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SYNTHESIS AND CONFORMATIONAL ASPECTS OF CORANDS INCORPORATING PYRYLIUM, THIOPYRYLIUM AND PYRIDINE SUBUNITS

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Abstract The pyrylium corands **1a**, **1b** and the thiopyrylium corands **2a**, **2b**, were prepared in good yields by heterocyclization of the macrocyclic 1,5-pentanediones **4a**, **4b**, whereas the pyridine corands **3a**, **3b** were obtained by reacting **1a** and **1b**, respectively, with ammonium acetate NMR data and molecular mechanics calculations suggest that the heteroaromatic nuclei tend to fill the cavity of the macrorings

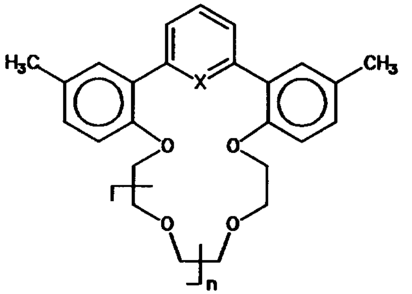
Introduction

Recently Reinhoudt and co-workers[1] reported the preparation of hemispherand-like[2] macrocycles containing the pyrylium subunit As stressed by the authors, this subunit is a useful building block which allows further variation in the structure of a molecular cavity However the preparation of the highly structured pyrylium hemispherands required nine steps with low global yields (≅ 2%) [1,3]

This is, to our knowledge, the only example in the literature in which a pyrylium ring has been incorporated into a polyether macrocyclic structure No examples have been reported so far for the thiopyrylium ring

Of course it would be useful to develop simple and high yielding methods to prepare such macrocycles, also in view of the interesting electrochemical behavior of pyrylium and thiopyrylium ions,[4] which could be exploited in the area of redox responsive receptors [5]

Here we report a simple synthesis of corands[2] **1a**, **1b** and **2a**, **2b**, and, as an example of the synthetic versatility of pyrylium ions, the conversion of corands **1a** and **1b** into the respective pyridine corands **3a** and **3b** In the light of ^{1}H NMR results and molecular mechanics calculations, some conformational aspects of the corands **1-3** will also be discussed

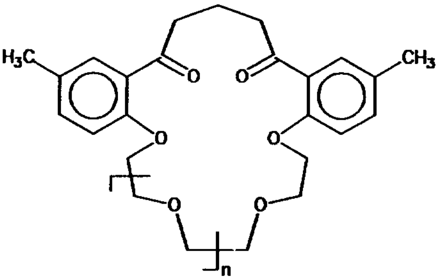


1a, X = O^+, n = 1
1b, X = O^+, n = 2
2a, X = S^+, n = 1
2b, X = S^+, n = 2
3a, X = N, n = 1
3b, X = N, n = 2

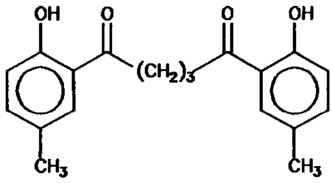
Results and Discussion

Syntheses. Our synthetic approach to corands **1** and **2** is based on the easy conversion of 1,5-pentanediones into both pyrylium[4,6] and thiopyrylium[7] cations, so that **1** and **2** share the precursor **4** This approach is more convenient with respect to one in which the pyran[1,3] or thiopyran ring is formed before macrocyclization, not only because in this way the synthetic sequence diverges only in the last step, but also because macrocyclization of a flexible chain is easier than that of a more rigid structure in which unavoidable repulsions between donor sites are built during the cyclization process We have followed the approach[8] of making the structure rigid after macrocyclization, by constructing an additional aromatic ring, so that the aromatization reaction provides the energy to compensate for the increased repulsions

The building blocks for the preparation of **4a** and **4b** were triethylene and tetraethylene glycol ditosylate, respectively, and the diketone **5** The latter was synthesized from *p*-methylanisole Reaction with glutaryl dichloride and AlCl3 in dichloromethane gave the acylated and demethylated compound **5** in a yield of 86% Compound **5** had already been synthesized, though less efficiently, by double Fries rearrangement of di-*p*-tolyl glutarate [9]



4a, n = 1
4b, n = 2



5

Two-component macrocyclization of **5** with triethylene or tetraethylene glycol ditosylate, and tetramethylammonium methoxide as a base in tetrahydrofuran, was carried out under influxion (Ziegler high dilution) conditions [10] Products **4a** and **4b** were obtained in 53% and 23% yield, respectively

We have anticipated that the 1,5-pentanedione moiety may be regarded as a synthetic precursor of both pyrylium and thiopyrylium cations Conversion of the diketones **4a** and **4b** into the pyrylium corands **1a** and **1b** could be accomplished in high yield (93%) in acetic anhydride by oxidation with triphenylcarbenium tetrafluoroborate generated *in situ*

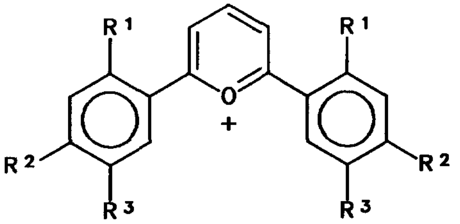
Heterocyclization of **4a** and **4b** to the thiopyrylium corands **2a** and **2b** was carried out according to the method of Strzelecka and Gionis,[7b] *i e* by reaction with P_4S_{10} in acetic acid and in the presence of lithium perchlorate The yields of **2a** and **2b** were 57% and 53%, respectively

Pyrylium ions are useful synthons because of their reactivity toward nucleophiles These attack the α- and γ-carbon atoms yielding *2H* and *4H* adducts with variable selectivities [4] *2H* Adducts often give rise to other aromatic systems by a ring opening-ring closure sequence. The most important of such transformations is the conversion of the pyrylium ring into that of pyridine [4] Conversion of the pyrylium corands **1a** and **1b** into the corresponding pyridine derivatives **3a** and **3b** was accomplished by reaction with ammonium acetate in acetic acid with yields of 53% and 75%, respectively

Conformational Aspects In the Table are reported the chemical shifts of the β and γ heteroaromatic protons of compounds **1-3** It is interesting to note that on increasing the length of the poly(oxyethylene) bridge, while the γ protons are slightly shifted upfield, the β protons are deshielded by *ca* 0 2 ppm This causes, in the case of **2a**, **2b**, and **3a**, **3b**, the inversion of the order of the Hβ and Hγ chemical shifts, so that the spin systems change in both cases from AB_2 to A_2B In order to clarify the role of the poly(oxyethylene) bridge it has been useful to examine the ^1H NMR data in CD_3CN of the following pyrylium ions which are devoid of the bridge 2,6-bis(2-methoxy-5-methylphenyl)pyrylium (**6**) (Hβ 8 61 ppm, Hγ 8 74 ppm, J = 8 4 Hz),[11] 2,6-bis(4- methoxyphenyl)pyrylium (**7**) (Hβ 8 19 ppm, Hγ 8 66 ppm, J = 8 4 Hz),[11] 2,6-diphenylpyrylium (**8**) (Hβ 8 51 ppm, Hγ 8 95 ppm, J = 8 6 Hz) [12]The chemical shift of Hγ can be considered a probe for the electronic effect of the α-phenyl rings, the Hγ chemical shift order, **8** > **6** ≅ **7**, indicates, as expected, that the substituted phenyl rings are electron-releasing and that their effect is similar In contrast the Hβ chemical shift order, **6** > **8** > **7**, is clearly indicative of a proximity effect in **6**, probably due to through-space electrostatic interactions between the *ortho*-oxygens and the β-protons If one compares the Hβ chemical shifts of **1a** and **1b** with those of **6** and **7**, the following order is found **6** ≅ **1b** > **1a** > **7** This order indicates that the proximity effect between *ortho*-oxygens and

Table Chemical Shifts of β and γ Protons of Compounds **1-3** in CD_3CN

Compound	δ Hβ (ppm)	δ Hγ (ppm)
1a	8 41	8 86
1b	8 57	8 84
2a	8 60	8 85
2b	8 83	8 78
3a	7 53	7 76
3b	7 78	7 74

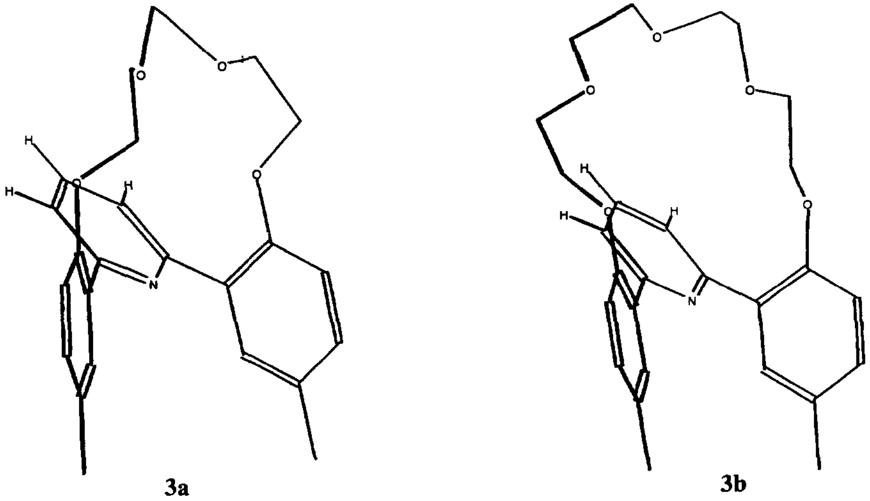


6, R^1 = OMe, R^2 = H, R^3 = Me

7, R^1 = R^3 = H, R^2 = OMe

8, R^1 = R^2 = R^3 = H

β-protons is partially hindered by the poly(oxyethylene) bridge, in particular by the shorter one This conclusion, in view of the chemical shift patterns shown in the Table, would also hold for the thiopyrylium and pyridine corands. Since the NMR data suggest the existence of a conformation of minimum energy in which the *ortho*-oxygens are in close proximity to the β-protons, we have carried out molecular mechanics calculations[13] on the neutral compounds **3a** and **3b**, in that analogous calculations on charged species, like **1** and **2**, would be less reliable Indeed the results of the calculations show a minimum in correspondence of the structures shown in the Figure In both structures the pyridine nucleus tends to fill the cavity of the macroring, the effect being more pronounced with the longer bridge This phenomenon which can be considered a sort of self-complexation, was first recognized by Reinhoudt *et al* [14] in the case of 2,6-pyrido and benzo crown ethers



3a **3b**

Figure. Conformations of Minimum Energy of **3a** and **3b**. Only the Hydrogens on the Pyridine Rings have been reported for clarity

Experimental

Melting points are uncorrected. ^{1}H NMR spectra were recorded with a Varian Gemini 200 and XL-300 spectrometers Chemical shifts are expressed in ppm (δ) from TMS internal standard High resolution EI and FAB mass spectra were obtained with a Kratos MS-80 spectrometer The experimental details to obtain high resolution FAB mass spectra of pyrylium and thiopyrylium ions have been previously reported [15] TLC analyses were performed on Merck 60 F_{254} silica gel plates Column chromatography separations were carried out on Merck 60 silica gel (70-230 mesh) Tetrahydrofuran (THF) was freshly distilled from sodium wires before use Triethylene and tetraethylene glycol ditosylates were prepared according to a literature procedure [16]

1,5-Bis(2-hydroxy-5-methylphenyl)pentane-1,5-dione (5). The reaction was carried out in a dry 500-mL three-necked flask, fitted with reflux condenser and dropping funnel, and connected to a suitable HCl-trap To a mixture of 75 g (0 56 mol) of anhydrous $AlCl_3$ in 125 mL of CH_2Cl_2 were cautiously added 31 g (0 25 mol) of *p*-methylanisole Glutaryl dichloride (21 5 g, 0 125 mol) in 50 mL of CH_2Cl_2 was added dropwise to the resulting solution at a rate that maintained a gentle reflux When the addition was complete, the mixture was heated to maintain reflux for 1 h After cooling to room temperature the reaction solution was poured into a mixture of ice (250 g) and concentrated HCl (150 mL) After separation of the organic phase, the water layer was extracted with methylene chloride The combined organic layers were washed with water and dried ($CaCl_2$), and the solvent was evaporated under reduced pressure to give a solid material The product was recrystallized from ethanol to give pure **5** yield 86%, mp 139-141 C (lit 140-141 C,[9a] 143 C[9b]), ^{1}H NMR (300 MHz) ($CDCl_3$) 2 19 and 2 30 (m and s, 8H, $COCH_2C\mathit{H}_2CH_2CO$ and CH_3), 3 13 (t, J = 6 0 Hz, 4H, $COCH_2$), 6 88 (d, J = 8 6 Hz, 2H, H_3), 7 27 (dd, J = 8 6, 2 Hz, 2H, H_4), 7 55 (d, J = 2 Hz, 2H, H_6), 12 12 (s, 2H, OH)

5',4"-Dimethyl-8,11,14,17-tetraoxa-6,7;18,19-dibenzocyclononadeca-6,18-diene-1,5-dione (4a) A 100 mL solution of **5** (5 0 g, 16 mmol) and triethylene glycol ditosylate (7 3 g, 16 mmol) in THF, and a 100 mL solution of 16 mL of methanolic tetramethylammonium hydroxide (25 wt %, 2 2 M) in THF were simultaneously added over a 5-h period to 100 mL of boiling THF When the addition was complete, the mixture was refluxed for 1 h and then, after having reduced the volume to 50 mL by solvent distillation, was poured into water A solid separated which was collected and purified by column chromatography (silica gel, benzene/ethyl acetate 1 1) and recrystallized from EtOH yield 52 %; mp 136-138 C, ^{1}H NMR (300 MHz) ($CDCl_3$) 1 96 (m, 2H, $COCH_2C\mathit{H}_2CH_2CO$), 2 26 (s, 6H, CH_3), 3 16 (m, 4H, $COCH_2$), 3 71 (s, 4H, OCH_2CH_2O), 3 84 (m, 4H, $ArOCH_2C\mathit{H}_2O$), 4 16 (m, 4H, $ArOC\mathit{H}_2CH_2O$), 6 77 (d, J = 8 4 Hz, 2H, ArH), 7 20 (dd, J = 8 3, 2 4 Hz, 2H, ArH), 7 51 (d, J = 2 4 Hz, 2H, ArH), mass spectrum found M^+, 426 208 $C_{25}H_{30}O_6$ requires M^+, 426 204

5',4"-Dimethyl-8,11,14,17,20-pentaoxa-6,7;21,22-dibenzocyclodocosa-6,21-diene-1,5-dione (4b) was prepared from tetraethylene glycol ditosylate similarly to **4a.** After having reduced the volume of the final reaction mixture to 50 mL, it was poured into water and extracted with ethyl ether The combined ethereal extracts were washed with a 0 25 M NaOH aqueous solution, with water and dried (Na_2SO_4) By removal of the solvent an oil was obtained that was purified by column chromatography (silica gel, ethyl ether) to give a solid product yield 23 %, mp (EtOH) 86-87 C; ^1H NMR (300 MHz) ($CDCl_3$) 2 06 (m, 2H, $COCH_2C\mathit{H}_2CH_2CO$), 2 28 (s, 6H, CH_3), 3 15 (m, 4H, $COCH_2$), 3 67 (s, 8H, OCH_2CH_2O), 3 85 (m, 4H, $ArOCH_2C\mathit{H}_2O$), 4.18 (m, 4H, $ArOC\mathit{H}_2CH_2O$), 6.80 (d, J = 8 4 Hz, 2H, ArH), 7 21 (dd, J = 8 4, 2 4 Hz, 2H, ArH), 7 50 (d, J = 2 4 Hz, 2H, ArH); mass spectrum found· M^+, 470 223 $C_{27}H_{34}O_7$ requires M^+, 470 230

5',4''-Dimethyl-4,7,10,13-tetraoxa-20-oxonia-2,3;14,15-dibenzobicyclo[14,3,1]icosa-1(20),2,14,16,18-pentaene tetrafluoroborate (1a) Compound **4a** (0 89 g, 2 1 mmol) and triphenylmethanol (0 59 g, 2 3 mmol) were dissolved in 15 mL of warm acetic anhydride To the well-stirred solution was added dropwise a solution of 50% HBF_4 (0 84 g, 4 8 mmol) in 10 mL of acetic anhydride (this solution must be prepared by adding the HBF_4 in drops to the ice-cooled and well stirred Ac_2O) The reaction mixture was warmed to 50 C for 30 m After cooling to room temperature, ether was added until complete precipitation of the product **1a**, which was collected and washed with ether The crude solid was purified by dissolution in the least amount of CH_2Cl_2 followed by precipitation with dry ether yield 93 %, mp 218-220 C, ^1H NMR (300 MHz) (CD_3CN) 2 40 (s, 6H, CH_3), 3 06 (s, 4H, OCH_2CH_2O), 3 45 (m, 4H, $ArOCH_2C\mathit{H}_2O$), 4 29 (m, 4H, $ArOC\mathit{H}_2CH_2O$), 7 22 (d, J = 8 4 Hz, 2H, ArH), 7.57 (dd, J = 8 4, 2 1 Hz, 2H, ArH), 7 75 (d, J = 2 1 Hz, 2H, ArH), 8 41 (d, J = 8 1 Hz, 2H, H_{17} and H_{19}), 8 86 (t, J = 8.1 Hz, 1H, H_{18}), FAB mass spectrum, found M^+, 407 188. $C_{25}H_{27}O_5$ requires M^+, 407 186

5',4''-Dimethyl-4,7,10,13,16-pentaoxa-23-oxonia-2,3;17,18-dibenzobicyclo[17,3,1]tricosa-1(23),2,17,19,21-pentaene tetrafluoroborate (1b) was prepared from **4b** similarly to **1a** yield 93%, mp 188-189 C, ^1H NMR (300 MHz) (CD_3CN) 2 43 (s, 6H, CH_3), 3 28 and 3 34 (m, 8H, OCH_2CH_2O), 3 71 (m, 4H, $ArOCH_2C\mathit{H}_2O$), 4 31 (m, 4H, $ArOC\mathit{H}_2CH_2O$), 7 20 (d, J = 8 5 Hz, 2H, ArH), 7 57 (dd, J = 8 5, 2 2 Hz, 2H, ArH), 7 88 (d, J = 2 2 Hz, 2H, ArH), 8 57 (AB_2-system, J = 8 3 Hz, 2H, H_{20} and H_{22}), 8 84 (AB_2-system, J = 8 3 Hz, 1H, H_{21}), FAB mass spectrum, found M^+, 451 213 $C_{27}H_{31}O_6$ requires M^+, 451 212

5',4''-Dimethyl-4,7,10,13-tetraoxa-20-thionia-2,3;14,15-dibenzobicyclo[14,3,1]icosa-1(20),2,14,16,18-pentaene perchlorate (2a) [17] A mixture of **4a** (0 85 g, 2 mmol), phosphorous pentasulfide (0 67 g, 3 mmol) and lithium perchlorate (1 28 g, 12 mmol) was refluxed with stirring in 10 mL of acetic acid After 2 h a white precipitate was filtered off and washed with hot acetic acid A crude solid was precipitated by addition of diethyl ether to the filtrate This was dissolved in the least amount of CH_3CN and reprecipitated with ether The ^1H NMR spectrum of this material was consistent with the expected thiopyrylium cation contaminated by the corresponding pyrylium ion (molar ratio **2a** **1a** = 4 1) The purification of **2a** relied on the higher reactivity toward nucleophiles of the pyrylium with respect to the thiopyrylium ring [18] Addition of the proper amount of methoxide ion which, selectively adds to the pyrylium ring, allows the isolation of **2a**. The purification procedure had been already experimented in analogous cases and described in detail [7c] Yield 57 %, mp 184-185 C, ^1H NMR (200 MHz) (CD_3CN) 2 43 (s, 6H, CH_3), 3 40 (s, 4H, OCH_2CH_2O), 3 70 (m, 4H, $ArOCH_2C\mathit{H}_2O$), 4 32 (m , 4H, $ArOC\mathit{H}_2CH_2O$), 7 18 (d, J = 8 8 Hz, 2H, ArH), 7 46-7 56 (m, 4H, ArH), 8 60 (AB_2-system, J = 8 7 Hz, 2H, H_{17} and H_{19}), 8 85 (AB_2- system, J = 8 7Hz, 1H, H_{18}), FAB mass spectrum, found M^+, 423 1585 $C_{25}H_{27}O_4S$ requires M^+, 423 163

5',4"-Dimethyl-4,7,10,13,16-pentaoxa-23-thionia-2,3;17,18-dibenzobicyclo[17,3,1]tricosa-1(23),2,17,19, 21-pentaene perchlorate (2b) [17] was prepared from **4b** similarly to **2a** yield 53 %; mp 101 C (dec), ^1H NMR (300 MHz) (CD_3CN) 2 40 (s, 6H, CH_3), 3 31 and 3.38 (m, 8H, OCH_2CH_2O), 3.72 (m, 4H, $\mathrm{ArOCH_2C}H_2\mathrm{O}$), 4 28 (m, 4H, $\mathrm{ArOC}H_2\mathrm{CH_2O}$), 7 20 (d, J = 8 5 Hz, 2H, ArH), 7 48-7.58 (m, 4H, ArH), 8 78 (A_2B-system, J = 8.8 Hz, 1H, H_{21}), 8 83 (A_2B-system, J = 8 8 Hz, 2H, H_{20} and H_{22}), FAB mass spectrum, found M^+, 467 194 $C_{27}H_{31}O_5S$ requires M^+, 467 189

5',4"-Dimethyl-4,7,10,13-tetraoxa-20-aza-2,3;14,15-dibenzobicyclo[14,3,1]icosa-1(20),2,14,16,18-pentaene (3a) A solution of **1a** (0.95 g, 1 92 mmmol) and ammonium acetate (1 5 g, 19 5 mmol) in 10 mL of glacial acetic acid was heated under reflux for 4 h After being cooled to room temperature, the reaction mixture was poured into water The mixture was made alkaline with NaOH and extracted with ether. The organic extracts were washed with water and dried over Na_2SO_4, and the solvent was removed under reduced pressure The product was purified by column chromatography (benzene/ethyl acetate 1 1) and recrystallized from acetone yield 53 %, mp 122-123 C, ^1H NMR (300 MHz) (CD_3COCD_3) 2 34 (s, 6H, CH_3), 3 10 (s, 4H, OCH_2CH_2O), 3.49 (m, 4H, $\mathrm{ArOCH_2C}H_2\mathrm{O}$), 4 07 (m, 4H, $\mathrm{ArOC}H_2\mathrm{CH_2O}$), 7 00 (d, J = 8 3 Hz, 2H, ArH), 7 18 (dd, J = 8 3, 2 2Hz, 2H, ArH), 7.43 (d, J = 2.2 Hz, 2H, ArH), 7 53 (AB_2- system, J = 7 7 Hz, 2H, H_{17} and H_{19}), 7 76 (AB_2-system, J = 7 7 Hz, 1H, H_{18}), mass spectrum, found: M^+, 405 1945 $C_{25}H_{27}NO_4$ requires M^+, 405 194

5',4"-Dimethyl-4,7,10,13,16-pentaoxa-23-aza-2,3;17,18- dibenzobicyclo[17,3,1]tricosa-1(23),2,17,19,21-pentaene (3b) was prepared from **1b** similarly to **3a** yield 76 %, mp (acetone) 149-150 C, ^1H NMR (300 MHz) (CD_3COCD_3) 2 34 (s, 6H, CH_3), 3 31 and 3 38 (m, 8H, OCH_2CH_2O), 3 72 (m, 4H, $\mathrm{ArOCH_2C}H_2\mathrm{O}$), 4 11 (m, 4H, $\mathrm{ArOC}H_2\mathrm{CH_2O}$), 6 98 (d, J = 8 4 Hz, 2H, ArH), 7 16 (dd, J = 8 3, 2 4 Hz, 2H, ArH), 7 70 (d, J = 2 4 Hz, 2H, ArH), 7 74 (A_2B-system, J = 7 9 Hz, 1H, H_{21}), 7 78 (A_2B-system, J = 7 9 Hz, 2H, H_{21} and H_{22}), mass spectrum, found M^+, 449 222 $C_{27}H_{31}NO_5$ requires M^+, 449 220

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(17) **CAUTION** Organic perchlorates are potentially explosive Small quantities of the material should be handled with all necessary precautions

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