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Organic Metal-Complexes. XXI [1]

Synthesis and Structure of 3,5,15,17-Tetraoxo-1,7,10,13,19,22-hexaoxacyclotetracosane and 2,12,14,24-Tetraoxo-4,7,10,16,19,22-hexaoxa-25-mercurato-bicyclo[11.11.1]pentacosane

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Abstract. A new synthesis of the title crown *via* isoxazolo crown ether **7** and macrocyclic bis-β-eneaminoketone **10** is described. **7** can be synthesized in 14% yield by a non-template double-[3+2] cycloaddition of dinitrileoxide **5** prepared *in situ* from dinitropolyether **19** by dehydration with Ph–NCO and alkyne **6**. The compounds **16**, **17** and **18** are synthesized by the same synthetic strategy. Comparable IR and ^{1}H NMR spectroscopic data of macrocyclic and non-cyclic compounds show, that macrocyclic conformation stabilizing effects can be ruled out. The structures of the macrocycles **1**, **7**, **10** and that of the Hg(II)-complex **25**, synthesized by reaction of **1** with $Hg(OAc)_2$ were established by single-crystal X-ray structure analyses. Both inter- and intramolecular hydrogen bonds are observed for the macrocyclic bis-β-eneaminoketone **10**, whereas only intramolecular hydrogen bonds are formed by **1**.

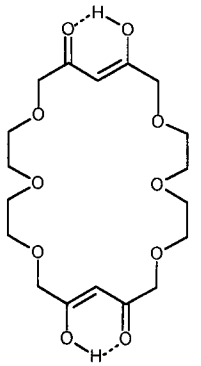
In the Hg(II)-complex of **1** the mercury is bonded to two methylene groups. C–Hg–C is almost linear [177(1)°], the mean Hg–C distance amounts to 215(1) pm. In addition to the Hg–C bonds, each Hg makes a short contact to a carbonyl oxygen in a neighbouring molecule in the plane perpendicular to the C–Hg–C axis [Hg(1)–O(1) = 279(1) pm, Hg(2)–O(5) = 284(1) pm].

Nearly all metal cations form oxygen chelated complexes like **2** with β-dicarbonyl compounds [1], that are soluble in organic solvents. Whereas in most cases polymeric precipitates are formed, if solutions of mercury(II)-salts and β-dicarbonyl compounds are mixed. Therefore X-ray structure determination was successful only in a few cases of sterically hindered complexes, showing mercury–carbon bonds and bond angles of nearly 180° at the mercury atom **3**. Oxygen bonded Hg(II) enolates such as **4** could only be found in solution [2, 3].

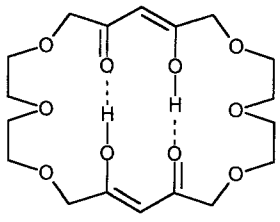
We expected that a crown ether with incorporated β-dicarbonyl-units such as **1** is suitable for the synthesis of a monomeric oxygen chelated Hg(II)-β-dicarbonyl compound, because of the ability of crown ethers to act as complexing agents – a fascinating aspect of modern chemistry [4a–t]. The resulting coronate should furthermore be soluble to give useful cystals for X-ray structure determination.

The procedures described by Alberts and Cram [5] for the synthesis of macrocyclic acetylacetone ligand **1**, as well as its aliphatic analogue and metall complex by Saegusa and co-workers [6] did not give crystals useful for X-ray structure analyses, so that hardly anything is known about their structures. Only transannular hydrogen bonding in **1** (structure **1b**) has been ruled out on the basis of pK_a-relationships between macrocyclic acetylacetone ligands and similiar open chain compounds [7].

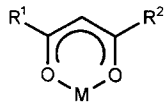
The preparation of **1** according to the literature procedure [7] includes a multiple deprotection step in the course of which 1,3-dithiane groups are transformed into keto groups, which is difficult to accomplish [8]. This difficulty and the limitations of the known procedure with regard to the choice of hetero atoms restricted to oxygen in the crown structure prompted us to look for a different synthesis, described in Scheme 1. The



1a



1b



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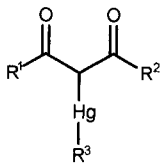

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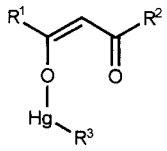


4

synthesis of the macrocycles is combined with the formation of isoxazole groups by [3+2]-cyclo- addition of nitrileoxides [9] to alkynes. The isoxazole groups can afterwards be hydrogenated to the ene-amino ketone and hydrolized to the β-dicarbonyl functionality.

The [3+2]-cycloaddition of **5** to **6** has the advantage to give **7** as the major macrocyclic product with syn-oriented isoxazole groups, whereas [3+2]-cycloaddition of **8** to itself gives a mixture of the macrocycles **9a–c,** with *anti*-oriented isoxazole groups for **9b**. This could lead to the specific synthesis of the two isomeric macrocycles **10** and **11**.

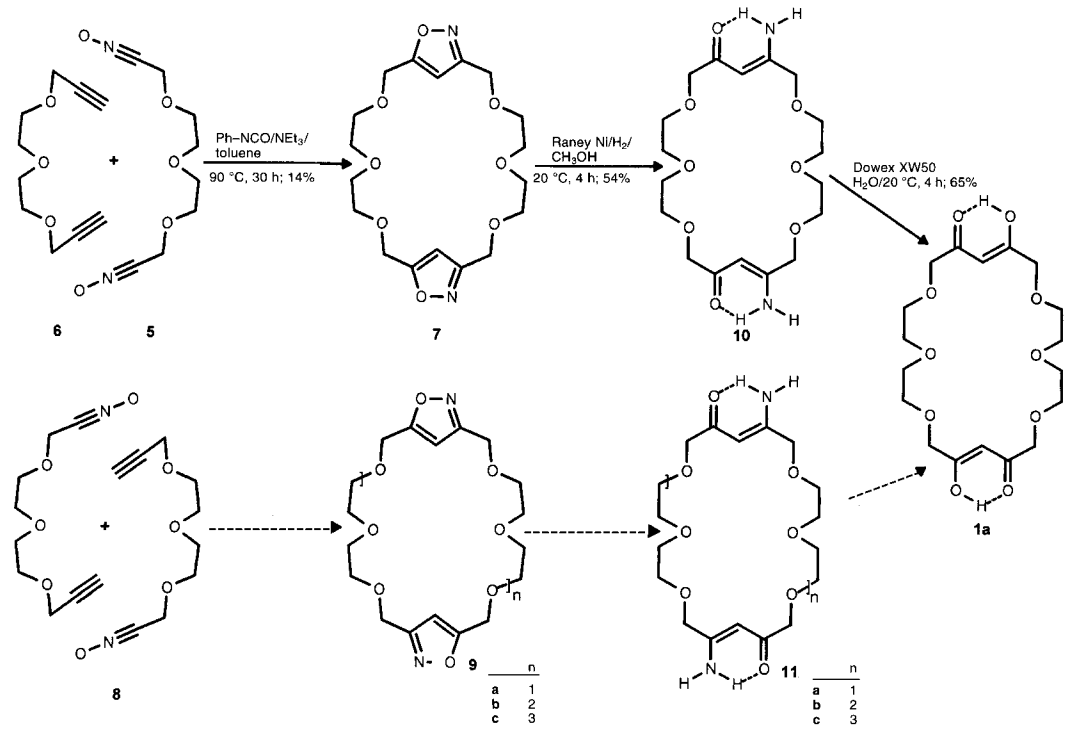
It seems to be adaptable to hetero atoms other than oxygen and avoids synthetic steps involving metal cations as reactants or templates to eliminate product contamination, due to strong complexation with the target compound.

In this article, we describe a new synthesis of the macrocyclic acetylacetone ligand **1**, the X-ray molecular structure of the free ligand as well as those of the compounds **7**, **10** and of the Hg(II) compound **25**.

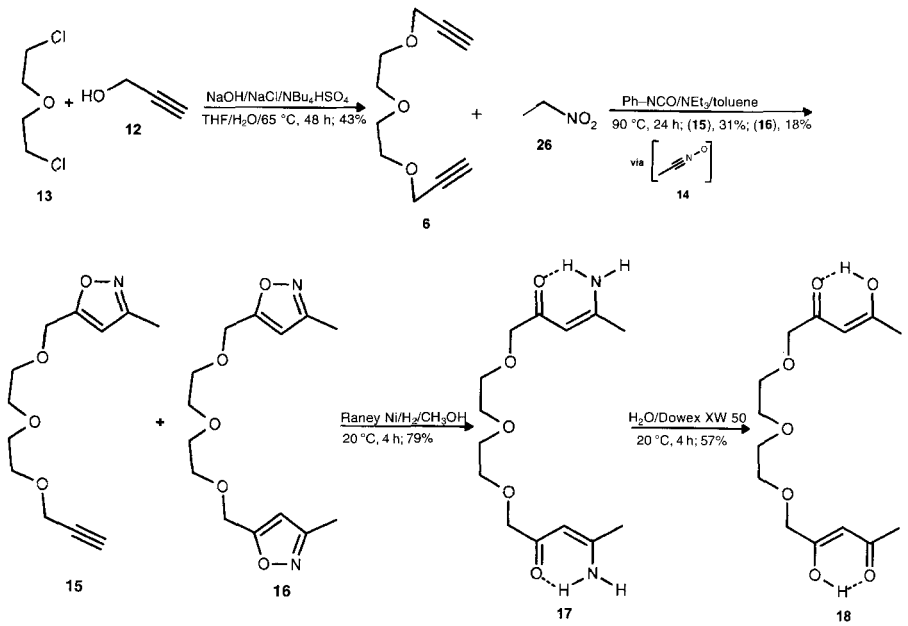
Synthesis

In order to verify the efficiency of the intended synthesis, we synthesized the open chain compound **18** according to Scheme 2.

The [3+2]-cycloaddition of diine **6** synthesized by treating a mixture of propargylic alcohol **12** and dichloride **13** with NaOH under phase-transfer conditions (43%), and nitrileoxide **14** formed in situ by the reaction of commercially available nitroethane **26** with Ph-NCO and NEt_3, gives **15** (31%) and **16** (18%). Hydrogenation of **16** with Raney-Nickel gives **17** (79%),



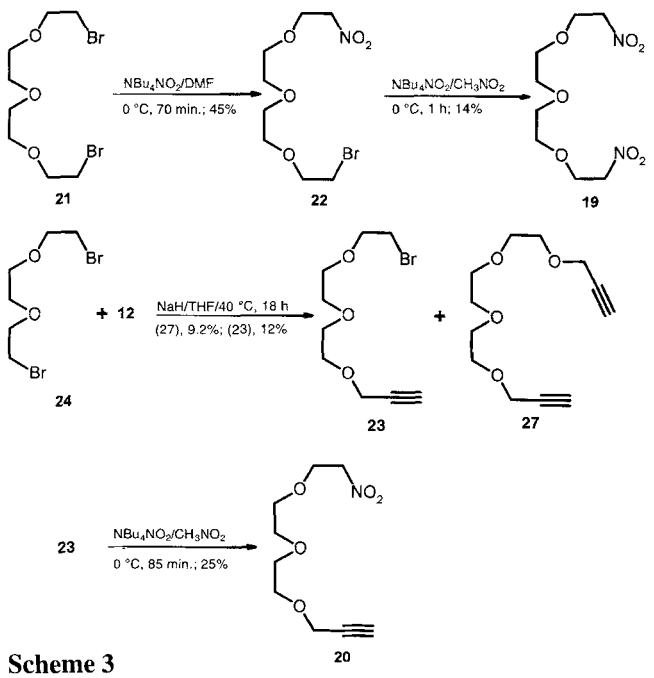
Scheme 1



Scheme 2

which is hydrolyzed to **18** (57%) by adsorbing the formed NH_3 with an acidic ion-exchange resin.

For the synthesis of the isoxazolo crown ethers **7** and **9a–c** (Scheme 1) the nitro compounds **19** and **20** have to be prepared (Scheme 3). Classical procedures [10], reaction of **21**, **22** and **23** with $AgNO_2$ or $NaNO_2$ lead to decomposition of the starting material. Minor amounts of the desired compounds can be detected by ^1H NMR spectroscopy, but no pure product could be isolated.



Scheme 3

We believe that the nucleophilic displacement of the bromine in the polyether substrates **21**, **22** and **23** by the ambident nitrite ion, which gives the corresponding nitro compounds is an equilibrium reaction. Therefore in the course of the reaction a growing amount of unstable nitrous acid esters are formed instead.

The substitution reaction is successful when a variant of the procedure published by Simchen and co-workers [11] is applied, by using NBu_4NO_2 in DMF.

In order to synthesize **19**, it is necessary to use a two step procedure, involving concentrated solutions of NBu_4NO_2 at 0 °C with significant excess of the bromo-compound. Furthermore it is necessary to remove nearly all NBu_4-salts by precipitation in ether. Immediate flash chromatography gives **22** (45%) and **19** (14%).

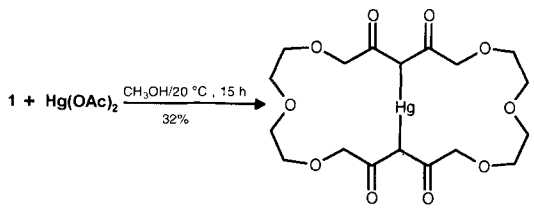
For the synthesis of **20** a comparable procedure can be applied to **23** as starting material, synthesized by treating dibromide **24** with **12** and NaH in THF (12%). Because of the difficulty in purifying **20** and the low yield (25%), the synthesis of **9a–c** was abandoned.

Under the reaction conditions reported in the literature [9] for the formation of isoxazoles described above starting with **20** and **6** isoxazolo crown ether **7** can only be isolated in low yield (5%). The yield can nearly be tripled (14%) by starting the reaction at 30 °C with a minor amount of Ph–NCO, elevating the temperature to 90 °C, diluting the reaction system and adding the final amount of Ph–NCO.

When the 1,3-dipolar cycloaddition reaction is carried out in very dilute solution only polymeric material is found. It is further impossible to improve the yield by using the template effect of the potassium ion, be-

cause of decomposition reactions caused by the counter ions, for reasons discussed above. Hydrogenation of **7** gives **10** (54%), which gives **1** (65%) when hydrolyzed and freed of NH_3.

The Hg(II) β-diketonato coronate **25** forms spontaneously and precipitates after combining methanolic solutions of **1** and $Hg(AcO)_2$ (Scheme 4). Elemental analysis showed a ligand-to-Hg(II) ratio of 1:1. The block shaped crystals are unstable, become turbid and have to be recrystallized (32% isolated yield).



25

Scheme 4

Structural Features of Macrocyclic and Linear Ligands

The open chain compounds **16**, **17**, and **18** show IR spectroscopic bands and ^1H NMR spectroscopic signals comparable to those for the crown ethers with equivalent functional groups **7**, **10** and **1**.

The IR spectra of **18** (neat) and **1** (KBr) show three bands in the carbonyl range: sharp bands at 1709 and 1730 and a broad band at 1612 cm^{-1} for **18** and very weak bands at 1730 and 1745 and an intense broad band at 1615 cm^{-1} for **1**. Additionally in the spectrum of **1** an olefinic band at 3112 cm^{-1} is found.

The ^1H NMR chemical shifts of **1**, **7**, **10**, **16**, **17** and **18** are comparable to those found in the literature for compounds with equivalent functional groups: 3,5-dimethyl-isoxazole [13], 4-amino-pent-3-en-2-one [14], acetylacetone [14, 15] and 1,3,13,15-tetraoxotetracosane [4].

The ^1H NMR signals of **7** at 4.64 and 4.66 ppm are assigned by comparing ^1H NMR-data with those of a similiar macrocycle [16] and comparing line shape and intensity with those of **16**.

The signals of **1** for the hydroxyl hydrogen, the olefinic hydrogen and the CH_2 group flanking the β-dicarbonyl system are each split into two signals. Each signal group shows the same intensity ratio, which is dependent upon temperature, concentration and solvent. The signals of the hydroxyl hydrogen (15.10 and 15.05 ppm) can be recorded separately below −10 °C. Above this temperature only one signal is found. Furthermore, if the concentration of **1** in $CDCl_3$ is below 0.05M, it can only be recorded at temperatures below 0 °C.

Alberts and Cram [7] did not find a signal at 15.1 ppm in the ^1H NMR spectrum of **1** and therefore ascribed a signal found at 6.5 ppm to this hydrogen. They further described two signals found at 4.2 and 4.1 ppm with an intensity correlation of four to one and that the protons that cause the signal at 4.1 ppm could rapidly be exchanged by deuterium.

We find signals at 6.32 and 6.27 ppm (olefinic hydrogen) and at 4.18 and 4.10 ppm (CH_2 group flanking the β-dicarbonyl system) with an intensity correlation of approximately one to four (23 °C). The protons that cause the last two signals cannot be exchanged rapidly by deuterium even in D_2O. ^{13}C NMR spectroscopic comparison between the signals found for **1** and those found in the literature for acetylacetone [15] proves that **1** is partly enolized in solution. The signal of the intermediate CH_2 group of the non-enolized β-dicarbonyl system is found at 3.64 ppm in the ^1H-^{13}C NMR COSY spectrum of **1**, which also supports our interpretation of the ^1H NMR data given above.

It is known that the concentration of the enolic structure of β-dicarbonyl compounds depends on the state of aggregation, solvent polarity, temperature and neighbouring substituents [2, 12]. The percentage of the enolized β-dicarbonyl systems can be calculated by estimating the integrals of the signal at 4.18 ppm, corresponding to the CH_2 groups flanking the non-enolized, and at 4.10 ppm, corresponding to those CH_2 groups flanking the enolized β-dicarbonyl systems. At −30 °C (0.2M, $CDCl_3$) approximately 92% of the dicarbonyl groups are enolized, 84% at 0 °C and 74% at 23 °C, respectively. In D_2O at 23 °C only 14% enolization is found. The NMR data of **1** confirm that transannular hydrogen bonding can be ruled out.

Structural Features of the Mercury(II)-complex 25

In the IR-spectrum of **25** intense bands of the carbonyl stretching vibration and the C–O stretching vibrations of the ether bridges are found. The carbonyl band is found at significantly higher wave numbers (1671 cm^{-1} (br) and 1630 cm^{-1} (sh)) than those of typical oxygen bonded chelate complexes (1580–1280 cm^{-1}) [2b, 17].

The ^1H NMR spectrum shows a broad multiplet of the protons of the ether bridges, two doublets at 3.93 and 4.22 ppm of the four methylene protons flanking the β-dicarbonyl system (geminal coupling J = 15.1 Hz) and a singlet at 4.14 ppm, having two satellites due to the ^1H-^{199}Hg atom coupling ($J(^{199}Hg$-$^1H)$ = 234 Hz).

The ^{13}C NMR-spectrum shows four signals, which can be assigned by comparison with the ^{13}C NMR spectrum of **1**: at 205.46 ppm (C=O), at 75.22 ppm (O–CH_2–C=O), 71.15 ppm (CH_2–CH_2–OCH_2–CH_2) and at 69.19 ppm (CH_2–O–CH_2, O=C–CH_2–CO). DEPT- and ^1H-^{13}C COSY spectra prove, that the signal at 69.19

ppm originates from two different carbon atoms. It should be noted here that this means a downfield shift of nearly 19 ppm for the signal of the intermediate carbon of the β-dicarbonyl system in **25** relative to the corresponding carbon of the non-enolized β-dicarbonyl system in **1** (50.24 ppm).

These results show that Hg(II) is bonded to the methylene carbon of the β-dicarbonyl system and stabilizes a particular rigid conformation of **1** in compound **25** with an intense electronic anisotropy.

Crystal Structures

Compound 1 (Fig. 1)

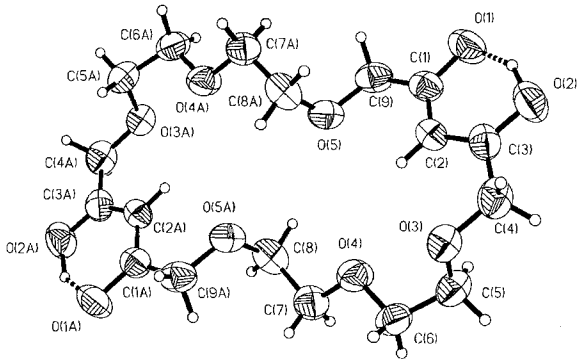


Fig. 1 Molecular structure of **1** with 50% probability displacement ellipsoids for the non-H atoms. H-atoms are represented by spheres of arbitrary size.

The asymmetric unit of **1** comprises half a formula unit, *i.e.* half of a macrocylic moiety, the molecule being located on a center of symmetry. It has two crystallographically equivalent intramolecular hydrogen bonds between O(1) and O(2) and the symmetry related O(1A) and O(2A) [O(1)···O(2) = 2.517(2) Å, O(2)–H = 1.20(3) Å, O(1) ···H = 1.41(3) Å, O(2)–H···O(1) = 150(3)°]. The relatively high vibration amplitude of H(1) [U = 0.15 Å^2] indicates a substantial hydrogen disorder. The molecule has an elliptical shape; it exhibits totally enolized β-dicarbonyl systems. There is no indication of transannular contacts; in particular, transannular hydrogen bonds can be ruled out, confirming previous results [7] which were inferred from ^{1}H NMR spectra. There are no intermolecular contacts closer than expected from the van der Waals radii.

Compound 7 (Fig. 2)

The macrocyclic polyether system does not show any unusual features, the two isoxazole rings being *syn*-oriented and almost perfectly planar (rms deviation of 0.005 Å of the ring atoms from the best plane). The individual molecules are separated by normal van der Waals contacts.

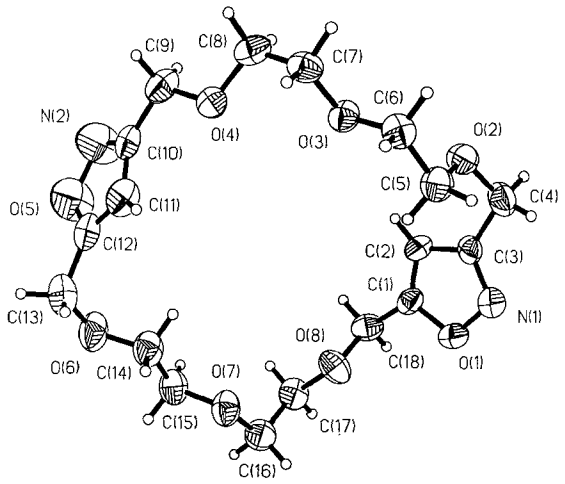


Fig. 2 Molecular structure of **7** with 50% probability displacement ellipsoids for the non-H atoms. H-atoms are represented by spheres of arbitrary size.

Compound 10 (Fig. 3)

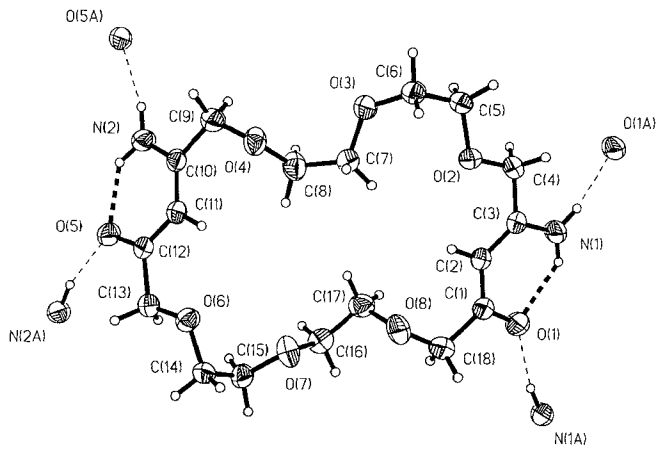


Fig. 3 Molecular structure of **10** with 50% probability displacement ellipsoids for the non-H atoms. H-atoms are represented by spheres of arbitrary size.

The macrocycle has an elliptical shape, the planar β-eneaminoketone systems forming an obtuse angle with each other. One of each of the two hydrogens at N(1) and N(2) is engaged in intramolecular hydrogen bonding N(1)···O(1) and N(2)···O(5) [N(1)···O(1) = 2.663(2) Å, N(1)–H = 0.86(2) Å, O(1)···H = 1.99(2) Å; N(2)···O(5) = 2.652(2) Å, N(2)–H = 0.93(2) Å, O(5)···H = 1.92(2) Å]. The remaining hydrogens at N(1) and N(2) are involved in intermolecular hydrogen bonds [N(1)···O'(1) = 2.848(2) Å, N(1)–H = 0.88(2) Å, O'(1)···H = 1.98(2) Å; N(2)···O'(5) = 2.850(2) Å, N(2)–

H = 0.90(2) Å, O'(5)···H = 1.97(2) Å]. The vibration parameters suggest that these hydrogens are all well ordered. Apart from the hydrogen bonding there are no intermolecular distances closer than normal van der Waals contacts.

Compound 25 (Fig. 4)

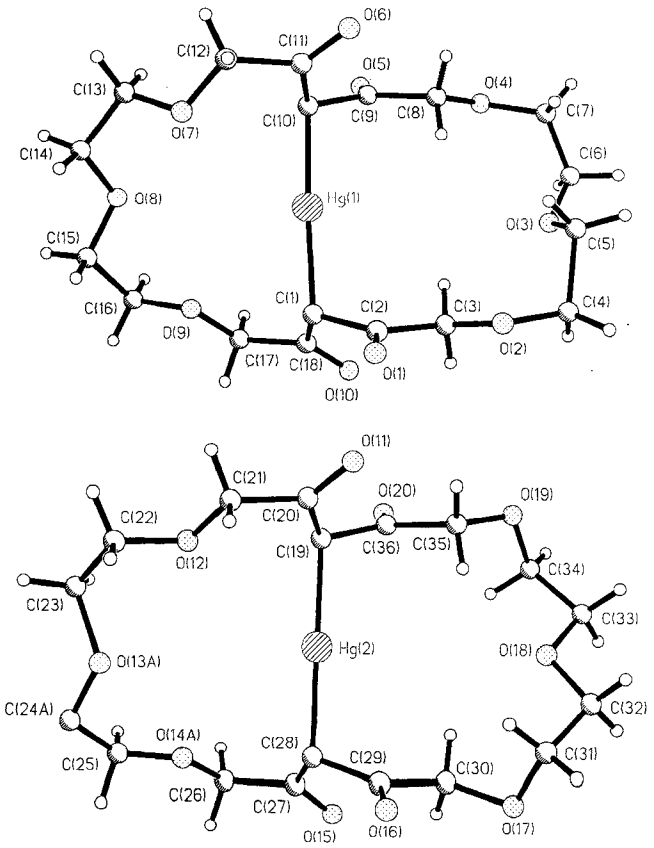


Fig. 4 Molecular structure of the two independent molecules of the Hg(II)-compound **25**. Atoms are represented by spheres of arbitrary size. Only one of the disordered C(24), O(13), and O(14) is shown.

The asymmetric unit of the Hg(II)-complex **25** comprises two crystallographically independent molecules of slightly different geometry. Atoms C(5) (molecule I) and C(24), O(13), O(14) (molecule II) were found to be disordered, probably due to decomposition in the X-ray beam.

Hg(II) is bonded to two carbon atoms with a nearly linear C–Hg–C [176.4(5)° and 177.7(5)°, respectively] and an average distance C–Hg of 215(1) pm [Hg(1)–C(1) = 216(1) pm, Hg(1)–C(10) = 214(1) pm, Hg(2)–C(28) = 215(1) pm, Hg(2)–C(19) = 216(1) pm]. In addition to the Hg–C bonds, each Hg makes a short contact to a carbonyl oxygen atoms in the plane perpendicular to the C–Hg–C axis [Hg(1)–O(1) = 279.4(9) pm, Hg(2)–O(5) = 283.7(9) pm]. Both Hg···O distances are slightly smaller than the sum of the van der Waals radii of metallic mercury and oxygen (140 + 151 = 291 pm) and similar to those found for bis-(dipivaloyl-methyl) mercury [6a] [Hg–C = 213(3) pm, 218(3) pm; Hg–O = 270(2) pm].

Internal fixation of Hg(II) into **1** causes a structural deformation of the ligand: the elliptic shape of **1** with nearly parallel polyether bridges is distorted to a structure with crossed polyether bridges and an inverted ratio of elliptic half-axes.

We gratefully acknowledge support of this work by the Deutsche Forschungsgemeinschaft and the Verband der chemischen Industrie. Special thanks to Prof. Dr. H. Volz for his aid after the death of Prof. Dr. H. Musso; to Mrs. I. Süß for IR spectra and elemental analysis; to Mrs. E. Fischer and P. Lang for NMR spectra; to Mr. D. Müller (Institute of Inorganic Chemistry Karlsruhe University), Mr. U. Tanger and Dr. U. I. Zachorsky for HRM spectra.

Experimental

Melting points: "Kofler Heiztischmikroskop", uncorrected; IR-spectra: Perkin Elmer Spectrophotometer 882; NMR-spectra: Bruker Cyrospec WM 250 and Bruker AM 400 (if not stated otherwise $CDCl_3$ as solvent; int. TMS standard for ^1H NMR ($\delta = 0$) and $CDCl_3$ ($\delta = 77.05$) for ^{13}C NMR, respectively); HRM-spectra: Finnigan 711 and Finnigan MAT 70; elemental analysis: Carlo Erba "Elemental Analizer" and "Analytische Laboratorien Prof. Dr. H. Malissa und G. Reuter, Gummersbach, Germany.

X-ray Structure Determination

Single-crystal X-ray diffraction data were collected at ambient temperature on a 4-circle diffractometer equipped with a graphite monochromator, using the $\omega/2\theta$-scan technique. Crystallographic data as well as details about data collection, data reduction, and refinement are summarized in Tab. 1.

In each case three reference reflections were measured every 200 reflections, which showed no significant intensity changes for samples **1**, **7**, and **10**. Crystals of the mercury(II)-complex **25**, however, steadily blackened throughout X-ray irradiation (unfortunately, data collection could not be performed below ambient temperature since the crystals cracked while being cooled). A significant intensity reduction of the standards was observed for **25**, which was corrected during subsequent data reduction (XTAL/SHELXTL: Sheldrick, 1983 [26a]; REDU4: Stoe & Cie, 1986a [26b]). Data reduction included a Lorentz-polarization correction and an empirical absorption correction for **25**, based on ψ-scans (EMPIR: Stoe & Cie, 1986b [26c]). Lattice parameters were obtained in each case by least-squares refinement against the angular diffractometer settings of 25 centered reflections in the range $0° \leq \theta \leq 20°$.

The structures were solved by direct methods and successive Fourier syntheses SHELXS86: Sheldrick, 1985 [27a]; Sheldrick, 1990 [27b]). Structure refinements (SHELXTL: Sheldrick, 1994 [27c]) were based on F^2 with weights $w = 1/[\sigma^2(F^2)$

+ $(p \cdot F^2)^2$], p = 0.035, 0.020, 0.020, 0.10 for **1**, **7**, **10**, and **25**, respectively (parameter p was chosen to minimize variation of mean $w\,\Delta^2$ as functions of both F_o^2 and $\sin\theta/\lambda$).

All atoms, except hydrogen, were refined anisotropically by full-matrix least-squares techniques. CH_2-hydrogens were constrained to ride on their parent carbon atom at a fixed distance C–H = 0.97 Å. The remaining H's were allowed to vary freely with isotropic Debye–Waller factors. For **25**, hydrogens at carbon atoms C(10) and C(28) could not be located in a difference Fourier synthesis; those at C(1) and C(19) could not be sensibly refined. These 4 hydrogens plus those at C(24) were therefore omitted from refinement of the mercury(II)-complex **25**.

For compound **7**, intensity statistics strongly suggest the absence of a center of symmetry; the Flack (1983) [28a] absolute structure parameter [0.15(97)] supports our choice of polarity. In addition, polar axis restraints were applied during refinement of **7**, using the method of Flack and Schwarzenbach (1988) [28b] to fix the origin along the *c*-glide plane.

Scattering factors for the neutral atoms were taken from the International Tables for Crystallography, Vol. C (Tables 4.2.6.8 and 6.1.1.4) [29a,b]. Anomalous dispersion corrections were taken from Cromer and Liberman [30].

Chromatography TLC

E. Merck, precoated (0.25 mm) silica gel plates "polygram Sil G/UV_{254}" and E. Merck precoated (0.25 mm) RP-silica gel plates "RP-18 F_{254}", corresponding R_f-values mentioned in the text by "R_f" and "R_f(RP-18)", if not mentioned otherwise compounds were visualized by I_2-vapour.

Flash column chromatography

different glass-columns were used, mentioned in the text "(height of sorbent (cm)× column diameter (cm))"; sorbent: silica gel, grain size 0.040– 0.063 mm and silanized silica gel, grain size 0.040–0.063 mm, mentioned in the text by "silica gel" and "RP-silica gel". *Solvents* used in the synthesis: dried and purified according to literature procedures [19], solvents used for chromatography: distilled and fractionated prior to use.

Reagents

NBu_4NO_2 (Tetrabutylammoniumnitrite) was prepared by literature procedure [20], except using CH_3CN instead of CH_2Cl_2 for recrystallization; (**b**) 1,8-dibromo-3,6-dioxaoctane (**24**) [21, 22] (*b.p.* (0.02 Torr) 89–90 °C, n_D^{20} = 1.5020) and 1,11-dibromo-3,6,9-tri-oxa-undecane (**21**) [22] (*b.p.* (0.015 mbar) 108–110 °C, n_D^{20} = 1.4964) were prepared according to the literature procedure in 40% yield; (c) the used cation-exchange resin named "Dowex XW 50" can be purchased from Fluka under the tradename "Dowex 50 WX 8". It was loaded by 2% HCl solution (suspension) and washed with water (distilled twice in quartz glass ware) until neutral.

4,7,10-Trioxatrideca-1,12-diine (**6**)

To a vigorously stirred solution of NaOH (400 g, 10 mol), NaCl (17 g, 0.3 mol) and NBu_4HSO_4 (17 g, 50 mmol) in H_2O (400 g) under Ar a mixture of 2,2'-dichlorodiethylether (**13**) (143 g, 1 mol) and propargylic alcohol (**12**) (336 g, 6 mol) in THF (250ml) is added, so that the temperature does not exceed 65 °C. After stirring for 48 h at 65 °C it is cooled by adding

Tab. 1 Crystallographic data of **1**, **7**, **10** and **25**. Summary of data collection, data reduction, and refinement.

	1	**7**	**10**	**25**
Molecular formula	$C_{18}H_{28}O_{10}$	$C_{18}H_{26}N_2O_8$	$C_{18}H_{30}N_2O_8$	$C_{18}H_{26}O_{10} \cdot Hg$
(Formula weight)	(404.40 g/mol)	(398.41 g/mol)	(402.44 g/mol)	(602.99 g/mol)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	C2/c, Z = 4	Cc, Z = 4	$P2_1/c$, Z = 4	$P2_1/c$, Z = 8
Cell parameters	a = 19.223(9) Å	a = 18.692(7) Å	a = 24.882(4) Å	a = 15.962(6) Å
	b = 8.291(4) Å	b = 13.075(4) Å	b = 10.138(2) Å	b = 13.849(6) Å
	c = 14.015(7) Å	c = 8.400(3) Å	c = 8.095(1) Å	c = 19.460(7) Å
	β = 116.82(4)°	β = 105.78(3)°	β = 93.42(1)°	β = 108.02(4)°
Unit cell volume	1994.4(17) Å^3	1975.6(13) Å^3	2038.4(6) Å^3	4090.8(28) Å^3
Density (calcd.)	1.347 Mg/m^3	1.340 Mg/m^3	1.311 Mg/m^3	1.952 Mg/m^3
μ(MoKα)	0.110 mm^{-1}	0.106 mm^{-1}	0.103 mm^{-1}	7.58 mm^{-1}
Crystal size (mm)	0.5 × 0.3 × 0.2	0.5 × 0.3 × 0.2	0.7 × 0.6 × 0.2	0.4 × 0.3 × 0.3
Diffractometer	Picker	Syntex R3	Syntex R3	Picker
Wavelength	0.71069 Å	0.71069 Å	0.71069 Å	0.71069 Å
θ_{max}	22.5°	25.0°	27.5°	25.0°
Reflections collected	3689	6782	12456	14428
Unique reflections	1308	3471	4684	7193
Observed ($I > 2\sigma$ (I))	1204	2339	3382	5642
R_{int} (I)	0.022	0.041	0.027	0.037
No. of parameters	141	273	289	634
No. of reflections	1308	3471	4684	7193
$R(F)$	0.031	0.042	0.043	0.071
$R_w(F^2)$	0.078	0.069	0.083	0.187
S (GOF)	1.054	0.984	1.133	1.183

ice, neutralized by 10N HCl and extracted with ether (6× 300ml). The etheral extract is washed with a saturated solution of $NaHCO_3$ (2 ×100 ml) and water (100 ml), dried (Na_2SO_4) and the solvent is distilled off to leave a tarry residue (204 g), which gives a colourless oil after fractional distillation, 80 g (43%, *b.p.* 102.5–103.5 °C/6 Torr, n_D^{20} = 1.4628). – IR (neat): ν/cm^{-1}= 3290 (C≡C-H), 2115 (C≡C), 1101. – ^{1}H NMR: δ/ppm= 2.45 (t, J = 2.42 Hz, 2H, C≡C<u>H</u>), 3.65–3.78 (m, 8H, OC<u>H</u>$_2$C<u>H</u>$_2$), 4.20 (d, J = 2.42 Hz, 2H, OC<u>H</u>$_2$C).

$C_{10}H_{14}O_3$ (182.21) calcd.: C 65.91 H 7.75
found: C 65.75 H 7.89.

6,9,12-Trioxa-4,2-epoxinitrilo-3-pentadecen-14-ine (**15**) *and 6,9,12-Trioxa-4,2,14,16-diepoxynitrilo-3,14-heptadecadiene* (**16**)

Ph–NCO (35 g, 300 mmol) is added dropwise over a period of 6 h to a stirred solution of diine (**6**) (18.2 g, 100 mmol), nitroethane (**26**) (18.8g, 250 mmol) and NEt_3 (2.5 g, 25 mmol) in toluene (500 ml) at 90 °C and subsequently stirred at this temperature for 24 h. After cooling, the mixture is filtered and the residual urea washed with toluene (100 ml × 4). The toluene is evaporated and gives a brown oil (30.6 g), which gives after silica gel Flash chromatography ((14 × 7.5), ether) monoisoxazole (**15**) (12.3 g, with 80% purity by ^{1}H NMR; R_f = 0.71) and diisooxazole (**16**) (10.6 g, with 60% purity by ^{1}H NMR; R_f = 0.32). Repeated Flash chromatography ((14×7.5), 35% EtOAc/toluene) of the major fraction gives (**15**) 7.5 g (31%, R_f 0.46) as slightly yellow oil. – IR (neat): ν/cm^{-1}= 3260 (C≡C-H, br), 3132 (C=C-H), 2114 (C≡C), 1613, 1103. – ^{1}H NMR: δ/ppm= 2.30 (s, 3H, C<u>H</u>$_3$C=N), 2.44 (t, J = 2.2 Hz, 1H, C≡C<u>H</u>), 3.64– 3.75 (br s, 8H, OC<u>H</u>$_2$C<u>H</u>$_2$), 4.20 (d, J = 2.2 Hz, 2H, OC<u>H</u>$_2$C≡C), 4.62 (s, 2H, OC<u>H</u>$_2$C=C), 6.12 (s, 1H, C=C<u>H</u>-C=N).

$C_{12}H_{17}NO_4$ calcd.: C 60.23 H 7.16 N 5.86
found: C 60.01 H 7.03 N 5.92
calcd.: 239.1157 found: 239.1162 (MS).

Repeated silica gel Flash chromatography ((14×7.5), 50% EtOAc/toluene) of the minor fraction gives (**16**) 5.6 g(18%, R_f = 0.33) as colourless oil. – IR (neat): ν/cm^{-1}= 3134 (C=C-H), 1613 (C=C), 1137, 1099. – ^{1}H NMR: δ/ppm= 2.29 (s, 6H, C<u>H</u>$_3$C=N), 3.62–3.74 (m, 8H, OC<u>H</u>$_2$C<u>H</u>$_2$), 4.62 (s, 4H, OC<u>H</u>$_2$CO), 6.10 (s, 1H, C=C<u>H</u>C=N).

$C_{14}H_{20}N_2O_5$ calcd.: C 56.74 H 6.80 N 9.46
found: C 56.65 H 6.86 N 9.36
calcd.: 296.1372 found: 296.1384 (MS).

2,16-Diamino-4,14-dioxo-6,9,12-trioxa-heptadeca-2,15-diene (**17**)

To Raney-Ni [23] (2 ml, 50% suspension in H_2O), washed with (4 × 20 ml) and suspended in (30 ml) CH_3OH under N_2, is added diisoxazole (**16**) (2 g, 6.75 mmol) in CH_3OH (5 ml). The system is flushed with H_2 and stirred mechanically under H_2 (20 °C). After 4 h the system is flushed with N_2, the suspension filtered through celite and the Raney-Ni residue washed with CH_3OH (3 × 10 ml). Solvent evaporation from the combined filtrate leaves impure (**17**) (2.01 g). Further purification by RP-silica gel Flash chromatography ((14 × 5), 30% CH_3OH/toluene) gives pure (**17**) (1.5 g, 79%; R_f (RP-18) = 0.55). – IR (neat): ν/cm^{-1}= 3352 (NH, vbr), 3200 (sh), 1625, 1536 (br), 1412 (br), 1292 (br), 1111 (br). – ^{1}H NMR: δ/ppm= 1.97 (s, 6H, C<u>H</u>$_3$C=C), 3.60–3.78 (m, 8H, OC<u>H</u>$_2$C<u>H</u>$_2$), 3.99 (s, 4H, OC<u>H</u>$_2$C=O), 5.25 (brs, 2H, N<u>H</u>), 5.36 (s, 2H, CC<u>H</u>=C), 9.84 (brs, 2H, N<u>H</u>···O).

$C_{14}H_{24}N_2O_5$ calcd.: C 55.98 H 8.05 N 9.33
found: C 55.75 H 7.93 N 9.16
calcd.: 300.1685 found: 300.1682 (MS).

6,9,12-Trioxa-2,4,14,16-tetraoxoheptadecane (**18**)

Bis-β-eneaminoketone (**17**) (90 mg, 0.22 mmol) in H_2O (1 ml) is added to a suspension of Dowex WX-50 ionexchange resin in H_2O (4 ml) and stirred (4 h, room temperature). The suspension is filtered and the resin is washed with H_2O (5 × 2 ml). Removal of the solvent from the combined filtrate (20 °C, 1 Torr) and *in vacuo* drying of the residue (20 °C, $5 \cdot 10^{-3}$ Torr) gives a yellow viscous oil (65 mg), which is further purified by RP-silica gel Flash chromatography ((11.5×2); 5% CH_3OH/toluene) and gives (**18**) (38 mg, 57%; indication by Fe(III)Cl_3 in CH_3OH) as a slightly yellow oil. – IR (neat): ν/cm^{-1}= 1730+1709 (C=O), 1612 (br), 1114. – ^{1}H NMR (0 °C; degree of enolization 85%): δ/ppm= 2.08 (s, 6H, C<u>H</u>$_3$CO, [enole]), 2.26 (s, 6H, C<u>H</u>$_3$C=O, [diketone]), 3.57–3.77 (m, 8H, OC<u>H</u>$_2$C<u>H</u>$_2$), 3.63 (s, 4H, O=CC<u>H</u>$_2$C=O, [diketone]), 4.07 (s, 4H, OC<u>H</u>$_2$CO, [enole]) 4.13 (s, OC<u>H</u>$_2$ C=O, [diketone]), 5.81 (s, 2H, C=C<u>H</u>C), 15.15 (s, 1H, O<u>H</u>).

$C_{14}H_{22}O_7$ calcd.: C 55.62 H 8.34
found: C 55.58 H 7.33
calcd.: 302.1366 found: 302.1359 (MS).

1-Nitro-11-bromo-3,6,9-trioxaundecane (**22**)

Dibromide (**21**) (42 g, 131 mmol) is added by syringe over a period of 2 min. to a stirred solution of NBu_4NO_2 (20 g, 69 mmol) in DMF (20 ml) at 0 °C and stirred for another 70 min. at this temperature. 15 min. after the addition of the reagent NBu_4Br begins to precipitate and the formerly colourless solution turns orange. The reaction mixture is poured into stirred ether (400 ml), stirred for 20 min., filtered, and the residual salt is extracted with ether (2 × 50 ml). The combined filtrate is washed with H_2O (4 × 25 ml), dried ($MgSO_4$, 5 min.) and gives a slightly yellow oil (37.6 g) after solvent evaporation, which is divided into two portions of equal mass. Each portion is separated by silica gel Flash chromatography ((14×7.5); 40% THF/hexane). This procedure gives the dibromide (**21**) (25.4 g, 79 mmol; R_f = 0.53) and compound (**22**) (9.3 g, 45%; R_f = 0.22). (**21**) and (**22**) can further be purified by bulb to bulb Kugelrohr-distillation but are sufficiently pure to be used for further synthesis: (**22**) *b.p.* 135 °C/$5 \cdot 10^{-3}$ Torr, n_D^{20} = 1.4793. – IR (neat): ν/cm^{-1}= 1560 + 1552 (NO_2), 1117. – ^{1}H NMR: δ/ppm= 3.48 (t, J = 6.2 Hz, 2H, C<u>H</u>$_2$Br), 3.58 – 3.74 (m, 8H, OC<u>H</u>$_2$C<u>H</u>$_2$), 3.81 (t, J = 6.2 Hz, 2H, OC<u>H</u>$_2$ CH_2Br), 4.06 (t, J = 5.1 Hz, 2H, OC<u>H</u>$_2$$CH_2$ NO_2), 4.55 (t, J = 5.1 Hz, 2H, C<u>H</u>$_2$$NO_2$).

$C_8H_{16}BrNO_5$ (286.12) calcd.: C 33.58 H 5.64 Br 27.93 N 4.90
found: C 33.51 H 5.57 Br 27.77 N 4.81
$C_8H_{17}{}^{79}BrNO_5$ calcd.: 286.0290 found: 286.0277 (MS+1)
$C_8H_{17}{}^{81}BrNO_5$ calcd.: 288.0270 found: 288.0283 (MS+1).

1,11-Dinitro-3,6,9-trioxaundecane (**19**)

NBu_4NO_2 (14.1 g, 49 mmol) is added to the mixture of

compound **22** (19.7 g, 69 mmol) in CH_3NO_2 (5 ml, 0 °C) and stirred for 1 h. Then the suspension is added dropwise into stirred ether (800 ml), stirred for 30 min., filtered and the precipitate extracted with ether (2×200 ml). The combined filtrate is washed with H_2O (4×20 ml) and dried ($MgSO_4$, 5 min.). The solvent and most of the volatile components are evaporated (finally: 100 °C, 0.1 Torr, 1 h) to leave a yellow oil (17.5 g), which is immediately separated by silica gel Flash chromatography ((14×7.5) 50% THF/hexane). This procedure delivers starting material (**22**) (10.3 g, 36 mmol; R_f=0.46) pure enough for further synthesis) and several further fractions containing (**19**) (total: 4.6 g; R_f=0.30). These are further purified by repeated silica gel Flash chromatography ((14×3), 5% EtOH/toluene) and give a colourless oil (1.95 g, 14%; R_f = 0.28), n_D^{20} = 1.4625. – When each column is eluated (60% THF/hexane; 1.3 l) and the solvent removed from the combined eluates, a red oil (1.5 g) is obtained containing ca. 30% dinitro compound **19**. This oil could be purified by the procedure described for the synthesis of **19**. – IR (neat): ν/cm^{-1}= 1564+ 1560 (NO_2), 1129 (br). – ^{1}H NMR: δ/ppm= 3.56–3.70 (m, 8H, OCH_2CH_2), 4.04 (t, J=5.1 Hz, 4H, $OCH_2CH_2NO_2$), 4.55 (t, J = 5.1 Hz, 4H, CH_2NO_2).

$C_8H_{16}N_2O_7$	calcd.:	C 38.09	H 6.39	N 11.11
(252.10)	found:	C 38.03	H 6.22	N 10.87

$C_8H_{15}N_2O_7$ calcd.: 251.0879 found: 251.0879 (MS-1)
$C_8H_{17}N_2O_7$ calcd.: 253.1036 found: 253.1032 (MS+1).

1-Bromo-3,6,9-trioxadodec-11-ine (**23**) *and 4,7,10,13-Tetraoxa-hexadeca-1,15-diine* (**27**)

Dibromide (**24**) (303 g, 1.1 mol) and propargylic alcohol (**12**) (61 g, 1.1 mol, freshly distilled) are added dropwise to the stirred suspension of NaH (33 g, 80% suspension in mineral oil, 1.1 mol, washed under Ar with pentane (5×50 ml) and dried *in vacuo*) in THF (500 ml) so that the temperature does not exceed 40 °C. The mixture is stirred at 40 °C for 18 h, then cooled (room temperature) and filtered through celite. The solvent is evaporated and gives an orange coloured oil (214 g), which is separated by silica gel Flash chromatography ((14×7.5), 5% ether/CH_2Cl_2, 20 g portions) and gives diine (**27**) (35 g, R_f=0.72), dibromide (**24**) (25 g, 90 mmol, R_f=0.58, sufficiently pure for further synthesis) and bromide (**23**) (34 g, R_f =0.36). Further purification of diine (**27**) can be done by silica gel Flash chromatography ((14×7.5), 50% THF/hexane, R_f= 0.56; 23g, 9.2%), n_D^{20} = 1.4660. – IR (neat): ν/cm^{-1}= 3290+ 3258 (C≡C-H), 2113(C≡C), 1745, 1101 (br). – ^{1}H NMR: δ/ppm= 2.44 (t, J = 2.4 Hz, 2H, C≡CH), 3.58–3.78 (m, 12H, OCH_2CH_2), 4.20 (t, J = 2.4 Hz, 4H, OCH_2C).

$C_{12}H_{18}O_4$	calcd.:	C 63.74	H 8.02	
(226.12)	found:	C 63.26	H 8.25	

$C_{12}H_{19}O_4$ calcd.: 227.1283 found: 227.1287 (MS+1).

Silica gel Flash chromatography of bromide (**23**) ((14×7.5), 10% ether/CH_2Cl_2) gives (**23**) as a colourless oil (31 g, 12%, R_f = 0.50), n_D^{20} = 1.4802. – IR (neat): ν/cm^{-1}= 3293+ 3250 (C≡C-H), 2115 (C≡C), 1101 (br), 664. – ^{1}H NMR: δ/ppm= 2.42 (t, J = 2.4 Hz, 1H, C≡CH), 3.46 (t, J = 6.3 Hz, 2H, CH_2Br), 3.60–3.73 (m, 8H, OCH_2CH_2O), 3.79 (t, J = 6.3 Hz, 2H, CH_2CH_2Br), 4.20 (d, J = 2.4 Hz, 2H, OCH_2C).

$C_9H_{15}BrO_3$	calcd.:	C 43.05	H 6.02	Br 31.82
(251.02)	found:	C 42.73	H 5.95	Br 32.20

$C_9H_{16}{}^{79}BrO_3$ calcd.: 251.0288 found: 251.0264 (MS+1)
$C_9H_{16}{}^{81}BrO_3$ calcd.: 253.0262 found: 253.0252 (MS+1).

1-Nitro-3,6,9-trioxadodec-11-ine (**20**)

NBu_4NO_2 (5.75 g, 20 mmol) is added to a solution of bromide (**23**) (5 g, 20 mmol) in CH_3NO_2 (5 ml) and stirred (0 °C, 85 min.). The reaction mixture is then added dropwise into stirred ether (300 ml) and stirred (room temperature, 20 min.). The precipitate is filtered and extracted with ether (2×100 ml). The combined filtrate is washed with H_2O (5×8 ml), dried ($MgSO_4$, 5 min.) and gives after solvent evaporation a tarry oil (3.9 g). Immediate silica gel Flash chromatography ((14×7.5), 15% ether/CH_2Cl_2) gives (**23**) (2.0 g, 8 mmol, R_f=0.70) and (**20**) (1.5 g, R_f=0.52). Compound **20** has further to be purified. Repeated silica gel Flash chromatography ((14×4), 10% CH_3OH/toluene) gives (**20**) as a colourless oil (1.1 g, 25%, R_f=0.60), n_D^{20} = 1.4632. – IR (neat): ν/cm^{-1}= 3296 (C≡C-H), 2114(C≡C), 1554 (NO_2), 1102 (br). – ^{1}H NMR: δ/ppm= 2.44 (t, J = 2.4 Hz, 2H, C≡CH), 3.58–3.74 (m, 8H, OCH_2CH_2), 4.06 (t, J = 5.1 Hz, 2H, $OCH_2CH_2NO_2$), 4.20 (d, J = 2.4 Hz, 2H, OCH_2C), 4.55 (t, J = 5.1 Hz, 2H, CH_2NO_2).

$C_9H_{15}NO_5$	calcd.:	C 49.76	H 6.96	N 6.45
(217.21)	found:	C 49.94	H 7.00	N 6.34.

6,9,12,19,22,25-Hexaoxa-1,4,17,14-diepoxynitrilo-tricyclo[22.2.1.1.^{14,17}]-1(27),17(28)-octacosadiene (**7**)

PhNCO (0.5 ml, 4.6 mmol) is added to a stirred solution of the dinitro compound (**19**) (2.52 g, 10 mmol), diine (**6**) (1.82 g, 10 mmol) and NEt_3 (1.4 ml, 10 mmol) in toluene (10 ml) and stirred (30 °C, 30 min.). In the course of the reaction a fluffy precipitate appears and the solution turns yellow. The stirred mixture is further diluted with toluene (200 ml), warmed (90 °C) and another portion of PhNCO (6.8 ml, 62.6 mmol) is added dropwise (5.75 h); afterwards it is stirred for 24 h at 90 °C. Then the precipitated urea is filtered and extracted with toluene (2×50 ml). The filtrate gives, after evaporation of all volatile compounds, a red–brown, tarry oil (5.3 g), which crystallizes at room temperature. The oil is fractionated twice by silica gel Flash chromatography ((14×7.5), 20% $CHCl_3$/THF) and gives an orange coloured oil (0.83 g, R_f =0.31), which crystallizes at room temperature. Recrystallization (50% EtOAc/EtOH, 4×1 ml/100 mg) gives pure (**7**) (590 mg, 14%): *m.p.* 77–78 °C. – IR (KBr): ν/cm^{-1}= 3213, 3170, 2749, 1609, 1095, 882. – ^{1}H NMR: δ/ppm= 3.60–3.76 (m, 16H, OCH_2CH_2), 4.64 (s, 4H, OCH_2C), 4.66 (s, 4H, OCH_2C=N), 6.41 (s, 2H, C=CH=N).

$C_{18}H_{26}N_2O_8$	calcd.:	C 54.26	H 6.58	N 7.03
	found:	C 54.43	H 6.83	N 7.01
	calcd.:	398.1689	found:	398.1687 (MS).

3,17-Dioxo-5,15-diamino-1,7,10,13,19,22-hexaoxa-4,15-cyclotetracosadiene (**10**)

To Raney Ni [23] (1.46 ml, 50 % suspension in H_2O), washed with (4×8 ml; under Ar) and suspended in CH_3OH (5 ml) is added a solution of (**7**) (1 g, 2.5 mmol) in CH_3OH (20 ml). The system is flushed with H_2 and stirred mechanically under H_2 (4 h, room temperature) and then flushed with Ar again. The suspension is filtered through RP-silica gel (5×2) and

the remaining filtercake is extracted with CH_3OH (5 × 5 ml). The solvent is removed from the combined filtrate and gives a colourless crystalline product (800 mg), which is recrystallized (10% CH_3OH/EtOAC, 2 ml/100 mg, 3×) to give pure (**7**) (55 mg, 54%): *m.p.* 116–118 °C. – IR (KBr): ν/cm^{-1} = 3400 (sh), 3281 (br, NH), 3123 (br), 1630, 1606, 1560, 1528, 1119, 1064. – ^1H NMR: δ/ppm = 3.58–3.73 (m, 16H, OCH_2CH_2), 4.02 (s, 4H, OCH_2CO), 4.22 (s, 4 H, OCH_2NH_2), 5.38 (s, 2H, C=CHC=O), 6.09 (s, 2H, NH), 9.78 (s, 2H, NH...O).

$C_{18}H_{30}N_2O_8$	calcd.:	C 53.72	H 7.51 N 6.96
	found:	C 53.84	H 7.68 N 6.94
	calcd.: 402.2002		found: 402.2007 (MS).

3,5,15,17-Tetraoxo-1,7,10,13,19,22-hexaoxacyclotetracosane (**1**)

Dowex XW-50 ion-exchange resin (2.06 g) is suspended in a solution of (**10**) (250 mg, 0.62 mmol) in H_2O (10.3 ml) and stirred (4 h, room temperature). Then the suspension is filtered through a glass filter funnel and the resin extracted with H_2O (5 × 4 ml). The solvent of the combined filtrate is evaporated (20 °C, 1 Torr), the residue is dried (20 °C, $5 \cdot 10^{-3}$ Torr) and gives a slightly yellow oil, which readily crystallizes. This product is dissolved in a warm mixture of 40% ether/hexane (40 ml) and filtered while being hot. Solvent evaporation, and recrystallization (CH_3OH) gives colourless pyramidal crystals (162 mg, 65%): *m.p.* 76–81 °C. – IR (KBr): ν/cm^{-1} = 3112(C=C-H), 1746+1730 (w), 1615 (br, C=O), 1096, 870. – ^1H NMR: δ/ppm = 3.57–3.81 (m, 16H, OCH_2CH_2), 3.64 (s, 4H, O=CCH_2C=O), 4.10 (s, 8H, OCH_2C=CH, [enole]), 4.18 (s, 4H, OCH_2C=O, [diketone]), 6.27 6.32 (s, 2H, C=CHC), 15.0 (brs, 2H, OH). – ^{13}C NMR (0 °C): δ/ppm = 50.24 (O=CCH_2C=O), 70.26 70.40 70.48 70.78 70.84 71.02 (OCH_2CH_2O), 71.87 71.90 (OCH_2C=C), 76.04 (OCH_2C=O), 94.13 94.17 (O=CCH=C), 191.92 (O–C=CH), 203.37 (O=CCH_2C=O).

$C_{18}H_{28}O_{10}$	calcd.:	C 53.46	H 6.98
	found:	C 53.42	H 6.91
	calcd.:	404.1682	found: 404.1686 (MS).

2,12,14,24-Tetraoxo-4,7,10,16,19,22-hexaoxa-25-mercurato-bicyclo[11.11.1.]pentacosane (**25**)

A solution of Hg(II)-acetate (20.5 mg, 64 µmol) in CH_3OH (0.5 ml) is added to a solution of (**1**) (26 mg, 64 µmol) in CH_3OH (0.8 ml) and left in the dark (15 h). The precipitate is filtered, washed (hexane, 2 × 5 ml), dried (20 °C, $5 \cdot 10^{-3}$ Torr) and recrystallized (THF, in the cold) to give clear, colourless, twisted brick-like crystals (12 mg, 32%): *m.p.* 110–112 °C (crystals become turbid): *m.p.* 157–170 °C. Crystals useful for X-ray structure determination have to be recrystallized from toluene/ethylacetate. – IR (KBr): ν/cm^{-1} = 1671 (br), 1630 (sh), 1122. – ^1H NMR: δ/ppm = 3.45–3.80 (m, 16H, OCH_2CH_2), 3.93 (d, J = 15.1 Hz, 4H, OCH_2C=O), 4.14 (s, 2H, O=CCHC=O), 4.22 (d, J = 15.1 Hz, 4H, OCH_2C=O). – ^{13}C NMR: δ/ppm = 69.19 (O=CCHC=O and $CH_2CH_2OCH_2CH_2$), 71.15 ($OCH_2CH_2OCH_2CH_2O$), 75.22 (OCH_2C=O), 205.46 (C=O).

$C_{18}H_{26}HgO_{10}$	calcd.:	C 35.85	H 4.35 Hg 33.27
(602.99)	found:	C 35.98	H 4.47 Hg 33.10
	calcd.:	404.1682	found: 404.1686 (MS-Hg).

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