Experimental

The 'keturet' was prepared from 1-methyl-1-phenyldithiobiuret and acetone, and crystallized from ethanol, using the procedure previously described by Fromm & Junius (1895) and Fairfull & Peak (1955) (yield 69%, m.p. 424–425 K).

Crystal data

$C_{12}H_{15}N_3S_2$
$M_r = 265.39$
Triclinic
$P\bar{1}$
$a = 9.871\ (2)$ Å
$b = 11.044\ (2)$ Å
$c = 13.117\ (3)$ Å
$\alpha = 87.403\ (8)°$
$\beta = 89.625\ (4)°$
$\gamma = 67.3872\ (11)°$
$V = 1318.6\ (4)$ Å^3
$Z = 4$
$D_x = 1.337$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 5212 reflections
$\theta = 2–30°$
$\mu = 0.385$ mm^{-1}
$T = 180$ K
Plate
0.35 × 0.20 × 0.05 mm
Colorless

Data collection

Rigaku/ADSC CCD diffractometer
CCD scans
Absorption correction: multi-scan (*d*TREK*; Molecular Structure Corporation, 1997*a*)
$T_{\min} = 0.85$, $T_{\max} = 0.98$
12 370 measured reflections

5927 independent reflections
2257 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.050$
$\theta_{\max} = 30.07°$
$h = -11 \rightarrow 13$
$k = -11 \rightarrow 15$
$l = -15 \rightarrow 18$

Refinement

Refinement on F^2
$R(F) = 0.040$
$wR(F^2) = 0.077$
$S = 1.020$
5927 reflections
315 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2)]$
$(\Delta/\sigma)_{\max} = 0.005$

$\Delta\rho_{\max} = 1.00$ e Å^3 (0.8 Å from H10, bonded to C6)
$\Delta\rho_{\min} = -0.90$ e Å^3 (0.4 Å from H8, bonded to C6)
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

S1—C2	1.774 (3)	S3—C14	1.775 (3)
S1—C3	1.822 (4)	S3—C15	1.842 (3)
S2—C1	1.711 (3)	S4—C13	1.689 (3)
N1—C1	1.324 (4)	N4—C13	1.350 (4)
N2—C2	1.307 (4)	N5—C14	1.307 (4)
C2—S1—C3	96.7 (2)	C14—S3—C15	95.7 (2)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···S4$^{\rm i}$	1.02 (3)	2.39 (3)	3.353 (3)	157 (2)
N4—H16···S2$^{\rm ii}$	0.96 (3)	2.65 (4)	3.522 (3)	152 (3)

Symmetry codes: (i) $1 + x, y - 1, z$; (ii) $x - 1, 1 + y, z$.

The U_{ij} values are quite small (low-temperature data), but physically very reasonable, with atoms near the centers of the molecules having the lowest displacement parameters and those on the periphery the highest. The highest correlation coefficient in the refinement is 0.51, for U_{22} and U_{12} of atom C12 (see *Comment* for a discussion of the pseudosymmetry). The higher than usual value of $R_{\rm int}$ resulted from lower than usual crystal quality. All parameters were refined for the two H atoms bonded to N; the other H atoms were placed on calculated sites, with C—H = 0.98 Å and U(H) equal to 1.2 times U of the C atom to which they were bonded. Methyl group H atoms were placed from a difference synthesis.

Data collection: *d*TREK* (Molecular Structure Corporation, 1997*a*). Cell refinement: *d*TREK*. Data reduction: *d*TREK*. Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993). Program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1997*b*). Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1159). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). **C55**, 436–439

Two dioxane derivatives of anthraquinone

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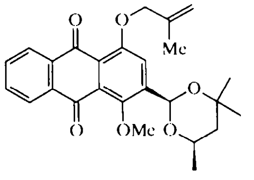
Abstract

The structures of 1-methoxy-4-(2-methylprop-2-enyloxy)-2-[(2*R*,6*R*)-4,4,6-trimethyl-1,3-dioxan-2-yl]anthraquinone, $C_{26}H_{28}O_6$, and 4-hydroxy-3-(2-methylprop-2-

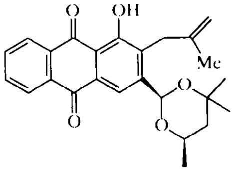
enyl)-2-[(2*R*,6*R*)-4,4,6-trimethyl-1,3-dioxan-2-yl]anthraquinone, $C_{25}H_{26}O_5$, have been determined to compare their conformations with those determined for solutions by ^{1}H NOESY (nuclear Overhauser effect spectroscopy) spectra.

Comment

During studies on the Lewis-acid-initiated intramolecular cyclization of chiral 2′-anthraquinonyl-4′,4′,6′-trimethyl-1′,3′-dioxanes to form anthracyclinones, it appeared that the stereochemical course of the reactions was dependent on the overall three-dimensional structure of the substrate, rather than on complexation of the Lewis acid to a preferred binding site. ^{1}H NOESY (nuclear Overhauser effect spectroscopy) spectra (Lorimer, 1998) indicated that these substrates adopted very specific conformations in solution. For example, the dioxane O atoms were invariably directed towards the smallest *ortho* substituent on the anthraquinone moiety, and in the acetal 1-methoxy-4-(2-methylprop-2-enyloxy)-2-[(2*R*,6*R*)-4,4,6-trimethyl-1,3-dioxan-2-yl]anthraquinone, (I), the acetal hydrogen (H2′) was oriented towards the methoxy group. In order to compare the solid-state conformations with those in solution, single-crystal structure analyses were carried out on (I), and on its reductive Claisen rearrangement product, 4-hydroxy-3-(2-methylprop-2-enyl)-2-[(2*R*,6*R*)-4,4,6-trimethyl-1,3-dioxan-2-yl]anthraquinone, (II).



(I)



(II)

In both structures, the 1,3-dioxane ring adopts a chair conformation. In (I), the dioxane O1′ atom is oriented towards the unsubstituted C3 atom, whereas in (II), O1′ is oriented towards the unsubstituted C1 atom. The mean plane of the dioxane rings is tilted with respect to the plane of the anthraquinone rings, the interplanar angles being 49.10 (6) and 59.38 (5)° for the two molecules in (I), and 56.18 (5)° for (II). Thus, even though the dioxane rings are rotated by 180° about the C2—C2′ bond in the two structures to position the O atoms adjacent to the smallest *ortho* substituent, the angles made by the planes are very similar. The conclusion is that the conformations in the solid and solution states are very similar.

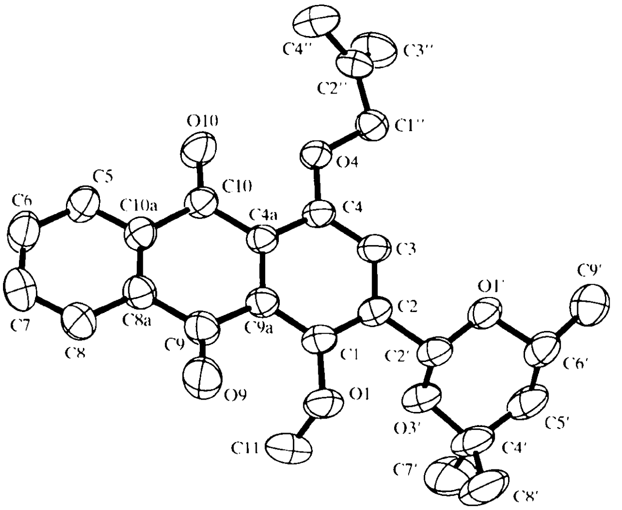


Fig. 1. The structure of one of the independent molecules in (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

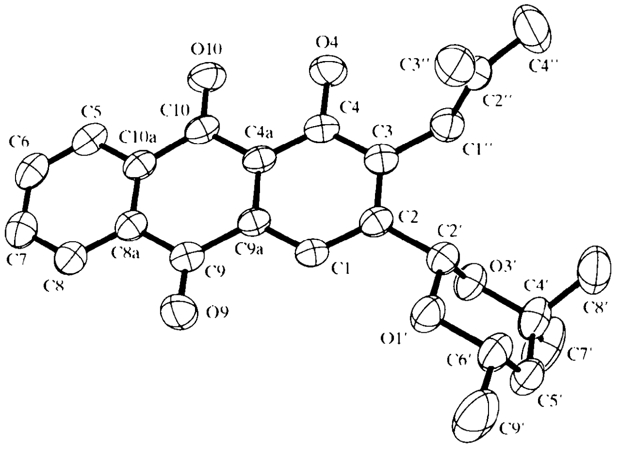


Fig. 2. The structure of (II), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

In both structures, the anthraquinone moiety shows significant deviations from planarity. The molecules are bowed, with the central part below the mean plane and the ends above the plane, with r.m.s. deviations of up to 0.22 Å. There is no obvious reason for this distortion. Otherwise, the molecular dimensions of the anthraquinones are normal. There are no significant differences between the geometries of the independent molecules in (I). There is an intramolecular hydrogen bond in (II), in which the hydroxyl oxygen, O4, makes an approach of 2.562 (2) Å to O10 (see Table 1).

Experimental

Both compounds were prepared in synthetic sequences starting from the anthraquinone anthrarufin. Their syntheses will be reported elsewhere (Cambie *et al.*, 1999). Compound (I) was obtained as yellow–orange crystals [m.p. 388.5–389 K, $[\alpha]_D^{20}$ +1.6° (concentration 0.94 g/100 ml in CH_2Cl_2); found: C 71.5, H 6.4%, M^+ = 436.1880; calculated for $C_{26}H_{28}O_6$: C 71.5, H 6.5%, M = 436.1886]. Compound (II) was obtained as orange crystals [m.p. 443–444 K, $[\alpha]_D^{20}$ −40.0 (concentration 0.07 g/100 ml in CH_2Cl_2); found: C 73.9, H 6.5%, M^+ = 406.1786; calculated for $C_{25}H_{26}O_5$: C 74.1, H 6.7%, M = 406.1780]. Crystals suitable for X-ray analysis were obtained from methanol solutions of the compounds.

Compound (I)

Crystal data

$C_{26}H_{28}O_6$
$M_r = 436.48$
Monoclinic
$P2_1$
$a = 8.2103\,(1)$ Å
$b = 25.6785\,(6)$ Å
$c = 11.6874\,(2)$ Å
$\beta = 105.004\,(1)^\circ$
$V = 2380.03\,(7)$ Å^3
$Z = 4$
$D_x = 1.218$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 8192 reflections
$\theta = 2$–26°
$\mu = 0.086$ mm^{-1}
$T = 203\,(2)$ K
Needle
0.56 × 0.24 × 0.22 mm
Yellow

Data collection

Siemens SMART CCD diffractometer
Area-detector ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{\min} = 0.953$, $T_{\max} = 0.981$
14 259 measured reflections
9283 independent reflections

7319 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.015$
$\theta_{\max} = 26.32^\circ$
$h = -10 \rightarrow 9$
$k = -32 \rightarrow 30$
$l = 0 \rightarrow 14$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.110$
$S = 1.051$
9283 reflections
585 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0527P)^2 + 0.1956P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.16$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.2 (7); not determined reliably

Compound (II)

Crystal data

$C_{25}H_{26}O_5$
$M_r = 406.46$
Orthorhombic
$P2_12_12_1$
$a = 6.7930\,(1)$ Å
$b = 14.0076\,(2)$ Å
$c = 22.2770\,(1)$ Å
$V = 2119.77\,(4)$ Å^3
$Z = 4$
$D_x = 1.274$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 7212 reflections
$\theta = 2.0$–24.5°
$\mu = 0.088$ mm^{-1}
$T = 203\,(2)$ K
Needle
0.47 × 0.18 × 0.18 mm
Orange

Data collection

Siemens SMART CCD diffractometer
Area-detector ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{\min} = 0.960$, $T_{\max} = 0.984$
12 565 measured reflections
3734 independent reflections

3232 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$
$\theta_{\max} = 25^\circ$
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 26$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.086$
$S = 1.035$
3734 reflections
276 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0407P)^2 + 0.2833P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.15$ e Å^{-3}
$\Delta\rho_{\min} = -0.11$ e Å^{-3}

Extinction correction: SHELXL97 (Sheldrick, 1997)
Extinction coefficient: 0.0082 (9)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.5 (10); not determined reliably

Table 1. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···O10	0.83	1.83	2.562 (2)	146

The data collection nominally covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. The crystal-to-detector distance was 4.94 cm. Coverage of the unique set is over 97% complete to at least 26° in θ. Crystal decay was monitored by repeating the initial frames at the end of data collection and analysing the duplicate reflections, and was found to be negligible. The absolute configurations were established from the known stereochemistry of the dioxane rings. Compound (I) has two independent molecules in the asymmetric unit. H atoms were placed geometrically and refined with a riding model (including free rotation about C—C bonds for methyl groups), and with $U_{\rm iso}$ constrained to be 1.2 (1.5 for methyl groups) times $U_{\rm eq}$ of the carrier atom. Standard uncertainties on the C—C distances do not exceed 0.004 Å in (I) and 0.003 Å in (II).

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structures: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1293). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 439–441

Dipeptide (Z)-Pro-ψ[CO-N(NH$_2$)]-Ala-NH^{i}Pr

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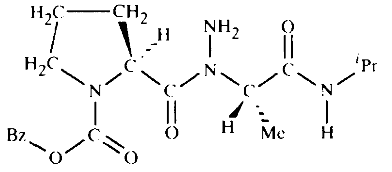
Abstract

The dipeptide, *N*-benzyloxycarbonylprolyl-*N*-aminoalanine isopropylamide, $C_{19}H_{28}N_4O_4$, assumes an extended conformation at variance with the β-folded conformation of its *N*-amino glycine-containing analogue. The *N*-amino amide is *trans* planar and has similar dimensions to the standard peptide group. One of the *N*-amino H atoms is intramolecularly hydrogen bonded to the C-terminal amide carbonyl group.

Comment

In contrast to *N*-methylation, *N*-amination of the peptide group has received little attention, mainly because of difficulties in obtaining optically pure α-hydrazino acids ($N^{\beta}H_2$-N^{α}H-CH*R*-CO$_2$H) and regioselective acylation of their α-nitrogen (Vidal *et al.*, 1993, 1997). The conformational analysis of the ^{t}BuCO-Pro-ψ[CO-N(NH$_2$)]-Gly-NH^{i}Pr *N*-amino dipeptide in solution and in the solid state has revealed a βII-folded structure with a *trans* *N*-amino amide group (Marraud *et al.*, 1993; Dupont *et al.*, 1993).

The absolute (*S*,*S*) configuration of the dipeptide, (I), is known from that of the starting proline and alanine materials. The three-dimensional structure shows that the *N*-amino amide group is *trans* planar with dimensions similar to those of the standard peptide group (Benedetti, 1977), and the *N*-amino group is practically bisected by the amide plane. The molecule assumes an extended conformation (Fig. 1) and engages in intermolecular hydrogen bonds of the N—H···O=C type (Table 2). One of the *N*-amino H atoms is at a hydrogen-bond distance from the C-terminal oxygen of the same molecule, so closing a six-membered pseudocycle.



(I)

This open conformation is also present in solution, as revealed by the large solvent sensitivity of the ^{i}PrNH resonance in NMR spectroscopy [1.91 p.p.m. shift from

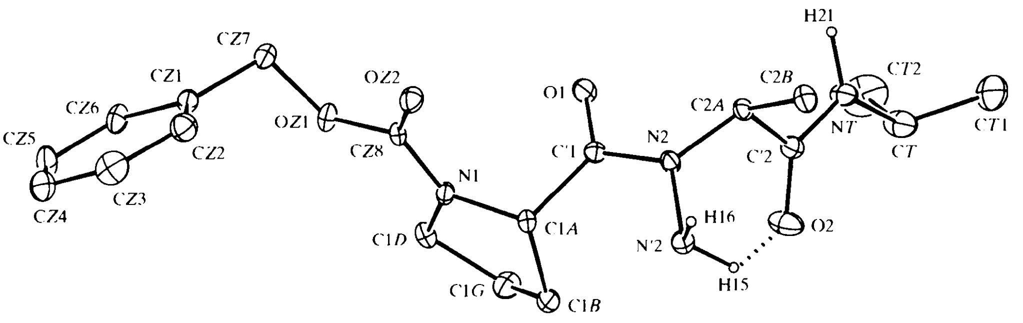


Fig. 1. Conformation of the title molecule showing the intramolecular hydrogen bond (broken line) between the *N*-amino group and the O2 atom. The displacement ellipsoids are drawn at the 25% probability level and H atoms linked to N atoms are included as small circles of an arbitrary radius.