Fig. 1. *ORTEP* plot (Johnson, 1965) of HYNONA showing atom numbering and thermal ellipsoids (50% probability level) of the non-H atoms. The H atoms were given an arbitrary 0·07 Å radius and were numbered to correspond to their carrier atom followed by a sequence number.
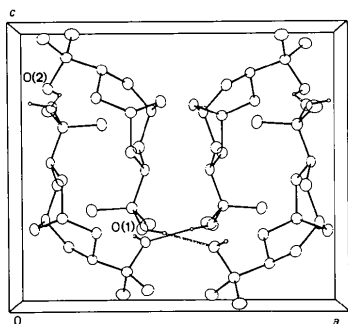

Fig. 2. Drawing of the unit-cell contents viewed down **b**. Short O···O contacts are indicated by open bonds.

torsion angles with those of the twist-boat conformation of cyclohexane as calculated by molecular mechanics (Table 2) (van de Graaf, Baas & van Veen, 1980, and references cited therein) shows that both wings of the bicyclo[3.3.1]nonane skeleton are flattened. Similar geometries were calculated for several analogous 3α,7α-disubstituted bicyclo[3.3.1]nonanes with the use of molecular mechanics (Peters *et al.*, 1978).

The packing of the molecules is illustrated in Fig. 2. There are two short intermolecular O···O contacts which can be considered as (weak) hydrogen bonds; their geometrical details are added in Table 2.

References

BHATTACHARJEE, S. K. & CHACKO, K. K. (1980). *Tetrahedron*, **35**, 1999–2007.
GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.
GRAAF, B. VAN DE, BAAS, J. M. A. & VAN VEEN, A. (1980). *Recl Trav. Chim. Pays-Bas*, **99**, 175–178.
JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
KONINGSVELD, H. VAN (1981). *Cryst. Struct. Commun.* **10**, 775–780.
KONINGSVELD, H. VAN & PETERS, J. A. (1981). *Cryst. Struct. Commun.* **10**, 723–729.
PETERS, J. A., BAAS, J. M. A., VAN DE GRAAF, B., VAN DER TOORN, J. M. & VAN BEKKUM, H. (1978). *Tetrahedron*, **34**, 3313–3323.
PETERS, J. A., VAN DER TOORN, J. M. & VAN BEKKUM, H. (1975). *Tetrahedron*, **31**, 2273–2281.
STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. W. & HALL, S. R. (1972). The XRAY72 system—version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Bis[2-(*o*-methoxyphenoxy)ethyl] Ether–Urea (1:1) Complex, $C_{18}H_{22}O_5.CH_4N_2O$

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Dedicated to Professor Friedrich Cramer on the occasion of his 60th birthday

Abstract. $M_r = 378.2$, monoclinic, C2, $a = 26.084$ (8), $b = 4.732$ (2), $c = 7.612$ (3) Å, $\beta = 101.75$ (5)°, $Z = 2$, $D_m = 1.32$ Mg m^{-3}, $D_x = 1.315$ Mg m^{-3}, λ(Cu $K\alpha$) $= 1.5418$ Å, μ(Cu $K\alpha$) $= 0.83$ mm^{-1}, $F(000) = 404$, room temperature. The structure of the linear polyether–urea complex was solved from 774 diffractometer-measured reflections and refined to an R of 0·052. The polyether ligand, which has five O atoms in the chain, does not wrap circularly around the urea molecule to have the expected 'monomer' type of

interaction as in other polyether metal–ligand complexes. On the contrary it exists in an 'S'-type conformation with each half of the 'S' loop bound to one half of two urea molecules through weak, bifurcated N—H⋯O hydrogen bonds (stoichiometry 1:2). The urea molecules themselves are bound head to tail through N—H⋯O hydrogen bonds to form an infinite chain along the *b* axis of the crystal.

Introduction. The complexing abilities of linear polyether ligands with cations are of biological interest as they serve as model compounds of ionophore antibiotics (Saenger, Brand, Vögtle & Weber, 1977; Vögtle & Weber, 1979; Hilgenfeld & Saenger, 1982). In this context structure analyses of several polyether ligands of different lengths and different cations have been carried out (Saenger, Suh & Weber, 1979; Suh, Weber, Kaftory & Saenger, 1980; Chacko & Saenger, 1980, 1981). Besides metal ions, linear polyethers are also found capable of forming stable 1:1 adducts with neutral guest molecules like urea and thiourea. Such complexes are of particular clinical interest because they can be used to accelerate dialysis (Vögtle & Weber, 1979) and they serve as models for biological receptor systems. The crystal structure of a 1:1 complex of thiourea with a linear polyether containing seven O atoms namely, bis[2-(o-methoxyphenoxy)-ethoxyethyl] ether–thiourea (hereafter called MPEEET) has already been determined (Suh & Saenger, 1978). In the present report we describe the crystal structure of (I) which is the complex of urea with a shorter linear polyether containing five O atoms.

Experimental. Needle-shaped crystals of (I) obtained by recrystallization of material made available by Professor Vögtle, University of Bonn, approximate cell dimensions from precession photographs which also established the space group $C2$ from systematic absences; density measurements showed there to be only two molecules of the complex in the unit cell ($Z = 2$) demanding (I) to have a twofold axis of symmetry. Crystal $0.15 \times 0.20 \times 0.30$ mm, Nonius CAD-4 automatic diffractometer, Cu $K\alpha$ radiation, lattice parameters by least squares from 15 reflections, 774 measured reflections with $I > 2\sigma(I)$ ($2\theta_{max} = 118°$, $\pm h,k,l$) used for structure determination, no absorption correction, intensity variation of three standard reflections within experimental errors with no systematic trend; direct methods [$MULTAN80$ (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980)], refinement on F by full-matrix least squares (Gantzel, Sparks & Trueblood, 1961), anisotropic thermal corrections assigned to the non-hydrogen atoms, in final cycles $w = 5.0$ for $|F_o| < 5.0$ and $w = |F_o|$ for $F_o > 5.0$, H-atom positions computed on the basis of stereochemical considerations (with B values corresponding to those of the attached C or N) and included in the

structure factor calculations but not refined; final $R = 0.052$, $R_w = 0.018$, $S = 0.052$, $(\Delta/\sigma)_{max} = 0.79$; scattering factors from *International Tables for X-ray Crystallography* (1962).

Discussion. The final atomic parameters are given in Table 1.* The molecule is shown schematically in Fig. 1. Geometrical data of (I) are presented in Fig. 2. The bond lengths and angles agree fairly well with average values reported (Saenger, Suh & Weber, 1979) for linear polyether metal complexes [*i.e.* 1.49 Å for aliphatic C—C, 1.42 Å for aliphatic C—O and 1.37 Å for aromatic C—O, bond angles are 108 and 111° for aliphatic C—C—O and C—O—C respectively and 117° for (aromatic)C—O—C(aliphatic)]. With regard to the urea molecule, the C=O distance of 1.226 (10) Å and the N—C—N' bond angle of 115.0 (4)° are significantly different from the reported values of 1.270 (7) Å and 118.1 (6)° for the structure of urea (Caros & Donohue, 1969) probably due to the special location of urea on the twofold axis and to the particular hydrogen-bonding scheme (see below). The torsion angles along the polyether chain are *trans* and *gauche* about the C—O and C—C bonds respectively, as generally observed (Saenger, Suh & Weber, 1979).

The molecular packing and hydrogen-bonding scheme in this crystal structure are depicted in Fig. 3. The most prominent motif is, bands of urea molecules located with their C=O axes along crystallographic dyads in (000). They are connected by hydrogen bonds between the two *endo*-positioned NH groups of one urea to oxygen of the urea translated along [010] immediately 'above'.

Each band of urea molecules is surrounded by polyether molecules which are located with their central O(7) atoms on crystallographic dyads at $(0,0,\frac{1}{2})$. The polyether adops an 'S'-like arrangement folded into a 'V'-shape, Figs. 1–3. The two loops of the 'S' are in hydrogen-bonding contact with the *exo*-NH groups of two *c*-translation equivalent urea molecules such that each *exo*-NH forms bidentate contacts with the aromatic oxygens O(1) and O(4), with H⋯O distances given in Table 2. Polyether oxygen O(7) is not involved in any obvious interactions.

Because both partners of the complex (I) are located on crystallographic dyads, the overall stoichiometry of the crystals is 1:1, yet the local stoichiometry is 1:2. This situation is quite different from MPEEET with 1:1 ratio, *i.e.* one thiourea molecule is circularly surrounded by a linear polyether molecule with seven O atoms which are all engaged in hydrogen bonds (some

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bifurcated) to *exo* as well as *endo* NH groups. It appears that such a geometry or a 1:1 complex formation is prohibited for (I) by the shorter length of the ligand with only five oxygens, which in a 1:1 complex could satisfy only the hydrogen-bonding capacity of the *endo* NH groups of urea, leaving the *exo* NH's free. The system avoids this unfavourable geometry by urea–urea self complexation (which is also observed in other crystal structures) and only the *exo* NH's interact with polyether aromatic oxygens, leaving O(7) free. Another interpretation could be that urea–urea hydrogen bonding is stronger (and more preferred) than urea–polyether interactions and, therefore, the band-like urea motif determines the crystal structure, with polyether molecules acting only to satisfy the *exo*-NH groups *via* hydrogen bonding. This interpretation is also in agreement with N···O distances, being rather long for N···O(1), 3·080 (4) Å, and N···O(4), 3·385 (3) Å, whereas N···O(urea) is only 3·007 (8) Å (Table 2). A possible strategy to decide between these two alternatives would be the investigation of the crystal structure of the thiourea analogue of (I) where thiourea–thiourea interactions are weaker compared to the urea case.

The authors are grateful to Professor F. Vögtle, Bonn, for initiating this study and for providing the material. They thank the Regional Sophisticated Instruments Centre, IIT, Madras, for the data collection on the CAD-4 diffractometer. Calculations were carried out using the IBM 370/155 System at the IIT Computer Centre, Madras.

Fig. 1. Chemical structure and numbering scheme of bis[2-(*o*-methoxyphenoxy)ethyl] ether–urea complex.

Fig. 2. Bond angles (°), distances (Å) and hydrogen bonding (dashed lines) in the complex. Bond angles in the urea molecule: O–C–N 122·5 (4), O–C–N' 122·5 (4), N–C–N' 115·0 (4)°.

Table 1. *Fractional atomic coordinates* (×10⁴) *and equivalent isotropic thermal parameters* (×10²) *with e.s.d.'s in parentheses*

	x	y	z	$B_{eq}(\text{Å}^2)$
O(1)	3716 (1)	6636	6912 (3)	419 (8)
C(2)	3414 (1)	6517 (13)	5231 (4)	319 (21)
C(3)	3560 (1)	8336 (13)	3962 (5)	303 (18)
O(4)	3973 (1)	9964 (12)	4584 (3)	372 (17)
C(5)	4154 (1)	11642 (15)	3278 (5)	393 (21)
C(6)	4579 (1)	13466 (14)	4247 (6)	413 (22)
O(7)	5000	11741 (13)	5000	403 (21)
C(8)	3280 (2)	8335 (14)	2216 (5)	387 (20)
C(9)	2862 (1)	6593 (15)	1738 (5)	432 (21)
C(10)	2722 (1)	4825 (15)	2988 (5)	412 (21)
C(11)	3002 (1)	4780 (15)	4735 (5)	380 (21)
C(12)	3633 (2)	4553 (16)	8180 (6)	514 (23)
O	5000	5646 (13)	10000	627 (26)
C	5000	8236 (17)	10000	356 (20)
N	4676 (1)	9756 (13)	8803 (5)	506 (19)

Table 2. *Hydrogen-bond distances*

D–H···A	D···A (Å)	H···A (Å)	D–H···A (°)
N–H1(N)···O(1)	3·080 (4)	2·16	153
N–H1(N)···O(4)	3·385 (3)	2·58	138
N–H2(N)···Oⁱ	3·007 (8)	2·07	150

Symmetry code: (i) x, 1 + y, z.

Fig. 3. Crystal structure viewed along **c*** to show band of urea molecules and V-folding of molecules. Distances in Å.

References

CAROS, A. & DONOHUE, J. (1969). *Acta Cryst.* B25, 404.
CHACKO, K. K. & SAENGER, W. (1980). *Z. Naturforsch. Teil B*, 35, 1533–1537.

CHACKO, K. K. & SAENGER, W. (1981). Z. Naturforsch. Teil B, 36, 102–107.

GANTZEL, P. K., SPARKS, R. A. & TRUEBLOOD, K. N. (1961). Program UCLALS 1, Univ. of California.

HILGENFELD, R. & SAENGER, W. (1982). Top. Curr. Chem. 101, 1–75.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univs. of York, England, and Louvain, Belgium.

SAENGER, W., BRAND, H., VÖGTLE, F. & WEBER, E. (1977). Metal Ligand Interactions in Organic Chemistry and Biochemistry, edited by B. PULLMAN & G. GOLDBLUM, Part I, pp. 363–374. Dordrecht: Reidel.

SAENGER, W., SUH, I.-H. & WEBER, G. (1979). Isr. J. Chem. 18, 253–258.

SUH, I.-H. & SAENGER, W. (1978). Angew. Chem. Int. Ed. Engl. 17, 534.

SUH, I.-H., WEBER, G., KAFTORY, M. & SAENGER, W. (1980). Z. Naturforsch. Teil B, 35, 352–359.

VÖGTLE, F. & WEBER, E. (1979). Angew. Chem. Int. Ed. Engl. 18, 753–776.

Structure and Absolute Configuration of (+)-Doronine–Benzene (1:1), C₂₁H₃₀ClNO₈.C₆H₆

$C_{21}H_{30}ClNO_8.C_6H_6$

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Abstract. $M_r = 538.1$, orthorhombic, $P2_12_12_1$, $a = 10.873$ (4), $b = 12.678$ (3), $c = 20.511$ (9) Å, $V = 2827.4$ Å³, $Z = 4$, $D_x = 1.26$ g cm⁻³, Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å, $\mu = 16.1$ cm⁻¹, $F(000) = 1144$, room temperature, $R = 0.08$, 2162 independent reflections. The absolute configuration of the molecule was determined. The X-ray results show the presence of a benzene molecule of crystallization in the crystal structure. An intramolecular transannular interaction is postulated between the N and carbonyl C atoms across the eight-membered ring: the N···C(8) distance is 2.231 Å and the C(8)=O(23) bond length is 1.221 Å. Molecules of (+)-doronine are stabilized in the crystal structure by a single intermolecular hydrogen bond and van der Waals interactions.

Introduction. (+)-Doronine,* a Cl-containing seco-pyrrolizidine alkaloid first isolated by Russian workers from *Doronicum macrophyllum* (Alieva, Abdullaev, Telezhenetskaya & Yunosov, 1976) was isolated from the methanol extract of *Senecio clevelandii* E. L. Greene. The physiological properties of seco-pyrrolizidine alkaloids have not been extensively in-

vestigated (Culvenor, 1976). It has been suggested that the stereochemical disposition of groups attached to C(15) and C(20) can influence toxicological properties such as carcinogenicity (Hirata, 1978). Furthermore, it has been proposed that the intramolecular N···C=O interaction in the structure may be relevant to the physiological activity of pyrrolizidine alkaloids (Bürgi, Dunitz & Shefter, 1973). The structure (I) (empirical formula $C_{21}H_{30}ClNO_8$) based on spectral and chemical data (Alieva *et al.*, 1976) was ascribed to (+)-doronine. The present X-ray analysis was undertaken to determine the configuration at all the chiral centers. The X-ray results confirm the proposed structure and show that a benzene molecule of crystallization is present.
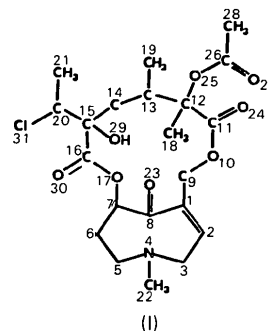
* Systematic name (*Chemical Abstracts*): (15α,20R)-12-acet-oxy-20-chloro-15,20-dihydro-15-hydroxy-4-methyl-4,8ʹ-secosenecio-nan-8,11,16-trione.

(I)