures listed in the Cambridge Crystallographic Data Base,[25] tetraorganotin compounds generally have 4-coordinate tin centres with near tetrahedral geometries. This is a consequence of the poor acceptor strength of the tin centre: however, in a limited number of rigid tetraorganotin compounds with suitably sited donor groups, intramolecular complexation can occur with the formation of 5- and even 6-coordinate tin centres.[26] Clearly the tin centres in (*Z,Z*)-**3** (Ar = Ph, R = Ph_3SnCH_2) are not complexed to any of the donor centres. The Lewis acidity of organotin halides, $R_{4-n}SnX_n$, invariably increases with the value of n. The reactions of (*Z,Z*)-**3** (Ar = Ph, R = Ph_3SnCH_2) with iodine (2n mol equivalents) were undertaken to obtain the stronger Lewis acids, (*Z,Z*)-**3** (Ar = Ph, R = $I_nPh_{3-n}SnCH_2$, n = 1 or 2): as indicated by the solution NMR parameters, especially δ^{119}Sn values, (*Z,Z*)-**3** (Ar = Ph, R = IPh_2SnCH_2) [δ^{119}Sn = -122.5ppm] and (*Z,Z*)-**3** (Ar = Ph, R = $I_2PhSnCH_2$) [δ^{119}Sn = -227ppm], were 4 and 5 coordinate, respectively.

Conclusions

Protection of 4 of the 6 hydroxyl groups in **2** can be achieved by standard alkylidene procedures: the bis alkylidene derivatives, **3**, can be further derivatised by standard means. Transformations of the bis-mercurated, **4**, and the bis stannylated, (*Z,Z*)-**3** (Ar = Ph, R = Ph_3SnCH_2), compounds provide further routes to selected derivatives**.**

Experimental

Melting points were determined using a Kofler hotstage and are uncorrected Solution NMR spectra were obtained on Bruker 250 MHz and Varian 400 MHz instruments. IR spectra were obtained on Philips Analytical PU 9800 FTIR and Nicolet 205 FTIR instruments.

*N,N' -Bis-[tris(hydroxymethyl)methyl]ethanediamide (**1**)*

A solution of tris(hydroxymethyl)aminomethane (10.00 g, 82.6 mmol) and diethyl oxalate (6.03g, 41.3 mmol) in methanol (25ml) was refluxed for 2h. The reaction mixture was cooled, filtered and the precipitate was recrystallised from aqueous EtOH (80%); yield 75-80%; m.p. 221-223 °C [lit.[6]m.p. 224 °C]. ^{1}H and ^{13}C NMR spectra were identical with those reported.[6] IR (ν_{max}/cm^{-1}): 3413, 3339 (NH), 3245 (OH), 1667, 1516 (amide),

N,N'-Bis-(5-hydroxymethyl-2,2-dimethyl-1,3-dioxan-5-yl)ethanediamide (**2**)

A reaction mixture of **1** (3.00g, 10mmol) and concentrated H_2SO_4 (1ml) in acetone (100ml) was stirred at room temperature for 16h and filtered. The filtrate was washed with aqueous sodium bicarbonate, dried and rotary evaporated. The solid residue was recrystallised from acetone, yield 15%, m. p. 157-159 °C. Anal. calcd. for $C_{16}H_{28}N_2O_8$: C, 51.1; H, 7.5; N, 7.4. Found: C, 51.0; H, 7.5; N, 7.4%. NMR data are listed in Table 1. IR (ν_{max}/cm^{-1}): 3312, 3211, 3147, 3048, 1663, 1574 (amide).

*N,N' -Bis-(5-hydroxymethyl-2-phenyl-1,3-dioxan-5-yl)ethanediamide, **3** (Ar = Ph, R = H)*

A reaction mixture of **1** (1.5g, 5.1mmol) and concentrated H_2SO_4 (0.5ml) in benzaldehyde (25ml) was stirred for 12h at room temperature. Diethyl ether (10ml) and water (25ml) were added, and the viscous organic layer separated. On standing, a finely divided solid was collected, yield 85-95%. NMR spectra of this crude product revealed the presence of three stereoisomers, (*Z,Z*)-, (*E,E*)- and (*Z,E*)-**3** (Ar = Ph, R = H), in mole ratios of 1.8:1.3:1. Recrystallisation of the crude product from aqueous acetone gave a 1:1 mixture of stereoisomers, (*Z,Z*)- and (*E,E*)-**3** (Ar = Ph, R = H), yields ranged between 45-60%. This 1:1 mixture had a melting range between 185-225 °C. Anal. calcd. for $C_{24}H_{28}N_2O_8$: C, 61.0; H, 6.0; N, 5.9. Found: C, 61.1; H, 6.0; N, 5.9 %. IR (ν_{max}/cm^{-1}): 3490, 3382, 3337, 1671, 1516.

All solvents were removed from the mother liquor under vacuo to leave a solid residue, which was recrystallised from ethyl acetate. The colourless crystalline solid obtained was the single steroisomer, (*Z,Z*)-**3** (Ar = Ph, R = H); m.p. 238-241 °C. The mother liquor from the second crystallisation, on concentration and further recrystallisation gave

crystals of stereoisomer, (*Z,E*)-**3** (Ar = Ph, R = H); m.p. 194-197 °C. NMR spectra of the three stereoisomers are displayed in Tables 1 and 2.

*N,N'-Bis-[(Z)-(5-hydroxymethyl-2-(p-methoxyphenyl)-1,3-dioxan-5-yl)]ethanediamide, (Z,Z)-**3** (Ar = p-MeOC$_6$H$_4$, R = H)*

A reaction mixture of **1** (1.5g, 5.1mmol) and concentrated H_2SO_4 (0.5ml) in *p*-methoxybenzaldehyde (25ml) was stirred for 12h at room temperature. Diethyl ether (10ml) and water (25ml) were added, and the viscous organic layer separated. On standing, a finely divided solid was collected. ^{1}H NMR spectrum of the solid, indicated the presence of a single stereoisomer, still contaminated with *p*-methoxybenzaldehyde. The latter was removed on Soxhlet extraction with toluene. The white residue was insoluble in most organic solvents and only sparingly soluble in DMSO. Yield: 78%; m.p. 245-248 °C. Anal. calcd. for $C_{26}H_{32}N_2O_{10}$: C, 58.6; H, 6.1; N, 5.3. Found: C, 58.1; H, 5.9; N, 5.6 %. IR (ν_{max}/cm^{-1}): 3467, 3412, 3374, 3341, 1676, 1518. NMR data, displayed in Tables 1 and 2, indicated that the stereoisomer was (*Z,Z*)-(**3**: Ar = *p*-MeOC$_6$H$_4$, R = H).

*N,N'-Bis-[(Z)-(5-hydroxymethyl-2-(p-methylphenyl)-1,3-dioxan-5-yl)]ethanediamide, (Z,Z)-**3** (Ar = p-MeC$_6$H$_4$, R = H)*

A reaction mixture of **1** (1.5g, 5.1mmol) and concentrated H_2SO_4 (0.5ml) in *p*-methylbenzaldehyde (25ml) was stirred for 12h at room temperature. Diethyl ether (10ml) and water (25ml) were added, and the viscous organic layer separated. On standing, a finely divided solid was collected. ^{1}H NMR spectrum of the solid, indicated the presence of a single stereoisomer, (*Z,Z*)-**3** (Ar = *p*-MeC$_6$H$_4$, R = H), still contaminated with *p*-methylbenzaldehyde, which was removed on Soxhlet extraction with toluene. The white residue was insoluble in most organic solvents and only sparingly soluble in DMSO. Yield: 73%; m.p. 240 °C dec. Anal. calcd. for $C_{26}H_{32}N_2O_8$: C, 62.4; H, 6.4; N, 5.6. Found: C, 61.7; H, 6.3; N, 5.6 %. IR (ν_{max}/cm^{-1}): 3488, 3366, 3336, 1686, 1508.

NMR data are displayed in Tables 1 and 2.

*N,N'-Bis-(Z)- and -(E)- (5-allyloxymethyl-2-phenyl-1,3-dioxan-5-yl)ethanediamide, (Z,Z)- and (E,E)-**3** (Ar = Ph, R = H$_2$C=CHCH$_2$)*

To a solution containing a 1:1 mixture of (*Z,Z*)-:(*E,E*)-**3** (Ar = Ph, R = H), (2.00g, 4.23mmol) and NaH (0.2g) in dry DMF (6ml) was added allyl bromide (3.07g, 25.4 mmol). After stirring the reaction mixture at room temperature for 24h, it was poured onto ice (25g) and filtered. The dried solid residue had a melting range from 137 to 184 °C, and was shown by the ^{1}H NMR spectrum to be a 4:3 mixture of stereoisomers, (*Z,Z*)-:(*E,E*)-**3** (Ar = Ph, R = H$_2$C=CHCH$_2$. Recrystallisation from acetone gave pure stereoisomer (*Z,Z*)-**3** (Ar = Ph, R = H$_2$C=CHCH$_2$), m.p. 155-156 °C. The mother liquor still contained both (*Z,Z*)-:(*E,E*)-**3** (Ar = Ph, R = H$_2$C=CHCH$_2$). NMR data are displayed in Tables 1 and 2.

*N,N'-Bis-{(Z)-[5-(3-chloromercuri-2-methoxypropyl-oxymethyl)-2-phenyl-1,3-dioxan-5-yl]}ethanediamide (**4**)*

To a suspension of (*Z,Z*)-**3** (Ar = Ph, R = H$_2$C=CHCH$_2$) (0.38g, 1.2 mmol) in MeOH (10ml) was added a solution of Hg(OAc)$_2$ (0.44g, 1.2mmol) in MeOH (20ml). After stirring overnight, a saturated solution of sodium chloride (20 ml) was added, followed by water (80 ml). The precipitate was collected, and recrystallised from acetone: ethyl acetate (2:1) to give colourless crystals of {*N*-(*Z*)-[[(*R*^{2})-5-(3-chloromercuri-2-methoxypropyl)oxymethyl]-2-phenyl-1,3-dioxan-5-yl]}{*N'*-(*Z*)-[[(*S*^{2})-5-(3-chloromercuri-2-methoxypropyl)oxymethyl]-2-phenyl-1,3-dioxan-5-yl]}ethanediamide (**4**). Yield 95%, m.p.169-171 °C. ^{1}H NMR (CDCl$_3$): δ: 1.84-1.97 (m, 4H, CH$_2$Hg), 3.31(s, 6H, OMe), 3.46-3.50 (m, 4H, ≡COCH$_2$), 3.74-3.82 (m, 4H, C*H*$_2$OCHPh), 3.94-4.03 (m, 6H, =C*H*OCH$_3$ + OC*H*$_2$CHOCH$_3$), 4.49-5.58 (m, 4H, C*H*$_2$OCHPh), 5.61 (s, 2H, C*H*Ph), 7.36-7.39 (m, 6H, aryl), 7.49-7.52 (m, 4H, aryl), 7.98 (s, 2H, NH). ^{13}C NMR (CDCl$_3$): δ: 31.8 (CH$_2$Hg), 53.9 (C$_{quart}$), 56.4 (OMe), 69.6 (≡C-*C*H$_2$O), 69.9 (CH$_2$), 70.3 (=*C*HOCH$_3$), 73.7 (*C*H$_2$CHOCH$_3$), 101.5(*C*HPh), 126.1, 128.2, 129.0 & 137.3 (aryl), 159.7 (CO).

*N,N'-Bis-[(Z)-(5-triphenylstannylmethyloxymethyl)-2-phenyl-1,3-dioxan-5-yl)]ethane-diamide, (Z,Z)-**3** (Ar = Ph, R = Ph$_3$SnCH$_2$)*

Sodium hydride (1.50g, 6.5 mmol), and (iodomethyl) triphenylstannane (4.28g, 8.72 mmol) were successively added to a solution of a 1:1 mixture of (*Z,Z*)-:(*E,E*)-**3** (Ar = Ph, R = H), (2.00g, 4.23 mmol) in anhydrous DMF (20ml). The mixture was stirred overnight at room temperature, water (20ml) and diethyl ether (20ml) were added, and the organic layer was collected, dried over magnesium sulfate, and rotary evaporated. The reaction residue had δ^{119}Sn values in the NMR spectrum in CDCl$_3$ solution of -145.2, -142.0, -142.4, -139.8 (major), -130.2, -107.5, -101.6, -92.6 and –78.7ppm. The residue was separated, on a chromatotron, using hexane/ethyl acetate (2:1) as

eluent. The major fraction contained the triphenylstannylmethyl derivative of (*Z,Z*)-**3** (Ar = Ph, R = H). It was recrystallised from ethyl acetate; yield 23%, m.p. 170-174 °C. Anal. calcd. for $C_{62}H_{60}N_2O_8Sn$: C, 62.1; H, 5.1; N, 2.3. Found: C, 63.0; H, 5.5; N, 2.2%. IR (ν_{max}/cm^{-1}) 3297, 1676, 1507.

NMR Data are displayed in Tables 1 and 2.

X-Ray crystallography

Data were collected on an Enraf-Nonius CAD-4 diffractometer: data collection: CAD-4/PC.[27] Cell refinement: SET4 and CELDIM Software.[27] Data reduction: DATRD2 in NRCVAX94.[28.] Program used to solve structure: SHELXS-97. [29] Program used to refine structure: SHELXL-97.[30] Preparation of material for publication: SHELXL-97 [30] and WordPerfect macro PRPKAPPA.[31] Diagrams were prepared with the aid of PLATON.[32]

The compound **4** was found to be unstable in the X-ray beam. The compound lies on an inversion centre in the crystal and has an overall *Z*-shape. H atoms were treated as riding atoms with C-H 0.93 to 0.98Å, N-H 0.86Å. Atoms C(7) to C(12) had anisotropic displacement parameter restraints applied to them. The C(14)-C(14)^a distance (symmetry operation: *a*: -x, 2-y, 1-z) was constrained to be 1.520(5)Å, this was the average distance found for this bond in the 3 molecules reported in **3** (Ar = Ph, R = H).[8] The largest peaks in the difference map were adjacent to the Hg atom at distances 1.11 to 1.06Å.

Crystal refinement data for the compound are listed in Table 5.

Table 5. Crystal refinement data for **4**

Molecular formula	$C_{32}H_{42}Cl_2Hg_2N_2O_{10}$
Formula weight	1086.76
T (K)	293(2)
Wavelength (Å) Mo *Ka*	0.71070
Crystal system	Triclinic
Space group	P-1
Cell dimensions	
a (Å)	8.088(3)
b (Å)	10.897(5)
c (Å)	11.486(4)
α (°)	66.75(3)
β (°)	88.85(3)
γ (°)	75.31(3)
Volume (Å^3)	896.1(7)
Z	1
Calculated density (Mg/m^3)	2.0139(16)
Absorption coefficient, mm^{-1}	8.762
F(000)	522
Crystal color	colourless
Crystal size (mm)	0.417x0.125x0.042
Theta range for data collection (°)	2.1 to 25.0
Index range	$-9 \le h \le 9$ $0 \le k \le 12$ $-12 \le l \le 13$
Refinement method	Full matrix least-squares on F^2
No. of reflections: no of parameters	3159, 219
Goodness-of-fit on F^2	0.99
Final R indices [I>2sigma(I)]	R = 0.094 wR = 0.2458
Largest diff. peak and hole e.A^{-3}	2.80, -4.15

Supplementary material

Supplementary X-ray data for **4** are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033) on request, quoting the deposition number CCDC 153008.

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