Bull Soc Chim Fr (1996) 133, 183-197

Radiochemical stability of the dicyclohexano-18-crown-6 ether (DCH18C6): synthesis and tests in radioactive medium of the DCH18C6 radiolytic products

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(Received 24 October 1995; accepted 12 January 1996)

Summary — The *cis-syn-cis* isomer of the dicyclohexano-18-crown-6 ether (DCH18C6) was subjected to hydrolysis and radiolysis with a ^{137}Cs gamma source, at different doses of irradiation. The *cis-syn-cis* DCH18C6 radiolytic products previously identified [1], were synthesized in their different configurations. These radiolytic products, all of *cis* configuration, were tested on aqueous synthetic solutions of spent nuclear fuels. Experiments in radioactive medium showed that, under continuous extraction conditions, the *cis-syn-cis* DCH18C6 radiolytic products cannot perturb a reprocessing process using the DCH18C6 as selective extractant. Good prospects for the application of DCH18C6 to spent nuclear fuel reprocessing were therefore demonstrated. An X-ray crystallographic study of the DCH18C6 *cis-syn-cis*-isomer with uranyl nitrate was investigated.

spent nuclear fuel reprocessing / DCH18C6 radiochemical stability / radiolytic product synthesis / crown ether

Résumé — Stabilité radiochimique du dicyclohexano-18-couronne-6 éther (DCH18C6): synthèse et tests en milieu radioactif des produits de radiolyse du DCH18C6. *L'isomère* cis-syn-cis *du dicyclohexano-18-couronne-6 éther (DCH18C6) a été hydrolysé et radiolysé avec les rayonnements gamma d'une source de ^{137}Cs, à différentes doses d'irradiation. Les produits de radiolyse du DCH18C6* cis-syn-cis, *identifiés auparavant [1], ont été synthétisés dans leurs différentes configurations relatives. Ces produits de radiolyse, tous de configuration* cis, *ont été testés dans des solutions aqueuses synthétiques de retraitement de combustibles nucléaires usés. Les essais en milieu radioactif ont montré que, dans les conditions d'un système d'extraction en continu, les produits de radiolyse du DCH18C6* cis-syn-cis *ne peuvent pas perturber un procédé de retraitement utilisant le DCH18C6 comme extractant sélectif. Ainsi, de bonnes perspectives pour l'application du DCH18C6 au retraitement des combustibles nucléaires usés a été démontré. Un cristal du DCH18C6* cis-syn-cis *avec le nitrate d'uranyle a été examiné en cristallographie de rayons X.*

retraitement des combustibles nucléaires usés / stabilité radiochimique du DCH18C6 / synthèse de produit de radiolyse / éther couronne

Introduction

In some industrialized countries, nuclear energy contribution has reached impressive levels. Uranium figures at the heart of nuclear production of electricity. Before and after its transit through the reactor, uranium undergoes many operations and chemical transformations which constitute the 'fuel cycle'. One step of the 'fuel cycle' is the reprocessing. The reprocessing consists of recovering, in the spent fuels, the reusable energetic materials (uranium and plutonium) and conditioning, to the best conditions of safety for man and the environment, the ultimate wastes with a view to their disposal. At their arrival at the reprocessing plant, the spent fuels are stored for two to three years in a pool, awaiting the natural decrease of their activity. Once taken out of the pool, the fuel assemblages are sheared and the nuclear material is dissolved in nitric acid. Extraction with organic solvent permits the chemical separation of uranium, plutonium and fission products. Uranium is concentrated in nitrate form whereas plutonium is conditioned under its oxide form, and these are then reused

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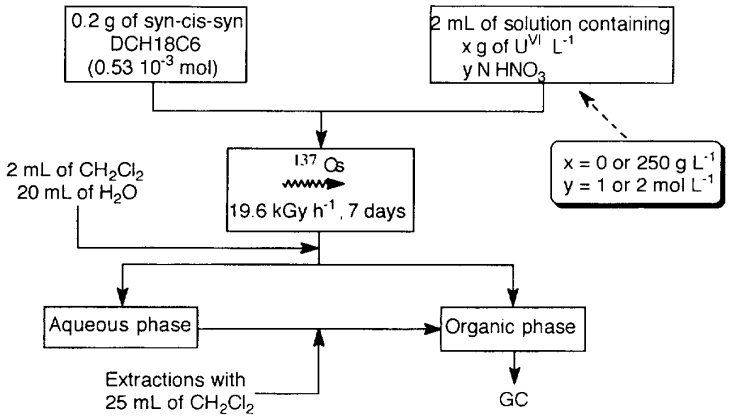

Fig 1. Radiolysis of *cis-syn-cis* DCH18C6 in nitric acid/uranium (VI) medium.

and contained in new fuels. The wastes that constitute the fission products undergo specific treatments with a view to their storage.

Extraction with organic solvents takes a dominant place in the reprocessing process. At present, the main facilities use the PUREX process (plutonium uranium refining by extraction) [2], based on liquid–liquid extraction of plutonium and uranium from the fission products by the tri-*n*-butylphosphate (TBP). The PUREX process, which is currently the most effective, presents several disadvantages however, essentially due to the degradation of TBP by radiolysis and hydrolysis. Plutonium and some fission products form complexes with the degradation products. In particular, mono- and dibutylphosphates interfere in the process and reduce its performance by forming interfacial precipitates (crud) [3]. Therefore, additional refining cycles are used for uranium and plutonium, and the solvent is subjected to many washings which generate effluents containing soluble organic products and radioelements which are difficult to eliminate. The radiolysis of the extraction system has also important negative consequences for technology.

Research of new more effective extractants has given rise to many works that show the importance of crown ethers in hydrometallurgy [4–10] and, in particular, of dicyclohexano-18-crown-6 (DCH18C6 **1**) for the reprocessing of spent nuclear fuels [11–13]. If we consider its good loading capacity and its excellent selectivity, interest in using DCH18C6 in spent nuclear fuel reprocessing arises also from its high stability in highly active solutions. Indeed, the recovery of radionucleides from low or high level radioactive wastes by solvent extraction cannot be achieved unless the extractant possesses a satisfactory radiation stability. During spent nuclear fuels reprocessing, the extractant can absorb a dose of the order of 630 kGy in one cycle of reprocessing [14]. Several papers have been published on the radiation chemistry of crown ethers [15, 16] and the considerable resistance of DCH18C6 to radiation has been shown [1, 17, 18].

The present work is aimed at studying the effect of gamma radiation on the structure and the physicochemical properties of DCH18C6. The *cis-syn-cis* DCH18C6 radiolytic products, identified in a previous study to evaluate their radiochemical yields [1], were synthesized in their different stereochemical configurations to assign their stereochemistry and to evaluate their possible interference with the reprocessing process. Influence of nitric acid and uranium concentrations on DCH18C6 radiolysis was examined, and an X-ray crystallographic study of the DCH18C6-uranyl nitrate compound was investigated. Finally, the behavior of the DCH18C6 radiolytic products in radioactive solutions was studied.

Results

Hydrolysis of cis-syn-cis *DCH18C6*

It has been shown that the chemical degradation behavior of some organic compounds is similar in both hydrolysis and radiolysis [3]. Study of the hydrolysis of DCH18C6 has therefore led to the identification of its degradation products while avoiding the undertaking of experiments in radioactive media.

Radiolysis of cis-syn-cis *DCH18C6*

Radiolysis of *cis-syn-cis* DCH18C6 was performed according to the procedure in figure 1.

Under these conditions of irradiation, a dose of 3293 kGy was absorbed by all the samples. Thus, the total absorbed dose in the study was in excess of that expected for one cycle of reprocessing [14].

Comparison of the structures of cis-syn-cis *DCH18C6 radiolysis and hydrolysis products*

The DCH18C6 radiolytic products have been identified in a previous study [1] (fig 2).

We have noted that no product exhibits a macrocyclic structure, and the dramatically lower complexing and extracting properties of open chain polyether compared to macrocyclic 'analogs' has been reported [19].

The hydrolysis and radiolysis DCH18C6 products were compared using gas chromatography. The degradation products showed the same retention times

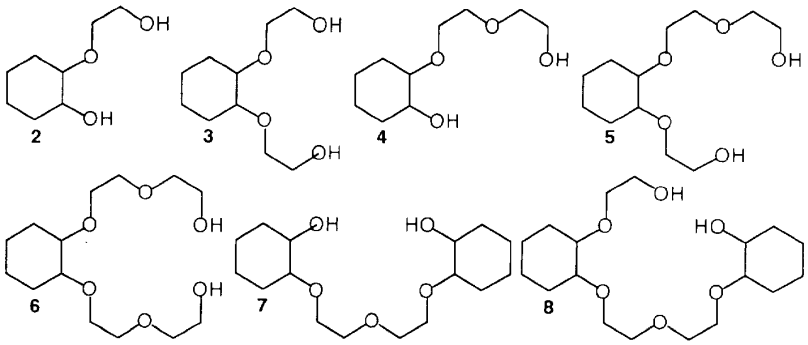

Fig 2. Structure of the DCH18C6 radiolytic products.

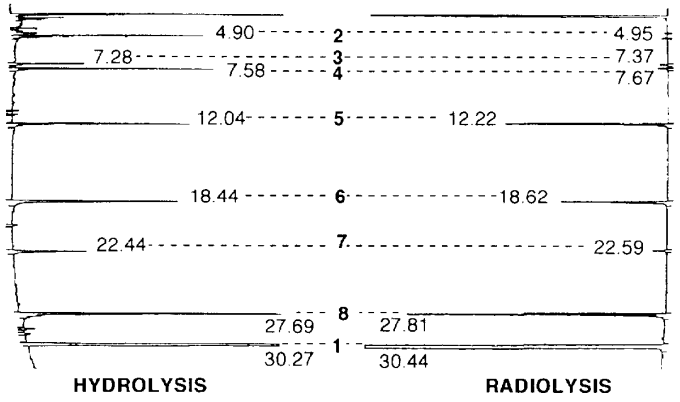

Fig 3. Comparison of radiolysis and hydrolysis chromatograms.

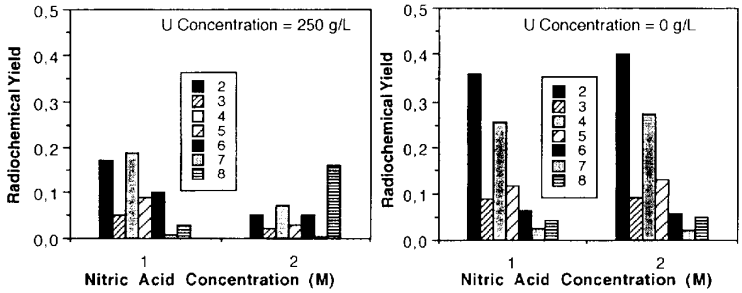

Fig 4. Acidity dependence of the DCH18C6 radiolysis in the presence and absence of uranium.

(fig 3); the DCH18C6 radiolysis products are qualitatively identical with the DCH18C6 hydrolysis products. Quantitatively, products of low mass are more abundant in the case of hydrolysis, whereas products of high mass are more abundant in the case of radiolysis. Indeed, protonation of the macrocycle sites starts a chain degradation reaction to give low mass products, but radiolysis, the most immediate phenomenum, essentially favors the high mass compounds.

Influence of acidity on the hydrolysis of cis-syn-cis *DCH18C6, in the presence and absence of uranium*

In the absence of uranium, an increase in acidity leads to an increase in DCH18C6 radiolysis. The presence of uranium in the DCH18C6 solution decreases, or slows down, radiolysis of DCH18C6, but this phenomenum is not independent of nitric acid concentration. Figure 4 shows the correlated action of nitric acid and uranium concentrations.

In the case of a high concentration of uranium, an increase in acidity from 1 to 2 M stabilizes the DCH18C6-uranyl nitrate compound and decreases the action of the γ radiation; compound **8**, the least fragmented product, was given in the highest yield. On the other hand, in the absence of uranium, an increase of the acidity from 1 to 2 M has no influence on the macrocycle degradation. The radiochemical yields were higher than in the presence of uranium but the degradation was only

governed by irradiation.The highest radiochemical yield was obtained for the most fragmented compound **2**.

A structural analysis of the cis-syn-cis *DCH18C6-uranyl nitrate compound*

cis-syn-cis DCH18C6 is more stable to radiolysis in the presence of uranium. Indeed, the presence of uranium disadvantaged macrocycle hydrolysis and radiolysis. This phenomenum was ascribable to the template effect of uranium that favors fragment recombination. Evidence for the structure of the DCH18C6-uranyl nitrate compound was obtained from a single X-ray analysis. An ORTEP view of the *cis-syn-cis* DCH18C6-uranyl nitrate is shown in figure 5.

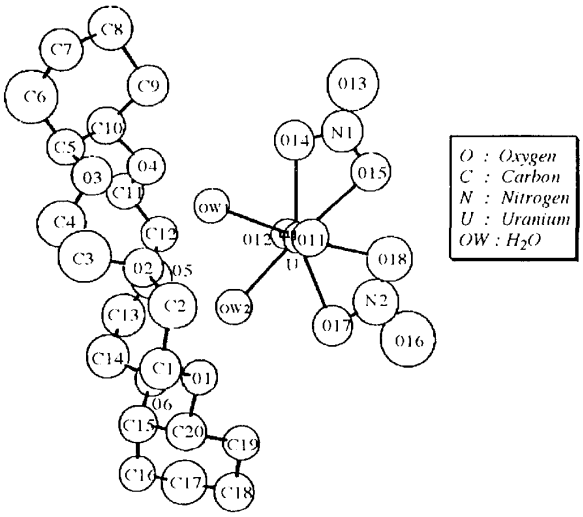

Fig 5. ORTEP drawing of the *cis-syn-cis* DCH18C6-uranyl nitrate compound.

Uranyl nitrate is bonded to the macrocycle via two water molecules. The uniqueness of the structure does not result from the presence of water molecules between the uranium atom and the macrocycle [20–22] but from their side-by-side arrangement, and in the non-linear position of the nitrate molecules in relation to uranium oxide. The ORTEP drawing of the asymmetric unit clearly shows that there is no bond between the uranium and the DCH18C6. Interaction between the macrocycle and the uranium complex is probably realized via hydrogen bonds between the two water molecules and the oxygen atoms of the macrocycle. Thus, all the oxygen atoms of the macrocycle are affected by the hydrogen bonds within a single unit $[(UO_2)(NO_3)_2(H_2O)_2]$. The six contacts assigned as being hydrogen bonds are summarized in table I.

Synthesis of DCH18C6 radiolysis products

In order to test their influence on spent nuclear fuel reprocessing, the DCH18C6 radiolytic products were synthesized.

Table I. Hydrogen bonding distances (Å).

OW1...04^{i}	2.68	OW2...01^{i}	2.60
OW1...02^{i}	2.75	OW2...05^{i}	2.78
OW1...03^{i}	3.02	OW2...06^{i}	2.87

Symmetry code: (i) $1-x$, $1/2+y$, $1/(-z)$.

• *Stereochemistry of the compounds synthesized*

Upon reduction, dibenzo-18-crown-6 ether (DB18C6) can yield up to five stereoisomers of DCH18C6. The ionoselective properties of these stereoisomers depend on their stereochemical configuration. For example, it has been shown that the selectivity of the isolation of plutonium is much higher when using the *cis-syn-cis*-isomer of the macrocycle [5]. We therefore had to determine the stereochemical configurations of the DCH18C6 radiolytic products in order to establish their complexing properties. However it is difficult, if not possible, to identify the stereochemical configurations with the usual techniques of analysis. Hydrolysis and radiolysis are expected to lead to degradation products with retention of configuration. So, in order to confirm this, we undertook synthesis of the DCH18C6 radiolytic products in their different stereochemical configurations (fig 6), without separation of the possible enantiomers.

Synthesis of 1,2-bis(2-hydroxyethoxy)cyclohexane **3**

Dialkylation of catechol with 2-chloroethanol in aqueous sodium hydroxide afforded the 1,2-bis(2-hydroxyethoxy)benzene **9** in 99% yield. The hydrogenation of aromatic compounds is well documented in the literature and heterogeneous catalysis has been the most thoroughly studied method. The reduction of **9** was first run according to the method described by Pedersen using Ru on alumina [23]. However, hydrogenation of phenol ether molecules leads to the formation of a hydrogenolysis by-product, the amount of which depends on the temperature of the reaction and the nature of the catalyst involved [24]. The phase transfer method of reduction previously described [25] gives rise to complete conversion, but the reaction mixture is difficult to purify due to the presence of trioctylamine, used as surfactant. With the Rh/C catalyst, the conversion is complete but the chimioselectivity varies from 63 to 95% as a function of the solvent polarity ($CHCl_3$ < $Cl(CH_2)_2Cl$ < MeOH).

Finally, the reduction of the 1,2-bis(2-hydroxyethoxy)-benzene **9** to 1,2-bis(2-hydroxyethoxy)cyclohexane **3** was performed by using the $Rh/SrTiO_3$ catalyst [26], under constant conditions of temperature and pressure. The synthesis is summarized in figure 7.

Synthesis of 2-(2-hydroxyethoxy)cyclohexanol cis **2**

Using another base and solvent, alkylation of catechol afforded mono- and dialkylated aromatic derivatives [27]. The monoalkylated aromatic derivative **10** was obtained in 30% yield, after simple silica gel chromatography. Then, reduction of compound **10** using $Rh/SrTiO_3$ catalyst led to the 2-(2-hydroxyethoxy)cyclohexanol *cis* **2** in 98% yield (fig 8).

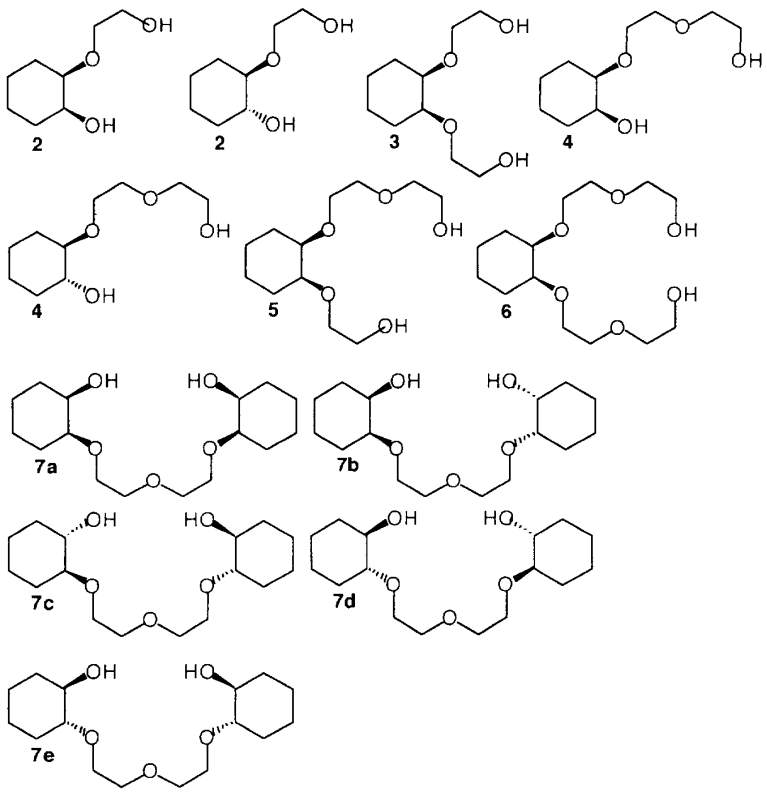

Fig 6. Potential stereochemical configurations of the DCH18C6 degradation products.

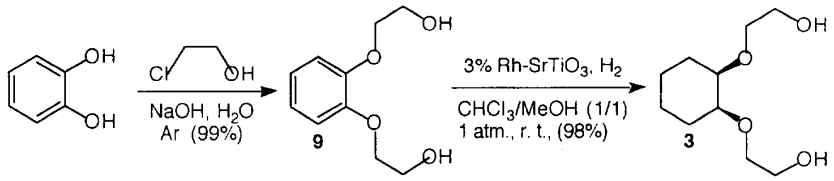

Fig 7. Synthesis of 1,2-bis(2-hydroxyethoxy)cyclohexane **3**.

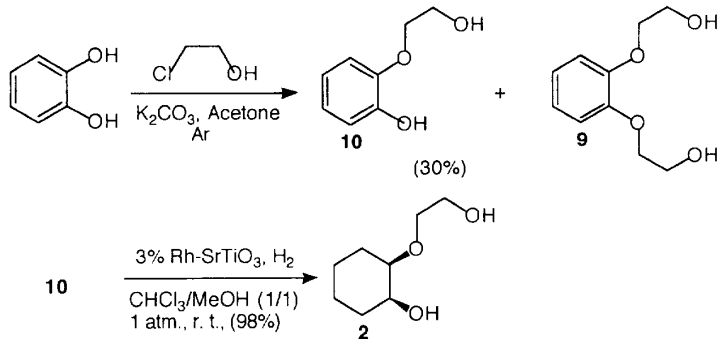

Fig 8. Synthesis of 2-(2-hydroxyethoxy)cyclohexanol *cis* **2**.

Synthesis of 2-(2-hydroxyethoxy)cyclohexanol trans **2**

The previously described method, involving the $Rh/SrTiO_3$ catalyst for the reduction of aromatic rings [26], preferentially yields the compound in the *cis* configuration. Conversely, epoxide opening in acidic medium is known to be directed to the *trans* configuration. This strategy, developed by Ikeda et al [28] for the synthesis of the cyclohexanol substituted at the 2-position, gives rise to a mixture of products which are difficult to purify. Direct treatment of the cyclohexeneoxide (7-oxabicyclo[4.1.0]heptane) with ethyleneglycol in the presence of catalytic sulfuric acid [29] led to the 2-(hydroxyethoxy)cyclohexanol *trans* **2** (fig 9).

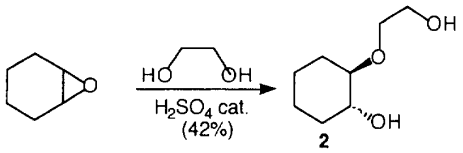

Fig 9. Synthesis of 2-(2-hydroxyethoxy)cyclohexanol *trans* **2**.

Synthesis of the 1,2-bis(5-hydroxy-3-oxapentyloxy)-cyclohexane cis **6**

The 1,2-bis(5-hydroxy-3-oxapentyloxy)cyclohexane in the *cis* configuration was readily obtained by quantitative reduction [26] of 1,2-bis(5-hydroxy-3-oxapentyloxy)benzene **11**, synthesized from the catechol according to the method previously described for compound **3** (fig 10). The dialkylated aromatic derivative **11** was reduced, affording the expected compound **6**.

Synthesis of 2-(5-hydroxy-3-oxapentyloxy)cyclohexanol cis **4**

Quantitative reduction of the 2-(5-hydroxy-3-oxapentyloxy)phenol **12**, arising as a secondary product of the dialkylated derivative synthesis, afforded the 2-(5-hydroxy-3-oxapentyloxy)cyclohexanol **7** in the *cis* configuration (fig 11).

Synthesis of 2-(5-hydroxy-3-oxapentyloxy)cyclohexanol cis **4**

2-(5-Hydroxy-3-oxapentyloxy)cyclohexanol *trans* **4** was obtained in 43% yield using previously described methodology (fig 12).

Synthesis of 1-(5-hydroxy-3-oxapentyloxy)-2-(2-hydroxyethoxy)cyclohexane cis **5**

1-(5-Hydroxy-3-oxapentyloxy)-2-(2-hydroxyethoxy)-cyclohexane *cis* **5** was obtained in two steps. Alkylation of 2-(5-hydroxy-3-oxapentyloxy)phenol **12** by 2-chloroethanol led to 1-(5-hydroxy-3-oxapentyloxy)-2-(hydroxyethoxy)benzene **13** in 31% yield. Reduction of compound **13** with the $Rh/SrTiO_3$ catalyst then gave the desired product **5** in 97% yield (fig 13).

Synthesis of 2,2'-[3-oxapentane-1,5-diylbis(oxy)diyl]-dicyclohexanol cis **7a, 7b**

The reaction conditions of Pedersen [23] for the direct synthesis of the cyclohexanols **7a** and **7b** *cis* lead to

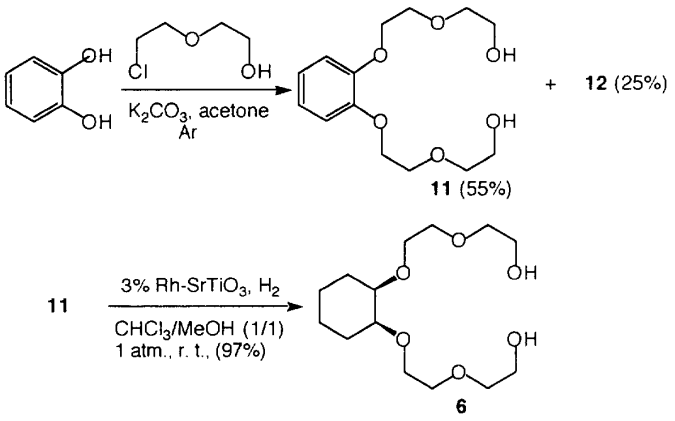

Fig 10. Synthesis of 1,2-bis(5-hydroxy-3-oxapentyloxy)cyclohexane *cis* **6**.

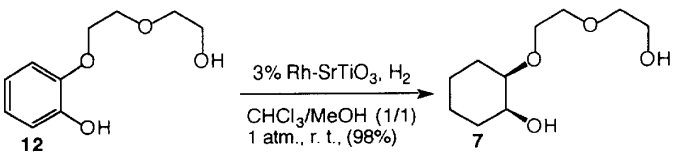

Fig 11. Synthesis of 2-bis(5-hydroxy-3-oxa-pentyloxy)cyclohexanol *cis* **4**.

a mixture which is difficult to purify. We now report a more convenient and simple method using guaiacol as starting material (fig 14). The key step of the synthesis is the deprotection of the phenoxy groups with trimethylsilyl iodide, by selective breaking of the methyl–oxygen bonds.

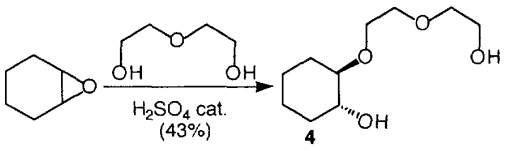

Fig 12. Synthesis of 2-(5-hydroxy-3-oxapentyloxy)cyclohexanol *trans* **4**.

Addition of bis(2-chloroethyl)ether to guaiacol afforded the aromatic dimethylated derivative **14** in 60% yield after recrystallization from ether. Deprotection of compound **14** with trimethylsilyl iodide in chloroform [30] led to the 2,2′-[3-oxapentane-1,5-diyl-bis(oxy)diyl]bis-phenol **15** after recrystallization from ether, in 97% yield. $Rh/SrTiO_3$ was inactive in the presence of the compound **15**, the complexing properties of which inhibit the reduction reaction. So aromatic derivative **15** was reduced by Rh/C catalyzed reaction. In this case, a total conversion was obtained, but the selectivity was a function of the polarity of the solvent used during the reduction (table II). Attempted increase of the catalyst concentration led to significant hydrogenolysis. The diastereoisomers crud was purified by thin layer chromatography.

Table II. Selectivity percentage as a function of solvent polarity.

Solvent	$CHCl_3$	$Cl(CH_2)_2Cl$	*MeOH*
Dipolar moment μ (10^{-3} C m)	3.8	5.2	5.7
Selectivity in **7**, (%)	39	56	60

Synthesis of 2,2′-[3-oxapentane-1,5-diylbis(oxy)diyl] dicyclohexanol trans **7c, 7d, 7e**

Synthesis of the stereoisomers **7c**, **7d**, **7e**, has been previously described [31]. We report a one-step procedure which leads to a mixture of the three stereoisomers.

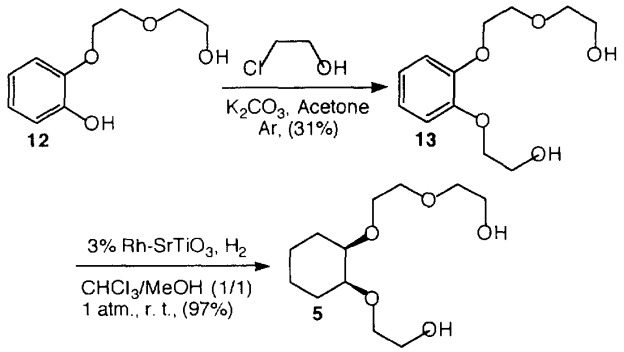

Fig 13. Synthesis of 1-(5-hydroxy-3-oxapentyloxy)-2-(2-hydroxyethoxy)cyclohexane *cis* **5**.

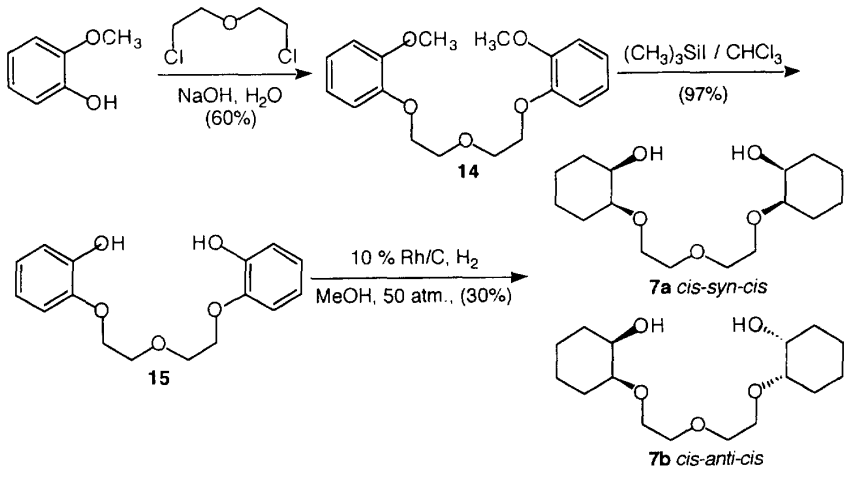

Fig 14. Synthesis of 2,2′-[3-oxapentane-1,5-diylbis(oxy)diyl]dicyclohexanol *cis* **7a** and **7b**.

Direct treatment of cyclohexene oxide with ethyleneglycol in the presence of catalytic sulfuric acid led to the cyclohexanols *trans* **7c**, **7d**, **7e** (fig 15). Distillation of the low mass compounds and thin layer chromatography of the diastereoisomers crud provided the *trans* mixture in 34% yield.

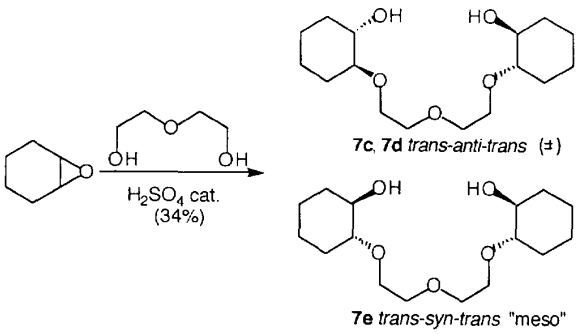

Fig 15. Synthesis of 2,2′-[3-oxapentane-1,5-diylbis(oxy)diyl]-dicyclohexanol *trans* **7c**, **7d**, **7e**.

Confirmation of the stereochemistry of the DCH18C6 radiolytic products

The different isomers of most of the degradation products were difficult to separate by GC analysis, although the peaks of the four isomers of the radiolysis compound **7** were all widely separated. So, the study of the stereochemistry of the radiolytic products was performed with compound **7** as reference. The stereochemical configuration of the compound **7**, obtained by radiolysis in the presence or absence of uranium, was determined by chromatography under conditions dependent on the mixture synthesized. The chromatograms in figure 16 show that, in all the cases studied, radiolysis of DCH18C6 led to product **7** with retention of configuration, ie, *cis* configuration.

As a general rule, γ radiation and hydrolysis give rise to degradation products of *cis* configuration.

Extraction tests in radioactive medium

Experiments were performed to test whether the degradation products of DCH18C6 modify the extraction of Pu, U and Sr by DCH18C6. For an acidity-adjusted second cycle solution of 4.9 N, compounds **2**, **3** and **7** were totally soluble in the aqueous phase. So, among the seven DCH18C6 radiolytic products, the influence of compounds **2**, **3** and **7** on Pu extraction with DCH18C6 was tested. Extraction of Pu was performed using a synthetic second cycle solution containing one or more of these radiolytic products. It is important to note that the concentration used was much higher than that expected in industrial reprocessing. Five tests were carried out: the first test was without a radiolytic product in the aqueous phase; the second, third and fourth tests were with only one radiolytic product in the aqueous phase; and the last one was with a mixture of the three radiolytic products in the aqueous phase (fig 17).

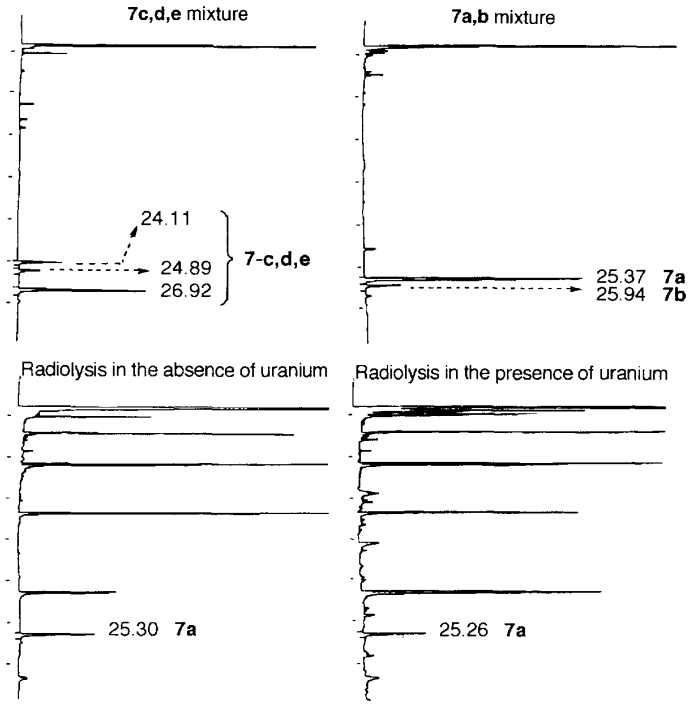

Fig 16. Chromatograms of the compound **7** obtained by synthesis and by radiolysis.

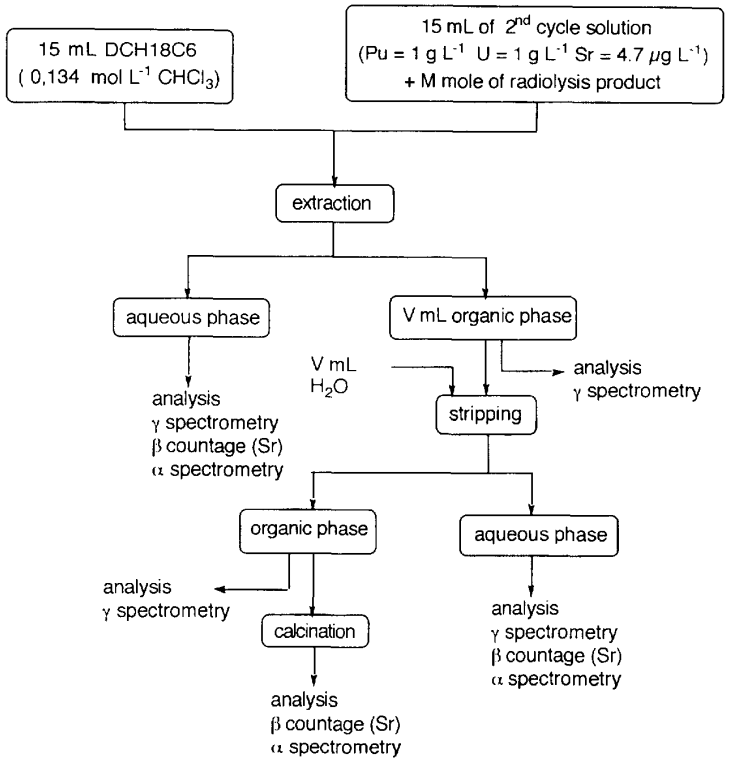

Fig 17. Procedure of Pu extraction by DCH18C6 in the presence of its radiolytic products.

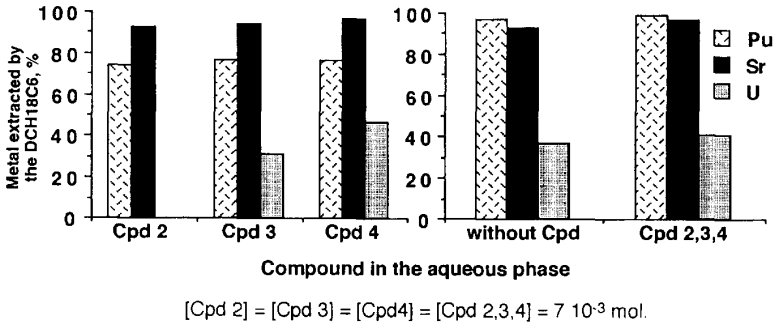

Fig 18. Effect of the radiolytic products of DCH18C6 on Pu, U and Sr extraction.

Effect of the radiolytic products on the extraction of Pu, U and Sr by DCH18C6

Figure 18 shows the effect of the DCH18C6 radiolytic products on the complexing properties of DCH18C6 in relation to Pu, U and Sr. A 20% decrease in the efficiency of Pu extraction was observed in the presence of one radiolytic product in the aqueous phase. In view of these results, two hypotheses can be put forward: (1) reduction of Pu from the IV to the III valence state, or (2) Pu IV retention and precipitation in the aqueous phase, by the DCH18C6 radiolytic products. Sr extraction capacity by the DCH18C6 was not modified by the presence of the synthesized radiolytic products in the aqueous phase. DCH18C6 radiolytic products have no effect on the concentration of γ emitters in the aqueous phase.

As in the absence of degradation compounds, the complexing properties of DCH18C6 are not modified by low or medium concentrations of the three radiolytic products in the aqueous medium. So, considering the low radiochemical yields observed for DCH18C6 radiolysis [1], the macrocycle radiolytic products do not perturb the extraction process.

Influence of a radiolytic product in the aqueous phase on Pu IV valence and concentration

In order to explain the influence of the DCH18C6 radiolytic products on Pu extraction, a radioactive second-

cycle solution was kept in contact with compound **2**. Concentrations of total Pu and Pu with valence states of III, IV and VI were determined as a function of the contact time between organic and aqueous phases (fig 19).

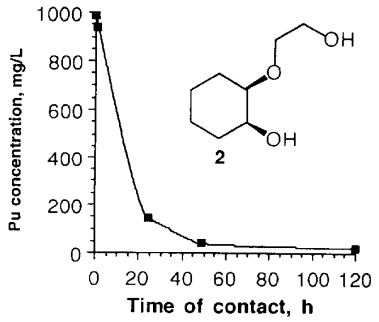

Fig 19. Variation of free Pu concentration as a function of the time of contact between the aqueous phase and a radiolytic product.

Pu III was not detected in any sample of aqueous phase; DCH18C6 radiolytic products do not reduce Pu. On the other hand, a precipitate was observed in the aqueous phase, the abundance of which was dependant on the aqueous phase–DCH18C6 time of contact, and decrease of free Pu in the aqueous phase was measured. Radiolytic product **2** precipitates Pu and retains it in the aqueous phase.

The presence of DCH18C6 radiolytic products could block out Pu extraction in a static liquid–liquid extraction system in which the degradation products inevitably accumulate. However they do perturb the process in a continuous extraction system.

Conclusion

DCH18C6, and specifically the *cis-syn-cis* isomer of this macrocycle, possesses a high stability toward radiolysis under conditions close to these established for its utilization. The *cis-syn-cis* DCH18C6 is more stable in the presence of uranium and this phenomenum is ascribable to a template effect of uranium that favors fragment recombination. We prepared a *cis-syn-cis* DCH18C6/U(VI) compound and determined its crystal structure by X-ray diffraction. In this compound there is no coordination bond between uranium and DCH18C6; interaction between the macrocycle and the uranium is realized via hydrogen bonds using the two water molecules of the complex and the oxygen atoms of the macrocycle. The *cis-syn-cis* DCH18C6 radiolytic products were synthesized in their different stereochemical configurations to assign their stereochemistry and to evaluate their possible interference with the reprocessing process. We have observed that γ radiation and hydrolysis give rise to degradation products of *cis* configuration. In a static liquid–liquid extraction system, the presence of DCH18C6 radiolytic products could block out Pu extraction. However, they will have no effect in the continuous extraction system used at industrial scale, in which the contact time between the radiolytic products and the extracting phase is shorter. Because of their solubility in the aqueous phase, the degradation products are not pollutant compounds and they can be eliminated using simple nitric acid scrubbing. DCH18C6 radiolytic and hydrolysis products have no effect on the extraction of γ emitters.

Altogether, its high selectivity and radiochemical stability make DCH18C6 an attractive candidate for the development of a new industrial technique for nuclear fuel reprocessing.

Experimental section

General methods

All syntheses were performed under a dry, inert Ar atmosphere. ^{1}H and ^{13}C NMR spectra were carried out on a Bruker 201 C spectrometer operating at 100.13 MHz (^{1}H) and 50.32 (^{13}C) MHz under broadband decoupling. Proton spectra are reported relative to tetramethylsilane and carbon spectra are reported relative to $CDCl_3$ (77 ppm/TMS) or CD_2Cl_2 (52.8 ppm/TMS). D_2O was introduced to identify OH functions.

FTIR spectra were recorded on a 1720-X Perkin Elmer spectrometer. Melting and boiling points are uncorrected. Mass spectrometry analyses were performed at the CNRS, Service central d'analyse, Laboratoire de spectrométrie de masse, Vernaison, France. GC spectra were recorded on a Shimadzu GC-14A spectrometer equipped with a J & W Scientific non-polar capillary column (60 m × 0.25 mm id) grafted with a 0.25 μm 5% diphenylmethylsiloxane film for all the compounds and with a Quadrex semi-polar capillary column (60 m × 0.25 id) grafted with a 0.25 μm 50% methylphenylsilicone film for the study of the stereochemistry of the DCH18C6 radiolytic products.

Tests in radioactive medium

• *Influence of the radiolytic products on Pu, Sr and U extraction by DCH18C6*

Extractions were carried out by shaking for 10 min 15 mL of a synthetic second-cycle solution containing (or not) radiolytic products, with 15 mL of a chloroformic DCH18C6 solution (5%, m/v). The organic solution (V mL) was washed with water (V mL), chloroform was evaporated, then the organic residue was calcinated and dissolved in nitric acid (68%). Extractions were carried out according to the procedure shown in figure 17.

[Cpd **2**] = [Cpd **3**] = [Cpd **4**] = 7.35 mmol; [Cpd **2**, **3**, **4**] = 2.45 × 3 = 7.35 mmol; [U] = 1 g L^{-1}; [Pu] = 1 g L^{-1}; [Sr] = 4.7 μg L^{-1}.

• *Influence of the presence of a radiolytic product in the aqueous phase on Pu valence and concentration*

Extractions were carried out by shaking 9.8×10^{-3} mol (1.5998 g) of radiolytic product **7** with 20 mL of a second-cycle solution. Four samples were taken as a function of time, to be analyzed.

• *Analytical procedure in radioactive medium*

■ *Measurements of the acidity [32]*

The acidities were measured on a Mettler DL 40 pH meter.

■ *Measurements of the activity by β counting [33]*

The strontium analyses were performed using β counting, and these measurements required the elimination of all other

radioelements. The Numelec ENU 16 equipment was composed of an argon/methane ionization chamber, a preamplifier, a high-voltage drawer and a counter. The precision of the analysis (±6%) was calculated from the variance and the deviation of the results obtained with eight measurements.

■ *Measurements of the activity by α spectrometry [34]*
Alpha activity measurements required actinide separation and were used to determine plutonium concentrations less than 0.5 mg L^{-1}. The Numelec equipment type ENU 15 B was composed of an argon/methane ionization chamber, a preamplifier, a high-voltage drawer and a Canberra multichannel analyzer. Efficiency analysis line standardization and energy adjustment were made using standard solutions. The concentrations were measured with a standard deviation of ±5–10%.

X-ray crystallography

• *Preparation of $(UO_2)(NO_3)_2(H_2O)_2$, (*cis-syn-cis *DCH18C6) compound*
To prepare suitable crystals, equimolar amounts of $(UO_2)(NO_3)_2$, $6(H_2O)$ and *cis-syn-cis* DCH18C6 (Fluka) were dissolved in acetonitrile, and the compound crystallized as the solution was evaporated. The crystals were pale yellow prisms, stable in air.

• *X-ray structure determination*
Crystal data for $(C_{20}O_6H_{36})(UO_2)(NO_3)_2(H_2O)_2$: Mr = 802.6, orthorhombic, $P2_12_12_1$, a = 10.896 (2), b = 15.899 (2), c = 16.890 (2) Å, V = 2 925 (1) Å^3, Z = 4, Dx = 1.823 g cm^{-3}, λ(Mo$K\alpha$) = 0.710 7 Å, μ = 53.3 cm^{-1}, T = 291 K.

The diffraction data were obtained from a single crystal of 0.15×0.3×0.4 mm studied on a Nonius CAD4 diffractometer using graphite monochromated Mo$K\alpha$ radiation. The cell parameters were refined from setting angles of 25 selected reflections ($13.7 < \theta < 22.6°$).

Intensities were collected using $\omega - \theta$ scan, in the range $1 < \theta < 30°$. The 8 568 measured reflections were reduced to 4 728 independent reflections. Only 1 887 were considered as observed ($I > 3\sigma(I)$). The intensity data were empirically corrected for absorption (Ψ scans).

The position of the U atom was determined from a Patterson map. The subsequent difference electron density maps gave the positions of the non-H atoms. The structure was refined by full-matrix least squares with anisotropic thermal parameters for U. The final R is 0.042 for 1 887 reflections. The atomic position parameters are listed in table III and selected interatomic distances and angles are listed in table IV. Lists of the structure factors and the anisotropic displacement parameters for U, atomic coordinates, interatomic distances and angles are included in the supplementary material data.

Organic synthesis

• *1,2-Bis(2-hydroxyethoxy)benzene* **9**
Catechol (3.3 g, 30 mmol) was added to a solution of NaOH (2.88 g, 72 mmol) in water (100 mL) under argon. The solution was heated to 60 °C and 2-chloroethanol (7.25 g, 90 mmol) was then added. After 12 h at 60 °C, NaOH (1.8 g, 45 mmol) and 2-chloroethanol (3.62 g, 45 mmol) were successively added. After 3 days at 60 °C the reaction was completed. After cooling, the product was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$, filtered, and CH_2Cl_2 was removed under reduced pressure. The residue was taken up in THF. Addition of heptane under stirring gave a white precipitate of the product **9**.

Table III. Atomic coordinates and isotropic parameters.

	X	Y	Z	B(A^2)
U	−0.0011(1)	0.58735(4)	0.2514(1)	2.530(8)*
O11	0.039(1)	0.4800(9)	0.240(1)	3.5(3)
O12	−0.041(1)	0.6933(8)	0.257(1)	2.8(2)
O13	−0.169(3)	0.563(2)	0.033(2)	7.6(7)
O14	−0.016(2)	0.583(1)	0.104(1)	4.4(4)
O15	−0.183(2)	0.553(1)	0.166(1)	4.6(4)
N1	− 0.129(2)	0.564(2)	0.099(2)	4.8(6)
O16	−0.253(3)	0.574(2)	0.441(2)	9.4(8)
O17	−0.067(2)	0.592(1)	0.398(1)	4.8(4)
O18	−0.215(2)	0.555(1)	0.307(1)	6.3(6)
N2	−0.183(3)	0.580(2)	0.374(2)	6.3(8)
Ow1	0.188(2)	0.614(1)	0.184(1)	3.2(3)
Ow2	0.155(2)	0.630(1)	0.345(1)	3.6(4)
O1	0.688(2)	0.031(1)	0.085(1)	3.0(3)
C1	0.585(3)	−0.014(2)	0.119(2)	3.7(5)
C2	0.619(3)	−0.036(2)	0.204(2)	4.9(7)
O2	0.605(1)	0.0424(9)	0.251(3)	3.7(3)
C3	0.485(4)	0.051(2)	0.280(2)	6.4(8)
C4	0.474(3)	0.132(2)	0.322(2)	5.5(8)
O3	0.559(2)	0.139(1)	0.384(1)	4.2(4)
C5	0.540(2)	0.217(2)	0.427(2)	3.7(5)
C6	0.475(4)	0.206(2)	0.506(2)	7(1)
C7	0.532(3)	0.147(2)	0.565(2)	4.3(6)
C8	0.667(3)	0.189(2)	0.590(2)	5.1(7)
C9	0.743(3)	0.197(2)	0.501(2)	4.6(6)
C10	0.658(3)	0.256(2)	0.450(2)	4.1(6)
O4	0.744(2)	0.262(1)	0.377(1)	4.2(4)
C11	0.713(3)	0.334(2)	0.338(2)	4.4(6)
C12	0.790(2)	0.337(2)	0.259(2)	4.2(5)
O5	0.728(2)	0.279(1)	0.198(1)	5.2(5)
C13	0.665(3)	0.327(2)	0.139(2)	6.0(8)
C14	0.584(3)	0.260(2)	0.093(2)	5.4(7)
O6	0.662(2)	0.206(1)	0.056(1)	3.3(3)
C15	0.589(3)	0.151(2)	0.007(2)	3.9(5)
C16	0.578(2)	0.175(2)	−0.076(2)	3.6(5)
C17	0.697(3)	0.199(2)	−0.115(2)	5.9(8)
C18	0.770(3)	0.111(2)	−0.122(2)	4.2(6)
C19	0.787(2)	0.076(2)	−0.038(2)	3.6(5)
C20	0.659(3)	0.066(2)	0.002(2)	3.9(6)

* B_{eq}, equivalent anisotropic thermal parameters: $B_{eq} = 4/3\ S_i S_j\ b_{ij}\ a_i\ a_j$.

Yield 5.89 g, 99%, mp 82 ± 1 °C.

IR (KBr): OH: 3 317, $\nu_{as}CH_2$: 2 939, ν_sCH_2: 2 869, ν=CH aromatic: 3 068, 3 030, νC=C aromatic: 1 596, 1 512, 1 560, 1 454, ν=C–O: 1 285, 1 256, 1 231, νO–CH_2: 1 070, 1 043 cm^{-1}.

^{1}H NMR (CD_2Cl_2): 2.5–2.6 (m, 4H, CH_2OH), 2.7–2.9 (m, 4H, CH_2O), 5.7–5.9 (m, 4H, ArH).

^{13}C NMR (CD_2Cl_2): 61.91, 72.62 (CH_2), 116.30, 122.99 (aromatic CH), 149.90 (aromatic Cquat).

• *General procedure of mono and dialkylation of catechol*
A mixture of catechol (1.65 g, 15 mmol) and K_2CO_3 (2.07 g, 15 mmol) in dry acetone was refluxed under argon for 1 h. The alkylating reagent was then added and the mixture was refluxed for 24 h. After cooling the solvent was evaporated to dryness. The residue was dissolved in CH_2Cl_2 and the resulting solution was washed with saturated NH_4Cl solution. The organic layer was dried over $MgSO_4$. After filtration, the solvent was evaporated to dryness.

Table IV. Selected bond distances and bond angles.

Interatomic distances (Å)					
U–O11	1.77(1)	O1–C1	1.45(3)	C10–O4	1.55(4)
U–O12	1.74(1)	O1–C20	1.53(3)	O4–C11	1.36(4)
U–O14	2.50(2)	C1–C2	1.54(4)	C11–C12	1.58(4)
U–O15	2.51(2)	C2–O2	1.48(4)	C12–O5	1.54(4)
U–O17	2.58(2)	O2–C3	1.41(5)	O5–C13	1.43(4)
U–O18	2.56(2)	C3–C4	1.47(5)	C13–C14	1.58(5)
U–Ow1	2.39(2)	C4–O3	1.40(4)	C14–O6	1.36(4)
U–Ow2	2.42(2)	O3–C5	1.46(3)	O6–C15	1.45(3)
O13–N1	1.20(4)	C5–C6	1.52(5)	C15–C16	1.45(4)
O14–N1	1.27(3)	C5–C10	1.48(4)	C15–C20	1.55(4)
O15–N1	1.29(3)	C6–C7	1.51(5)	C16–C17	1.51(5)
O16–N2	1.37(4)	C7–C8	1.68(4)	C17–C18	1.61(5)
O17–N2	1.34(4)	C8–C9	1.72(5)	C18–C19	1.54(4)
O18–N2	1.25(4)	C9–C10	1.58(5)	C19–C20	1.56(4)
Interatomic angles (°)					
O11–U–O12	177(1)	O17–U–Ow2	64.0(7)	C5–C6–C7	117.(3)
O11–U–O14	82.9(7)	O18–U–Ow1	173.2(7)	C6–C7–C8	106.(3)
O11–U–O15	85.6(7)	O18–U–Ow2	117.2(7)	C7–C8–C9	104.(2)
O11–U–O17	101.7(7)	Ow1–U–Ow2	69.6(6)	C8–C9–C10	104.(2)
O11–U–O18	94.2(8)	U–O14–N1	97.(2)	C5–C10–C9	114.(2)
O11–U–Ow1	84.4(6)	U–O15–N1	96.(2)	C5–C10–O4	111.(2)
O11–U–Ow2	99.7(7)	O13–N1–O14	114.(3)	C9–C10–O4	97.(2)
O12–U–O14	93.9(9)	O13–N1–O15	130.(3)	C10–O4–C11	107.(2)
O12–U–O15	92.7(7)	O14–N1–O15	115.(2)	O4–C11–C12	108.(2)
O12–U–O17	81.4(7)	U–O17–N2	88.(2)	C11–C12–O5	108.(2)
O12–U–O18	87.0(7)	U–O18–N2	91.(2)	C12–O5–C13	110.(2)
O12–U–Ow1	94.1(7)	O16–N2–O17	107.(3)	O5–C13–C14	104.(3)
O12–U–Ow2	82.3(7)	O16–N2–O18	125.(3)	C13–C14–O6	108.(3)
O14–U–O15	51.1(6)	O17–N2–O18	125.(3)	C14–O6–C15	108.(2)
O14–U–O17	160.2(7)	C1–O1–C20	112.(2)	O6–C15–C16	116.(2)
O14–U–O18	107.6(8)	O1–C1–C2	107.(2)	O6–C15–C20	107.(2)
O14–U–Ow1	65.7(6)	C1–C2–O2	106.(3)	C16–C15–C20	103.(2)
O14–U–Ow2	134.8(7)	C2–O2–C3	112.(2)	C15–C16–C17	115.(3)
O15–U–O17	109.6(7)	O2–C3–C4	110.(3)	C16–C17–C18	103.(3)
O15–U–O18	56.5(8)	C3–C4–O3	112.(3)	C17–C18–C19	108.(2)
O15–U–Ow1	116.7(7)	C4–O3–C5	110.(2)	C18–C19–C20	109.(2)
O15–U–Ow2	172.3(6)	O3–C5–C6	114.(2)	O1–C20–C15	111.(2)
O17–U–O18	53.2(7)	O3–C5–C10	111.(2)	O1–C20–C19	104.(2)
O17–U–Ow1	133.6(7)	C6–C5–C10	104.(2)	C15–C20–C19	112.(2)

■ *2-(2-Hydroxyethoxy)phenol* **10**

This was prepared from 2-chloroethanol (3.02 g, 37.5 mmol). The crude product was chromatographed over SiO_2 with ethyl acetate as eluent to afford **10** in 30% yield as a colorless oil and by-product **9** in 10% yield as a colorless oil.

10 Yield 0.69 g, 30%.

IR (NaCl): OH: 3 400, $\nu_{as}CH_2$: 2 930, ν_sCH_2: 2 870, ν=CH aromatic: 3 070, 3 030, νC=C aromatic: 1 610, 1 596, 1 505, ν=C–O: 1 270, 1 250, 1 220, νO–CH_2: 1 068, 1 050 cm^{-1}.

^1H NMR (CD_2Cl_2): 2.5–2.6 (m, 2H, CH_2OH), 2.8–3 (m, 2H, CH_2O), 5.8–6 (m, 5H, ArH).

^{13}C NMR (CD_2Cl_2): 61.91 (CH_2OH), 72.62 (CH_2O), 114.23, 116.13, 120.99, 123.91 (aromatic CH), 145.74, 147.54 (aromatic Cquat).

9 Yield 0.30 g, 10%.

■ *1,2-Bis(5-hydroxy-3-oxapentyloxy)benzene* **11**

This was prepared from 2-(2-chloroethoxy)ethanol (4.67 g, 37.5 mmol). The crude product was chromatographed over SiO_2 with ethyl acetate as eluent to afford **11** (R_F = 0.49) in 55% yield as a colorless oil and by-product **12** (R_F = 0.16) in 25% yield as a colorless oil.

11 Yield 6.30 g, 55%, R_F = 0.49.

IR (NaCl): OH: 3 375, $\nu_{as}CH_2$: 2 931, ν_sCH_2: 2 875, ν=CH aromatic: 3 067, 3 030, νC=C aromatic: 1 608, 1 594, 1 506, 1 457, ν=C–O: 1 267, 1 247, 1 224, νO–CH_2: 1 068, 1 053 cm^{-1}.

^1H NMR ($CDCl_3$): 2.4 (s, 2H, OH), 3.7 (m, 4H, CH_2OH), 3.8–3.9 (m, 8H, CH_2O), 4.2 (m, 4H, CH_2O), 6.9 (m, 5H, ArH).

^{13}C NMR ($CDCl_3$): 61.21 (CH_2OH), 68.10, 69.03, 72.53 (CH_2O), 113.32, 121.22 (aromatic CH), 146.13 (aromatic Cquat).

12 Yield 1.98 g, 25%, R_F = 0.16.

IR (NaCl): OH: 3 368, $\nu_{as}CH_2$: 2 930, ν_sCH_2: 2 875, ν=CH aromatic: 3 070, 3 030, νC=C aromatic: 1 608, 1 596, 1 505, 1 458, ν=C–O: 1 267, 1 247, 1 224, νO–CH_2: 1 071, 1 054 cm^{-1}.

^1H NMR (CD_2Cl_2): 3.5–3.7 (m, 4H, CH_2O), 3.7–4 (m, 2H, CH_2OH), 4.1–4.2 (m, 2H, CH_2O), 6.6–6.9 (m, 4H, ArH).

^{13}C NMR (CD_2Cl_2): 61.73 CH_2OH, 68.81, 69.83, 72.97 (CH_2O), 114.19, 116.14, 120.19, 122.93 (aromatic CH), 146.26, 147.25 (aromatic Cquat).

• *1-(5-Hydroxy-3-oxapentyloxy)-2-(2-hydroxyethoxy)-benzene* **13**

A mixture of **12** (4.70 g, 23.64 mmol) and K_2CO_3 (6.54 g, 47.29 mmol) in dry acetone was refluxed under argon for 1 h. 2-Chloroethanol (4.76 g, 59.1 mmol) was then added and the mixture was refluxed for 24 h. After cooling the solvent was evaporated to dryness. The residue was dissolved in CH_2Cl_2 and the resulting solution was washed with saturated NH_4Cl solution. The organic layer was dried over $MgSO_4$. After filtration, the solvent was evaporated to dryness. The crude product was chromatographed over SiO_2 with ethyl acetate as eluent to afford **13** in 31% yield.

13 Yield 1.77 g, 31%.

IR (NaCl): OH: 3 317, $\nu_{as}CH_2$: 2 941, ν_sCH_2: 2 879, ν=CH aromatic: 3 068, 3 030, νC=C aromatic: 1 608, 1 595, 1 506, 1 456, ν=C–O: 1 255, 1 247, 1 216, νO–CH_2: 1 076, 1 050 cm^{-1}.

^{1}H NMR (CD_2Cl_2): (m, H, CH_2OH), (m, H, CH_2O), (m, H, ArH).

^{13}C NMR (CD_2Cl_2): 60.71, 61.47 (CH_2OH), 68.30, 69.22, 71.52, 72.73 (CH_2O), 112.86, 114.23, 121.55, 121.66 (aromatic CH), 145.74, 147.54 (aromatic Cquat).

• *General procedure for the reduction of compounds* **9**, **10**, **11**, **12** *and* **13**

The reduction was performed by adding 10 mmol of each compound to a suspension of rhodium on strontium titanate catalyst (0.5%), oxidized 48 h in air, (6.17 g, 0.30 mmol of Rh) in MeOH/$CHCl_3$ (1:1, v/v) mixture. The reduction was completed in 12 h under 1 atm H_2 at room temperature under stirring. After filtration, the solvent was removed under reduced pressure.

■ *1,2-Bis(2-hydroxyethoxy)cyclohexane* **3**

This was prepared from compound **9** and obtained as a colorless oil.

3 Yield 2 g, 98%.

MS (CI, CH_4): m/z 99; 143; 205 (M + H$^+$); 206 (M + 2H$^+$).

MS (EI, 70 eV): m/z (%) 81 (100); 99 (53); 113 (11); 143 (8); 157 (2); 173 (4); 205 (3, [M + H]$^+$).

IR (NaCl): OH: 3 383, $\nu_{as}CH_2$: 2 935, ν_sCH_2: 2 862, δ_sCH_2: 1 457, $\nu_{as}CH_2OCH_2$: 1 100, 1 071, νCH cyclic: 989, $\nu_sCH_2OCH_2$: 900–800 cm^{-1}.

^{1}H NMR (CD_2Cl_2): 1.1–1.4 (m, 4H, CH_2), 1.4–1.65 (m, 4H, CH_2), 1.65–2.10 (m, 4H, CH_2), 3.4–3.5 (m, 4H, CH_2OH), 3.6–3.8 (m, 6H, CH_2O and CHO).

^{13}C NMR (CD_2Cl_2): 23.79, 29.57 (CH_2), 63.66 (CH_2OH), 72.31 (CH_2O), 79.8 (CHO).

■ *2-(2-Hydroxyethoxy)cyclohexanol* **2**

This was prepared from compound **10** and obtained as a colorless oil.

2 Yield 1.57 g, 98%.

MS (CI, CH_4) m/z 99; 143; 161 (M + H$^+$); 162 (M + 2H$^+$).

MS (EI, 70 eV) m/z 81 (100); 99 (85); 116 (3); 130 (4); 143 (12); 161 (2, [M + H]$^+$).

IR (NaCl): OH: 3 400, $\nu_{as}CH_2$: 2 993, ν_sCH_2: 2 862, δ_sCH_2: 1 458, $\nu_{as}CH_2OCH_2$: 1 126, 1 080, 1 040, νCH cyclic: 933, $\nu_sCH_2OCH_2$: 900–800 cm^{-1}.

^{1}H NMR ($CDCl_3$): 1.2–1.4 (m, 4H, CH_2), 1.6–1.7 (m, 2H, CH_2), 2–2.1 (m, 2H, CH_2), 3.1–3.2 (m, 1H, CH), 3.4–3.5 (m, 2H, CH_2), 3.8–4 (m, 3H, CHO and CH_2O), 4.3–4.4 (s, 2H, OH).

^{13}C NMR (CD_2Cl_2): 24.17, 24.27, 29.65, 32.75 (CH_2), 61.84 (CH_2OH), 70.18 (CHOH), 73.71 (CH_2O), 84.05 (CHO).

■ *1,2-Bis-(5-hydroxy-3-oxapentyloxy)cyclohexane* **4**

This was prepared from compound **12** and obtained as a colorless oil.

4 Yield 2 g, 98%.

MS (CI, CH_4) m/z 99; 127; 188; 205 (M + H$^+$); 206 (M + 2H$^+$).

MS (EI, 70 eV) m/z (%) 45 (44); 81 (100); 89 (16); 99 (77); 115 (2); 159 (7); 187 (3); 205 (4, [M + H]$^+$).

IR (NaCl): OH: 3 402, $\nu_{as}CH_2$: 2 993, ν_sCH_2: 2 862, δ_sCH_2: 1 452, $\nu_{as}CH_2OCH_2$: 1 124, 1 099, 1 041, νCH cyclic: 940, $\nu_sCH_2OCH_2$: 900–800 cm^{-1}.

^{1}H NMR ($CDCl_3$): 1.05–1.4 (m, 4H, CH_2), 1.5–1.8 (m, 2H, CH_2), 1.8–2.1 (m, 2H, CH_2), 3–3.2 (m, 1H, CH), 3.3–3.5 (m, 1H, CH), 3.5–4 (m, 8H, CH_2O and CH_2OH).

^{13}C NMR ($CDCl_3$): 24.02, 24.29, 29.73, 32.38 (CH_2), 61.32, 68.37 (CH_2O), 70.73 (CH_2OH), 72.73 (CH_2O), 73.59 (CHOH), 84.54 (CH).

■ *1-(5-Hydroxy-3-oxapentyloxy)-2-(2-hydroxyethoxy)-cyclohexane* **5**

This was prepared from compound **13** and obtained as a colorless oil.

5 Yield 1.65 g, 97%.

MS (CI, CH_4) m/z 99; 143; 187; 249 (M + H$^+$); 250 (M + 2H$^+$); 251 (M + 3H$^+$).

MS (EI, 70 eV) m/z (%) 45 (100); 89 (22); 99 (56); 114 (13); 127 (2); 143 (15); 156 (3).

IR (NaCl): OH: 3 356, $\nu_{as}CH_2$: 2 936, ν_sCH_2: 2 872, δ_sCH_2: 1 457, $\nu_{as}CH_2OCH_2$: 1 117, 1 082, 1 057, νCH cyclic: 990, $\nu_sCH_2OCH_2$: 900–800 cm^{-1}.

^{1}H NMR (CD_2Cl_2): 1.5–1.7 (m, 8H, CH_2), 2.6 (s, 2H, OH), 3.7–4 (m, 12H, CH_2 and CH).

^{13}C NMR (CD_2Cl_2): 21.75, 23.55, 27.30, 28.77 (CH_2), 64.52 (CH_2OH), 70.95, 71.21, 72.99, 73.45 (CH_2O), 77.89, 79.58 (CHO).

• *General synthesis of* trans *compounds*

A solution of cyclohexene oxide (4.9 g, 50 mmol) in glycol was stirred at 0 °C. Concentrated sulfuric acid (4 drops) was added and then the solution was slowly heated to 95 °C and stirred for 1 h at this temperature. After cooling CH_2Cl_2 was added. The organic layer was washed with a saturated $NaHCO_3$ solution and with water. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure.

■ *2-(2-Hydroxyethoxy)cyclohexanol* **2** trans

This was prepared from ethyleneglycol (9.31 g, 150 mmol) and isolated by distillation (bp 105 °C at 10^{-3} mbar).

2 Yield 3.36 g, 42%.

■ *2-(5-Hydroxy-3-oxapentyloxy)cyclohexanol* **4** trans

This was prepared from diethyleneglycol (15.92 g, 150 mmol) and isolated by distillation (bp 115 °C at 10^{-3} mbar).

4 Yield 4.39 g, 43%.

■ *2,2'-[3-Oxapentane-1,5-diylbis(oxy)diyl]dicyclohexanol* **7** trans

This was prepared from ethyleneglycol (3.72 g, 60 mmol) and isolated by thin layer chromatography with Et_2O as eluent).

7 Yield 2.57 g, 34%.

• *2,2'-[3-Oxapentane-1,5-diylbis(oxy)diyl]dianisole* **14**
Guaiacol (2-methoxyphenol) (111.73 g, 9 mol) was added to a solution of NaOH (43.2 g, 10.8 mol) in water (600 mL). The solution was heated to 60 °C and bis-(2-chloroethyl)ether was then added. After 48 h at 60 °C, the reaction was completed. After cooling, CH_2Cl_2 was added. The organic layer was washed with a NaOH solution (10%) and then with water. The organic layer was dried over $MgSO_4$ and concentrated. Addition of Et_2O gave the product as a white powder.

14 Yield 57.3 g, 60%, mp = 81 ± 1 °C.

IR (KBr): $\nu_{as}CH_2$: 2 914, $\nu_{as}CH_3$: 2 933, ν_sCH_2: 2 877, ν_sCH_3: 2 891, ν_sOCH_3: 2 802, ν=CH aromatic: 3 060, 3 029, νC=C aromatic: 1 607, 1 594, 1 508, 1 455, ν=C-O: 1 258, 1 244, 1 227, νO-CH_2: 1 070, 1 056 cm^{-1}.

^1H NMR (CD_2Cl_2): 3.7–4 (m, 8H, CH_2O), 4.1–4.2 (m, 6H, OCH_3), 6.8–7 (m, 8H, ArH).

^{13}C NMR (CD_2Cl_2): 56.09 (CH_3), 68.80, 70.24 (CH_2O), 112.43, 114.10, 121.10, 121.71 (aromatic CH), 148.76, 150.09 (aromatic Cquat).

• *2,2'-[3-Oxapentane-1,5-diylbis(oxy)diyl]bis-phenol* **15**

A solution of **14** (17.47 g, 54.9 mmol) in 75 mL of $CHCl_3$ was stirred under Ar at room temperature and iodotrimethylsilane (35.15 g, 175 mmol) was added. After the reaction was completed (typically 12 h) a MeOH/H_2O mixture (50:50, v/v) was added. Saturated $NaHSO_3$ solution (10 mL) was added and then CH_2Cl_2. The organic layer was concentrated under vacuum. Addition of Et_2O gave the product as a white powder.

15 Yield 15.60 g, 97%.

IR (KBr): OH: 3 317, $\nu_{as}CH_2$: 2 945, $\nu_{as}CH_3$: 2 933, ν_sCH_2: 2 885, ν_sCH_3: 2 891, ν_sOCH_3: 2 802, ν=CH aromatic: 3 070, 3 048, νC=C aromatic: 1 608, 1 597, 1 504, 1 461, ν=C-O: 1 268, 1 247, 1 224, νO-CH_2: 1 064, 1 047 cm^{-1}.

^1H NMR (CD_2Cl_2): 2.6–2.8 (m, 4H, CH_2O), 3.0–3.2 (m, 4H, CH_2O), 5.6–6 (m, 8H, ArH), 6.3 (s, 2H, OH).

^{13}C NMR (CD_2Cl_2): 70.59, 71 (CH_2O), 116.93, 117.06, 121.17, 124.4 (aromatic CH), 147.04, 148.62 (aromatic Cquat).

■ *2,2'-[3-Oxapentane-1,5-diylbis(oxy)diyl]dicyclohexanol* **7** cis

A mixture of **15** (1.45 g, 5 mmol) and rhodium on carbon (1 g, 0.48 mmol of Rh) in MeOH (15 mL) was placed in an autoclave. The reduction was completed in 2 h under 50 atm H_2 at room temperature under stirring. After filtration, the crude product was purified by thin layer chromatography with Et_2O as eluent.

7 Yield 0.45 g, 30%.

MS (CI, CH_4) m/z 99; 127; 143; 187; 205; 303 ($M + H^+$); 304 ($M + 2H^+$); 305 ($M + 3H^+$).

MS (EI, 70 eV) m/z (%) 45 (74); 81 (88); 89 (16); 99 (100); 143 (9); 187 (8); 205 (9); 156 (3).

IR (NaCl): OH: 3 446, $\nu_{as}CH_2$: 2 935, ν_sCH_2: 2 863, δ_sCH_2: 1 458, $\nu_{as}CH_2OCH_2$: 1 133, 1 096, 1 024 νCH cyclic: 990, $\nu_sCH_2OCH_2$: 900–800 cm^{-1}.

^1H NMR (CD_2Cl_2): 0.9–1.3 (m, 4H, CH_2), 1.3–1.6 (m, 8H, CH_2), 1.6–1.8 (m, 4H, CH_2), 3.2–3.3 (m, 2H, CHO), 3.4–3.7 (m, 8H, CH_2), 3.7–3.9 (m, 2H, CHOH), 4–4.1 (s, 2H, OH).

^{13}C NMR (CD_2Cl_2): 21.80, 21.87, 22.71, 27.47, 27.67, 30.79, 30.86 (CH_2), 67.63, 67.70 (CH_2O), 68.35, 68.57 (CH_2O), 70.96, 71.19 (CHOH), 79.84, 79.96 (CHO).

Acknowledgment

The authors are grateful to Graham Feast for helpful discussions.

Supplementary material available

Supplementary material data have been deposited with the British Library, Document Supply Center at Boston Spa, Wetherby, West Yorkshire, LS23 7BQ, UK as supplementary publication N° SUP = 90406 (45 pp) and are available on request from the Documentary Supply Center.

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