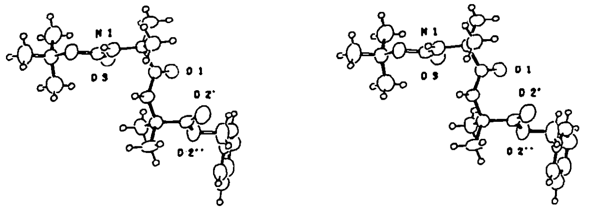

Fig. 2. Stereodiagram illustrating the observed conformation of Boc-Aib-Aib-OBzl.

molecule whose coordinates are listed in Table 1. This reversal in handedness of the C-terminal residue relative to the previous residues is frequently observed in peptides when this residue is not involved in intramolecular hydrogen bonding and reduces intramolecular contacts that would otherwise occur. Other examples include Boc-Pro-Aib-Ala-Aib-OBzl (Smith *et al.*, 1981), Z-$(Aib)_5$-OBu, Z-$(Aib)_4$-OH and Z-$(Aib)_3$-OBu (Benedetti *et al.*, 1982).

The molecules related by the *c*-glide plane are connected by hydrogen bonds of intermediate strength in which N(2) donates a hydrogen atom to O(1) of the molecule at $x, \frac{1}{2}-y, \frac{1}{2}+z$ with a geometry of N(2)···O(1) 3·013 (4), H(2N)···O(1) 2·19 (4) Å, and N(2)—H(2N)···O(1) 158 (3)°. No other intermolecular contacts are observed. The absence of short contacts involving N(1) represents a rare case where a potential hydrogen donor is not involved in hydrogen bonding. The molecules pack in alternate bands of hydrophobic and hydrophilic character parallel to the (*bc*) plane where the hydrophobic bands contain the phenyl and *tert*-butyl groups.

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*Acta Cryst.* (1983). C**39**, 896–899

# Structure of a 1:2 Adduct between 1,4,7,10,13,16-Hexaoxacyclooctadecane and *N,N'*-Dimethylthiourea, $C_{12}H_{24}O_6.2C_3H_8N_2S$

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(*Received* 25 *January* 1983; *accepted* 23 *February* 1983)

**Abstract.** $M_r = 472·67$, monoclinic, $P2_1/c$, $a = 9·629 (4)$, $b = 12·417 (5)$, $c = 11·063 (4)$ Å, $\beta = 103·95 (3)°$, $U = 1283·7$ Å$^3$, $Z = 2$, $D_x = 1·223$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·233$ mm$^{-1}$, $F(000) = 512$, $T = 291$ K. Final $R = 0·044$ for 2006 observed reflections. Each of the two guest molecules forms one (aminic) hydrogen bond of 2·08 (2) Å to one O atom of the macrocycle (approximate '$D_{3d}$' conformation). Complex units are linked by N—H···S bonds of 2·54 (1) Å.

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**Introduction.** X-ray analyses of complexes between urea and '18-crown-6' (Harkema, van Hummel, Daasvatn & Reinhoudt, 1981) and between thiourea and linear (Suh & Saenger, 1978; Weber & Saenger, 1980) or cyclic polyethers (Weber, 1982*b*) have shown O···H bridges to play a central rôle in stabilizing these compounds. Similar results have been obtained with aromatic amines (Hilgenfeld & Saenger, 1981; Weber & Sheldrick, 1981; Weber, 1981; Weber, 1982*a*,*c*) or amides (Knöchel, Kopf, Oehler & Rudolph, 1978; Galloy, Watson, Vögtle & Mueller, 1982) as guest molecules. Moreover, even with molecules containing acidic H atoms in $CH_2$ (Kaufmann, Knöchel, Kopf, Oehler & Rudolph, 1977; von Deuten, Knöchel, Kopf, Oehler & Rudolph, 1979) or $CH_3$ groups (Goldberg, 1975; Bandy, Truter & Vögtle, 1981; Weber, 1983), adduct formation *via* hydrogen bonds was observed.

In *N*,*N*′-dimethylthiourea the two aminic H atoms will probably serve as $e^-$ acceptors; the two methyl groups, however, might be involved either in secondary interactions or in steric effects. Hence a structural analysis of the title compound, to investigate the hydrogen-bond pattern formed, seemed worthwhile.

**Experimental.** Sample kindly provided by Professor F. Vögtle and Dr W. M. Mueller, University of Bonn (FRG); crystal (*ca* 0·6 × 0·4 × 0·2 mm) grown from methanol; Stoe–Siemens AED diffractometer; cell dimensions from $2\theta$ angles for 38 reflections ($20 < 2\theta < 25°$); 6862 profile-fitted (Clegg, 1981) data up to $2\theta = 50°$, 229 systematically absent ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$), 2263 unique ($R_{\rm int} = 0{\cdot}024$), 2008 intensities $>2\sigma(I)$, two erroneous reflections (machine fault) suppressed; no significant decline in intensity for three standard reflections; no absorption correction; structure solved by multisolution direct methods and subsequent Fourier syntheses; blocked-cascade refinement on $F$; $w^{-1} = \sigma^2(F) + 0{\cdot}0006F^2$; ligand H atoms in idealized positions (C—H = 0·96 Å) treated as 'riding atoms', methyl groups (C—H = 1·04 Å, H—C—H = 109·5°) as 'rigid groups', positions of aminic H atoms refined with N—H restrained to 0·96 Å (weights derived from $\sigma = 0{\cdot}01$ Å); all $U_{\rm iso}(H_i) = 1{\cdot}2\ U_{\rm eq}(C_i,\ N_i)$, for non-H atoms anisotropic thermal parameters; empirical extinction correction coefficient $x = 6{\cdot}2\,(3) \times 10^{-2}$ $[F_c' = F_c/(1{\cdot}0 + 0{\cdot}002xF_c^2/\sin 2\theta)^{0{\cdot}25}]$; 149 parameters; final $R = 0{\cdot}044$, $wR = 0{\cdot}049$, slope of normal probability plot = 1·54; max. shift/e.s.d. = 0·006, mean 0·001; largest peak/hole ≤ 0·25 e $Å^{-3}$; scattering factors from *International Tables for X-ray Crystallography* (1974); program for structure solution, refinement *etc.* (*SHELXTL*) written by Professor G. M. Sheldrick, for diffractometer control by Dr W. Clegg, both Göttingen (FRG).

Table 1. *Atomic coordinates* (×10⁴) *and* (*except for* H *atoms*) *equivalent isotropic thermal parameters* ($Å^2$ ×10⁴) *defined as one third of the trace of the orthogonalized* $U_{ij}$ *tensor*

| | *x* | *y* | *z* | $U_{\rm eq}/U_{\rm iso}$ |
|---|---|---|---|---|
| S(1) | 8277 (·6) | 1605 (·4) | 6034 (·4) | 623 (2) |
| C(10) | 7734 (2) | 2281 (1) | 4684 (1) | 426 (5) |
| N(11) | 6747 (2) | 3052 (1) | 4521 (1) | 582 (6) |
| H(11) | 6570 (22) | 3461 (15) | 3793 (13) | 679 |
| N(12) | 8288 (2) | 2052 (1) | 3708 (1) | 578 (6) |
| H(12) | 7970 (21) | 2472 (14) | 3000 (13) | 673 |
| C(11) | 6026 (3) | 3422 (2) | 5449 (2) | 730 (9) |
| H(11*a*) | 5193 | 3942 | 5058 | 857 |
| H(11*b*) | 6704 | 3791 | 6211 | 857 |
| H(11*c*) | 5611 | 2720 | 5738 | 857 |
| C(12) | 9334 (2) | 1239 (2) | 3696 (2) | 719 (8) |
| H(12*a*) | 8982 | 462 | 3810 | 840 |
| H(12*b*) | 10282 | 1385 | 4359 | 840 |
| H(12*c*) | 9511 | 1317 | 2809 | 840 |
| O(1) | 7335 (1) | 6004 (1) | 4400 (1) | 639 (5) |
| C(2) | 7710 (2) | 5608 (2) | 3318 (2) | 725 (9) |
| C(3) | 6421 (3) | 5502 (2) | 2294 (2) | 685 (8) |
| O(4) | 5573 (2) | 4647 (1) | 2559 (1) | 578 (4) |
| C(5) | 4286 (3) | 4514 (2) | 1622 (2) | 729 (8) |
| C(6) | 3363 (3) | 3715 (2) | 2047 (2) | 720 (8) |
| O(7) | 2880 (2) | 4148 (1) | 3049 (1) | 647 (5) |
| C(8) | 1981 (3) | 3429 (2) | 3489 (2) | 788 (9) |
| C(9) | 1511 (2) | 3950 (2) | 4552 (2) | 779 (9) |

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

| | | | |
|---|---|---|---|
| H(11)—N(11) | 0·93 (2) | C(2)—O(1) | 1·419 (6) |
| H(12)—N(12) | 0·93 (2) | C(2)—C(3) | 1·471 (6) |
| C(10)—S(1) | 1·683 (6) | C(3)—O(4) | 1·412 (6) |
| C(10)—N(11) | 1·330 (6) | C(5)—O(4) | 1·421 (6) |
| C(10)—N(12) | 1·345 (6) | C(5)—C(6) | 1·482 (7) |
| C(11)—N(11) | 1·446 (6) | C(6)—O(7) | 1·407 (6) |
| C(12)—N(12) | 1·429 (6) | C(8)—O(7) | 1·409 (6) |
| | | C(8)—C(9) | 1·505 (7) |
| | | C(9)—O(1)′ | 1·400 (6) |
| H(11)—N(11)—C(10) | 119 (1) | C(2)—O(1)—C(9)′ | 113·6 (3) |
| H(11)—N(11)—C(11) | 115 (1) | O(1)—C(2)—C(3) | 110·0 (4) |
| H(12)—N(12)—C(10) | 116 (1) | C(2)—C(3)—O(4) | 109·3 (3) |
| H(12)—N(12)—C(12) | 119 (1) | C(3)—O(4)—C(5) | 112·5 (3) |
| S(1)—C(10)—N(11) | 122·6 (3) | O(4)—C(5)—C(6) | 109·3 (3) |
| S(1)—C(10)—N(12) | 120·5 (3) | C(5)—C(6)—O(7) | 109·4 (3) |
| N(11)—C(10)—N(12) | 116·9 (3) | C(6)—O(7)—C(8) | 112·2 (3) |
| C(10)—N(11)—C(11) | 125·6 (3) | O(7)—C(8)—C(9) | 108·9 (4) |
| C(10)—N(12)—C(12) | 125·0 (3) | C(8)—C(9)—O(1)′ | 109·6 (3) |

For primed atoms see Fig. 1.

**Discussion.** Relevant atomic parameters are given in Table 1.* Bond lengths and angles (Table 2) reveal no unusual features as compared to other studies involving '18-crown-6' (for references see above and Maverick, Seiler, Schweizer & Dunitz, 1980) and *N*-methylurea (Huiszoon & Tiemessen, 1976; Harkema, ter Brake & Meutstege, 1979) or thiourea (Mullen, Heger & Treutmann, 1978; Mullen & Hellner, 1978; Elcombe & Taylor, 1968), respectively; only the present C(10)—S(1) distance appears slightly shortened [1·683 (6) Å], possibly due to the thermal motion of the S atom.

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* Lists of ligand H-atom parameters, anisotropic thermal parameters, torsion angles and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38453 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

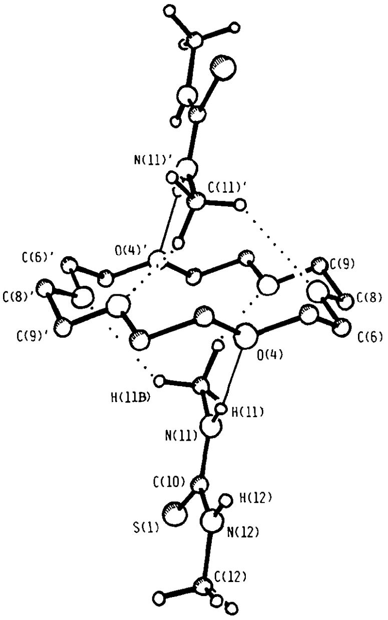

Fig. 1. A view of the adduct. Radii are arbitrary. Primed atoms are related to unprimed ones by inversion at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$. Dotted lines indicate (doubtful) C—H···O interactions of >2·6 Å, thin lines N—H···O bonds of 2·08 (2) Å.

Table 3. *Hydrogen-bond geometry (distances in* Å, *angles in* °)

| | | | |
|---|---|---|---|
| N(11)···O(4) | 2·955 (6) | H(11)···O(4) | 2·08 (2) |
| N(12)···S($1^{ii}$) | 3·394 (6) | H(12)···S($1^{ii}$) | 2·54 (1) |
| C($11^{i}$)···O(1) | 3·357 (6) | H($11a^{i}$)···O(1) | 2·645 (6) |
| C($11^{i}$)···O(7) | 3·484 (6) | H($11b^{i}$)···O(7) | 2·688 (6) |
| N(11)–H(11)···O(4) | 156 (1) | C($11^{i}$)–H($11a^{i}$)···O(1) | 125·5 (3) |
| N(12)–H(12)···S($1^{ii}$) | 153 (1) | C($11^{i}$)–H($11b^{i}$)···O(7) | 133·3 (3) |
| C(2)–O(1)···H($11a^{i}$) | 129·4 (3) | C(6)–O(7)···H($11b^{i}$) | 123·4 (3) |
| C($9^{i}$)–O(1)···H($11a^{i}$) | 113·7 (3) | C(8)–O(7)···H($11b^{i}$) | 123·8 (3) |
| C(3)–O(4)···H(11) | 118 (1) | C($10^{ii}$)–S($1^{ii}$)···H(12) | 117 (1) |
| C(5)–O(4)···H(11) | 125 (1) | | |

Symmetry code: (i) $1-x, 1-y, 1-z$ (primed atoms in Fig. 1); (ii) $x, 0·5-y, -0·5+z$.

As in many 1:2 complexes of '18-crown-6' with neutral $e^-$ acceptors (for references see above), the asymmetric unit contains only half the adduct; the two thioureas (tu's) (non-H atoms coplanar to within ±0·009 Å) are related by a centre of inversion at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ and are located 'above' and 'below' the hexagon of crown O atoms (coplanar to within ±0·24 Å) (Fig. 1), with dihedral angles between the tu plane and the plane of O atoms of 76·5 (8)° [step between tu planes: 1·19 (1) Å].

Examination of non-bonded distances between host and guests (Table 3) shows only one contact, namely N(11)···O(4) = 2·955 (6) Å, typical of a strong hydrogen bond [H(11)···O(4) = 2·08 (2) Å, N(11)–H(11)···O(4) = 156 (2)°]. It is thus surprising that the macrocycle displays the energetically less favoured (Bovill, Chadwick, Sutherland & Watkin, 1980) '$D_{3d}$' conformation with exclusively *anti–gauche–anti* units of alternating signs [mean O—C—C—O torsion = |170 (2)|, mean C—O—C—C = |177 (4)|°]* whilst with unsubstituted urea (Harkema *et al.*, 1981) or thiourea (Weber, unpublished) the 'biangular [99]' (Dale, 1973) conformation is found. However, the adopted '$D_{3d}$' conformation may be explained if contacts of one methyl group of each of the guest molecules to two crown O atoms (Table 3) are taken into account [though H···O distances of >2·6 Å and angles of about 130° indicate rather weak (if any) interactions], *i.e.* if each of the six O atoms accepts one hydrogen bond.

It seems that additional linkages between urea or thiourea molecules essentially assist in stabilizing the lattices of adducts with cyclic polyethers (Harkema *et al.*, 1981; Weber, 1982*b*). This also holds for the present structure. However, in accordance with the methyl substitution and in contrast to the three-dimensional network of hydrogen bonds in '18-crown-6'.5urea (Harkema *et al.*, 1981) and in 1,7,10,16-tetraoxa-4,13-diazacyclooctadecane.4tu (Weber, 1982*b*), the current compound contains only one tu···tu hydrogen bond [N—H···S 2·54 (1) Å] (Table 3), resulting in infinite chains of complex units approximately along *z*.

Without financial assistance from the Fonds der Chemischen Industrie this study could probably not have been carried out.

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* A list of torsion angles has also been deposited; see previous footnote.

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*Acta Cryst.* (1983). C**39**, 899–901

# The Structure of Gentiogenal: (±)-6-Methyl-1-oxo-3,4-dihydro-1*H*,6*H*-pyrano-[3,4-*c*]pyran-5-carbaldehyde, $C_{10}H_{10}O_4$

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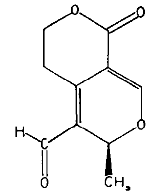
(*Received* 7 *February* 1983; *accepted* 1 *March* 1983)

**Abstract.** $M_r = 194{\cdot}19$, monoclinic, $P2_1/c$, $a = 9{\cdot}368\,(5)$, $b = 8{\cdot}282\,(5)$, $c = 11{\cdot}969\,(4)$ Å, $\beta = 103{\cdot}71\,(4)°$, $U = 902{\cdot}2\,(8)$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}431$ g cm$^{-3}$, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}2$ cm$^{-1}$, $F(000) = 408$, $T = 295$ K, $R = 0{\cdot}0515$ for 1033 observed reflections [$I > 2{\cdot}5\,\sigma(I)$]. The two fused six-membered rings are significantly puckered.



(I)

**Introduction.** Gentiopicrin (gentiopicroside), one of the major secoiridoid glucoside constituents of plant drugs originating from the Gentianaceae, is fungitoxic against *Penicillium expansum* on silica-gel thin-layer plates but only in the presence of $\beta$-glucosidase (van der Sluis, van der Nat & Labadie, 1983). Hydrolysis of this glucoside with $\beta$-glucosidase yields the aglucone. Absorbed on silica gel this aglucone is rapidly converted into an unknown compound, which was given the name gentiogenal. This compound proved to be active against our test organism *Penicillium expansum* (van der Sluis, van der Nat, Labadie, Spek & Ikeshiro, 1983). Gentiogenal was isolated in large amounts from an extract of *Blackstonia perfoliata* (L.) Hudson (Gentianaceae), a plant species known to be rich in gentiopicrin. Attempts to elucidate the structure of gentiogenal by means of $^1$H, $^{13}$C NMR and mass spectrometry resulted in two postulated structures, compatible with the available data. A subsequent X-ray structure determination was undertaken to secure the structure unequivocally. One of the proposed structures turned out to be the correct one (van der Sluis, van der Nat, Labadie, Spek & Ikeshiro, 1983). The 8*S* enantiomer is shown in (I).

**Experimental.** Good crystals obtained by recrystallization from chloroform, yellow crystal, 1·0 × 0·5 × 0·25 mm, Enraf–Nonius CAD4F diffractometer, accurate cell parameters calculated from the setting angles of 20 reflections and checked on the diffractometer *via* rotation photographs about the three crystal axes, unique data set $(+h, +k, \pm l)$ up to $\theta = 27{\cdot}5°$ collected with the $\omega/2\theta$ scan technique, Zr-filtered Mo $K\alpha$ radiation, 2088 reflections scanned; four reference reflections $(\bar{1}\bar{2}1;\ 1\bar{2}1;\ \bar{1}21;\ 12\bar{1})$ measured every hour of X-ray exposure time showed fluctuations less than 2% from the mean, the three groups of four reference reflections did not indicate any decay during the deliberately fast data collection (2·3 h of X-ray exposure time) contrary to what was expected from previous experience with another crystal; correction for the usual factors, excluding negligible absorption effects, 1033 unique reflections with $I > 2{\cdot}5\,\sigma(I)$, direct methods, refined on $F$ by full-matrix least-squares techniques, atoms located from difference Fourier; refined parameters included all positional parameters, anisotropic temperature factors for the non-hydrogen atoms and one overall temperature factor for the H

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