Keywords: biaryls · carboxylic acids · chirality · crystal engineering · hydrogen bonds

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[10] The dihedral angle between the least squares planes of the aromatic rings is 86.26(6)°. However, the pivot atoms of the substituents are displaced from the aromatic planes by as much as 0.190(3) Å (C11). The carboxyl groups, the hydrogen atoms of which were located and refined, are also essentially planar but adopt various orientations relative to their parent aromatic rings, with the dihedral angles of the carboxyl planes relative to the adjacent aromatic rings being 8.1(4)° for the C7-, 35.1(3)° for C8-, 14.2(3)° for C17-, and 44.5(2)° for C18-carboxyl. Steric bulk imposed by the carboxyl groups together with the crystal packing is assumed to be the responsible factor.

[11] There are two crystallographically independent double hydrogen bonds, both nearly planar and with asymmetrically disposed hydrogen atoms, one links O1 and O2 with O12′ and O11′ whereas the other links O3 and O4 with O14″ and O13″.

[12] According to Eliel,[13] no organic molecules of D_4 symmetry have yet been synthesized. Also, to the best of our knowledge, no hydrogen bond organized substructure of D_4 symmetry has been found in any previously known crystal structure.

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[17] Viability of this concept has been already demonstrated in our recent crystallographic study[5] of the chiral 2,2′-bipyridine-3,3′-dicarboxylic acid-1,1′-dioxide (C_2 symmetry), which revealed a self-assembly into a chiral "square" grid that was organized by the hydrogen bonding (−N−O···H−O−CO−) synthon.

[18] While generation of polar layers is relatively straightforward, their eclipsed stacking remains generally a great challenge for crystal engineering. The eclipsed stacking may be induced in the present case, for example, by introduction of the 4,4′-carboxyl groups into the tecton **2**, to allow the formation of an additional (orthogonal) network of intermolecular hydrogen bonds. A successful application of such a hydrogen-bond network in cross-linking supramolecular tapes has recently been reported.[19]

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High-Yielding Rotaxane Synthesis with an Anion Template**

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Molecules such as rotaxanes and catenanes that are noncovalently interlocked by mechanical bonds between two or more molecular components are of current interest. Their synthesis is usually based on some kind of template assistence such as the preorganization of building blocks by metal coordination, hydrophobic and donor-acceptor interactions, or hydrogen bonding.[1] Here we report on a new synthesis of rotaxanes based on the action of a supramolecular nucleophile, which is formed from the molecular recognition of an anionic stopper by a tetralactam wheel.

Some examples of recognition of anions by neutral organic ligands have been reported, and mostly feature several amide, sulfonamide, or urea groups as the hydrogen bond donors.[2] Macrocyclic lactams such as **1**, which have often been used in rotaxane and catenane syntheses,[1d] contain several aromatic

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[**] We thank Prof. J. L. Sessler, University of Texas, Austin, for fruitful discussions and cooperation in regard to anion complexation and Prof. K. Gloe, Universität Dresden, and Dr. H. Stephan, Forschungszentrum Rossendorf, for investigating anion extraction from aqueous phases. We also thank our co-workers J. Flörke, C. Heim, and A. Mohry for providing some of the substances used. This work was supported by the Deutsche Forschungsgemeinschaft (Vo 145/47-1).

amide groups, the NH protons of which point toward the macrocycle center, as revealed by several X-ray structures.[3]

Tetralactam **1a**[4] (see Scheme 1) binds secondary amides in CD_2Cl_2 where it clearly serves as a hydrogen-bond donor.[5] Semirotaxane complexes with in situ formed amide semiaxles[6] are most likely the decisive precursors[1d] in the corresponding rotaxane and catenane syntheses. We set out to elicit if anions that act as hydrogen-bond acceptors could also be bound in a similar way even if it can be ruled out on steric grounds that both isophthalic amide residues simultaneously contact one and the same anion.

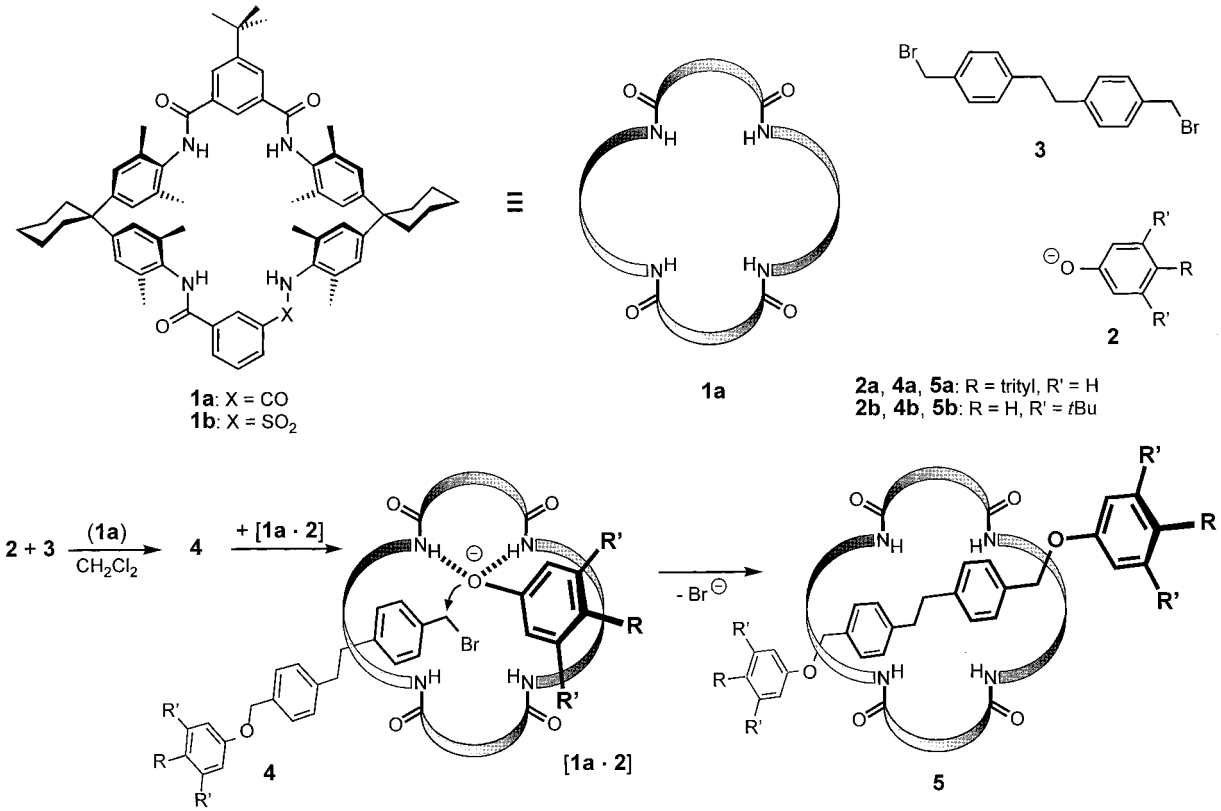
Indeed, NMR experiments with tetrabutylammonium salts of halides and some oxoanions in CD_2Cl_2 show the strong downfield shifts of the NH protons typical for hydrogen bonding; the "inner" (H-2) protons of the isophthalic acid moieties of **1a** are likewise affected but to a somewhat lesser extent.[7] Job plots confirm a 1:1 stoichiometry of the complexes.[8] In some cases the binding is too tight for an accurate determination of the association constants (probably $>10^5\,\text{M}^{-1}$) so that a 4:1 mixture of CD_2Cl_2 and CD_3OD had to be used for the titrations to reduce the affinities.[9] Monosulfonamide trilactam **1b** also serves as host, but the binding strength is considerably weaker, especially for halides. The anion binding properties are summarized in Table 1.

These results encouraged us to investigate the affinity of the macrocycles for organic anions that might serve as nucleophiles in S_N reactions, to evaluate their possible application in rotaxane syntheses. In fact, as revealed by NMR spectroscopy under typical synthetic conditions (5 mM tetralactam **1a**, CD_2Cl_2), phenolates, thiophenolates, and sulfonamide anions are bound close to quantitatively.[10] Even if the association is remarkably strong, it was not clear, however, if a complex of a macrolactam such as **1a** with, for example, a phenolate stopper or a phenolate axle center piece would be a suitable template for a threading-type phenyl ether rotaxane synthesis, since these anions would probably be positioned "on top" of the wheel rather than thread through it under formation of a prerotaxane. The reaction of *p*-tritylphenolate **2a**, dibromide **3**,[11] and wheel **1a**, nevertheless, produced the rotaxane **5a** in the surprisingly high yield of 95% (Scheme 1). This is

Table 1. Association constants K_a [M^{-1}] (error ±15%) of the macrocycles **1a** and **1b** with anions[a] determined by NMR titration at room temperature in CD_2Cl_2.

Ligand	Solvent	F^-	Cl^-	Br^-	I^-	AcO^-	NO_3^-	$H_2PO_4^-$
1a	CD_2Cl_2	200	–[b]	–[b]	–[b]	1.8×10^5	–[b]	–[b]
1a	CD_2Cl_2/CD_3OD (4/1)	–[c]	330	420	–[d]	120	250	–[d]
1b	CD_2Cl_2	–[c]	290	290	50	1.5×10^4	60	2.4×10^3

[a] The anions were added as tetrabutylammonium salts. [b] K_a is too high to be determined by NMR spectroscopy. [c] No binding detected. [d] Same order of magnitude as Cl^- and Br^-, but the shift values are small and the calculated values neither precise nor accurate.



Scheme 1. High-yielding anionic template synthesis of rotaxanes **5** with bis(phenyl ether) axles where phenolate–wheel complexes [**1a**·**2**] act as supramolecular nucleophiles for the reaction with semiaxles **4**.

  1433-7851/99/3803-0384 $ 17.50+.50/0 *Angew. Chem. Int. Ed.* **1999**, *38*, No. 3

probably the highest yield reported so far for this kind of synthesis. We assume that in a first step the dibromide **3** reacts with the stopper–wheel complex [**1a**·**2a**] to form the semiaxle **4a** and probably causes subsequent dissociation of the resulting semirotaxane complex.[12] Free **4a** then reacts with a second phenolate–lactam complex [**1a**·**2a**]—which acts as a supramolecular nucleophile—to furnish the rotaxane **5a**.[13]

To the best of our knowledge this is the first case of a rotaxane synthesis based on the assistence of an anionic template. The yield of rotaxane **5b** with 3,5-di-*tert*-butylphenolate **2b** as the stopper component was 57%.[14] With this smaller stopper the rotaxane is only metastable, that is, during the course of the synthesis at room temperature the axle slowly slips from the wheel and breaks the mechanical bond so that the free components remain. The process of decay can be monitored by NMR spectroscopy by the growth of signals of the free components. About 10% of dethreading is observed during 48 h at room temperature in $CDCl_3$.[15]

To sum up, lactam macrocycles exhibit strong affinities for small inorganic anions as well as organic anions in nonpolar solvents. Based on the latter we were able to introduce a new anionic template synthesis of rotaxanes with high yield, which possibly also opens the way for the formation of other types of mechanically interlocked molecules such as catenanes and knots. We are currently investigating the scope of application for other organic anions such as thiophenolates, sulfonamidates, and carboxylates as well as carbanions.[16]

Experimental Section

5a: A mixture of **1a**[4] (48.1 mg, 0.05 mmol), *p*-tritylphenol H-**2a** (33.6 mg, 0.1 mmol, Lancaster), and dibromide **3**[11] (18.4 mg, 0.05 mmol) in CH_2Cl_2 (10 mL) was stirred with solid K_2CO_3 (25 mg) for 7 d at room temperature. The solid was removed by filtration, and the organic solution washed with water and dried over $MgSO_4$. Column chromatography on silica gel with CH_2Cl_2/ethyl acetate (30/1) yielded **5a** (89 mg, 0.048 mmol, 95%) as a white powder. M.p. 175–177 °C; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.34$ (s, 9H, *t*Bu-CH_3), 1.56, 1.68, and 2.34 (b, 4H, 8H, and 8H, respectively, cyclohexanediyl CH_2), 1.93 (s, 24H, aryl CH_3), 2.49 (s, 4H, C_2H_4), 4.52 (s, 4H, OCH_2), 6.49 and 6.90 (AA′BB′, 8H, $J = 8.7$ Hz, phenoxy H-2/6 and H-3/5, respectively), 6.51 and 6.66 (AA′BB′, 8H, $J = 7.9$ Hz, *p*-xylylene), 7.02 (s, 8H, amidophenyl), 7.1–7.25 (m, 30H, trityl), 7.43 (s, 1H, isophthaloyl H-2), 7.60 (t, 1H, $J = 7.7$ Hz, isophthaloyl H-5), 7.65 (s, 1H, isophthaloyl H-2), 8.12 (d, 2H, $J = 7.7$ Hz, isophthaloyl H-4/6), 8.16 (s, 2H, 5-*t*Bu-isophthaloyl H-4/6); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 18.83$ (aryl CH_3), 23.00 (cyclohexanediyl CH_2), 26.34 (cyclohexanediyl CH_2), 31.16 (5-*t*Bu-isophthaloyl CH_3), 35.31 (5-*t*Bu-isophthaloyl C_q), 35.78 (cyclohexanediyl CH_2), 37.45 (C_2H_4), 45.41 (cyclohexanediyl C_q), 64.28 (Ph_3C), 69.86 (OCH_2), 113.27 (CH), 121.37 (CH), 125.97 (CH), 126.32 (C_q), 126.92 (CH), 127.48 (CH), 127.66 (CH), 128.10 (CH), 129.27 (CH), 130.36 (C_q), 130.91 (C_q), 131.01 (CH), 131.11 (C_q), 132.02 (CH), 132.36 (CH), 134.32 (C_q), 134.57 (C_q), 134.77 (C_q), 140.05 (C_q), 140.94 (C_q), 146.79 (C_q), 148.82 (C_q), 156.28 (C_q), 165.01 (CO), 165.45 (CO); MALDI-MS: *m/z*: 1863.2 [M^+].

5b: As above but 3,5-di-*tert*-butylphenol H-**2b** (Aldrich) was used as the stopper, 0.1 equivalents dibenzo[18]crown-6 were added to the mixture, stirring was continued for 3 d, and the chromatography eluent was petroleum ether (40–60)/ethyl acetate (15/1). The yield was 57%. M.p. 206–208 °C; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.23$ (s, 36H, 3,5-di-*t*Bu-phenyl CH_3), 1.38 (s, 9H, isophthaloyl-*t*Bu CH_3), 1.56, 1.68, and 2.35 (b, 4H, 8H, and 8H, cyclohexanediyl CH_2), 1.94 and 1.95 (2 s, 12H each, aryl CH_3), 2.45 (s, 4H, C_2H_4), 4.58 (s, 4H, OCH_2), 6.45 and 6.60 (AA′BB′, 8H, $J = 7.9$ Hz, *p*-xylylene H), 6.66 (s, 4H, phenoxy H-2/6), 7.04–7.08 (m, 10H, phenoxy H-4 and amidophenyl), 7.58 (s, 1H, isophthaloyl H-2), 7.62 (t, 1H, $J = 7.7$ Hz, isophthaloyl H-5), 7.74 (s, 1H, isophthaloyl H-2), 8.16 (d, 2H, $J = 7.7$ Hz, isophthaloyl H-4/6), 8.21 (s, 2H, 5-*t*Bu-isophthaloyl H-4/6); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 18.78$ (aryl CH_3), 22.97 (cyclohexanediyl CH_2), 26.32 (cyclohexanediyl CH_2), 31.14 (*t*Bu-isophthaloyl CH_3), 31.33 (stopper-*t*Bu CH_3), 34.93 (stopper-*t*Bu C_q), 35.30 (*t*Bu-isophthaloyl C_q), 35.66 (cyclohexanediyl CH_2), 37.56 (C_2H_4), 45.29 (cyclohexanediyl C_q), 69.96 (OCH_2), 108.77 (stopper CH), 115.74 (stopper CH), 121.46 (CH), 124.17 (CH), 126.21 (CH), 126.78 (CH), 127.93 (CH), 128.62 (CH), 129.41 (CH), 130.34 (CH), 130.98 (C_q), 131.12 (C_q), 132.10 (CH), 134.38 (C_q), 134.48 (C_q), 134.66 (C_q), 134.78 (C_q), 140.80 (C_q), 148.62 (C_q), 148.74 (C_q), 152.60 (C_q), 154.16 (C_q), 157.92 (C_q), 164.96 (CO), 165.37 (CO); FAB-MS: *m/z*: 1580.1 [MH^+].

Received: September 14, 1998 [Z12408IE]
German version: *Angew. Chem.* **1999**, *111*, 395–398

Keywords: host–guest chemistry · nucleophilic substitutions · rotaxanes · supramolecular chemistry · template synthesis

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[6] Rotaxanes are molecular compounds that consist of one or more wheels and penetrating axles that are mechanically bound together and sterically prevented from dethreading by bulky stopper groups at both ends of the axles. Semirotaxanes and pseudorotaxanes are analogous "conventional" inclusion complexes that are not restrained mechanically from dissociation since the axles (here semi- and pseudoaxles, respectively) carry only one stopper or no stopper at all, respectively. We propose semi- and pseudorotaxanes that act as precursors in rotaxane syntheses to be called prerotaxanes. Compare with P. R. Ashton, D. Philp, N. Spencer, J. F. Stoddart, *J. Chem. Soc. Chem. Commun.* **1991**, 1677 – 1679.

[7] The isophthaloylic H-2 proton signals of host **1a** in CD_2Cl_2 shift about 0.7 ppm downfield in the complex with bromide and 0.45 ppm with acetate anions relative to the free host. The complexation-induced shifts of the NH protons are 1.7 and 1.8 ppm, respectively (δ values for the complexes have been extrapolated from the titration curves). Preliminary studies also show that host **1a** can extract Cl^- and Br^- ions in the presence of tetrabutylammonium ions from an aqueous into an organic phase and maintain a clean 1:1 stoichiometry. The phase transfer of oxoanions is currently under investigation; H. Stephan, Forschungszentrum Rossendorf, personal communication.

[8] M. T. Blanda, J. H. Horner, M. Newcomb, *J. Org. Chem.* **1989**, *54*, 4626 – 4636.

[9] Titrations were made by the stepwise addition of a solution of one of the salts to a solution of a macrocycle. Nonlinear curve-fitting of the shift values of all nonoverlapped signals with significant complexation-induced shifts gave the association constants K_a, the average of which is given for each anion. See C. S. Wilcox in *Frontiers in Supramolecular Organic Chemistry and Photochemistry* (Eds.: H.-J. Schneider, H. Dürr), VCH, Weinheim, **1991**, pp. 123 – 143, and references therein.

[10] Addition of triethylammonium 3,5-di-*tert*-butylphenolate to **1a** in CD_2Cl_2 caused only weak chemical shifts. With protonated 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as the counterion, the binding constant was about $30\,M^{-1}$. A very tight binding only occured when the phosphazene base "P_4-*t*-Bu" (1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phosphoranylideneamino]-2λ^5,4λ^5-catenadiphosphazene; Fluka) was used to obtain the phenolate. The "free" anion is probably only formed in the nonpolar environment with this extremely strong, voluminous base. Line-broadening in the presence of less than one equivalent of phenolate **2** makes quantification difficult, but we estimate that at least 95% of the complex is formed at a concentration of 5 mM. The assiociation constant in a mixture of CD_2Cl_2/CD_3OD (4/1) is $280 \pm 10\,M^{-1}$, that is, similar to the inorganic anions. Thiophenol, toluene-4-sulfonamide, and *N*-(4-*tert*-butylphenyl)-4-*tert*-butylphenylsulfonamide behave in a similar way.

[11] H. Steinberg, D. J. Cram, *J. Am. Chem. Soc.* **1952**, *74*, 5388 – 5391.

[12] Addition of dibromide **3** or a diphenyl ether derived from it without voluminous stopper groups did not cause any significant NMR shifts of the wheel protons in CD_2Cl_2, hence we assume that the semirotaxanes formed with monoether **4** are not stable and thus do not act as prerotaxanes.

[13] In the syntheses of amide-based rotaxanes we often observed that highly reactive starting compounds such as aliphatic acid chlorides and aliphatic amines tended to produce considerably lower yields of rotaxanes relative to less active aromatic acid chlorides and anilines, respectively. We thus decided not to use preformed phenolate salts here, but rather to create them slowly in situ with a suspension of solid K_2CO_3 as the base.

[14] The rotaxanes show the typical upfield shifts ($\Delta\delta$) of proton signals relative to the free components in the NMR spectra recorded in $CDCl_3$. Selected $\Delta\delta$ values of **5a** (**5b**): Axle: C_2H_4 0.49 (0.46), OCH_2 0.53 (0.48), *p*-xylylene 0.72 (the signal at lower field is overlapped in the free axle here) (0.79 and 0.80), oxophenyl H-2/6 0.37 (0.33); wheel: isophthaloyl H-2 0.46 and 0.48 (0.34 and 0.41).

[15] Deslipping had earlier been observed with similar rotaxanes: M. Händel, M. Plevoets, S. Gestermann, F. Vögtle, *Angew. Chem.* **1997**, *109*, 1248 – 1250; *Angew. Chem. Int. Ed. Engl.* **1996**, *36*, 1199 – 1201. Newer results reveal the process being of first order; F. Vögtle, A. Affeld, C. Heim, unpublished results.

[16] The new method has already been applied successfully to the synthesis of analogous rotaxanes with ester, thioester, sulfide, and acetal axles since the submission of this communication.

Replacement of C–O by P–O in Cyclic Acetals and Ketals**

Feng Wang, Shuguang Ma, W. Andy Tao, and R. Graham Cooks*

Organophosphorus compounds are used in plasticizers, pharmaceuticals, pesticides, and warfare agents. Owing to their wide application, a variety of mass spectrometric techniques have been suggested for their identification[1] and used to study their gas-phase reactivity.[2] Phosphanylium ions (phosphenium ions, $R-P^+-R$), for example, participate in reactions that include insertion, proton transfer, hydride abstraction, electron transfer, cluster formation,[2–4] and [4+2$^+$] cycloaddition.[5] However, most gas-phase ion chemical studies of organophosphorus esters have been limited to characterization of molecular ions and reactions of the ions with their neutral precursors.[1, 4, 6] Methanol, formaldehyde, and alkene eliminations are commonly observed fragmentation processes. The generation and reaction of phosphorus-containing distonic ions has also received attention.[6a, 7]

Aiming to explore the chemistry of phosphoryl-containing cations, and ultimately contribute to increased understanding of the mechanism of hydrolysis of oxyphosphoranes[8] and related phosphoryl-transfer reactions in biomolecules,[9] we report here on the reactions of the phosphonium ions $CH_3P(O)OCH_3^+$ and $CH_3OP(O)OCH_3^+$. Alkyl-substituted 1,3-dioxolanes are chosen as the neutral reactants because of their reactivity with the analogous acylium ions.[10, 11]

In solution, acyl transfer is a well-documented method of converting aldehydes and ketones into acetals and ketals and so protecting or, in the case of transacetalization, transferring the carbonyl group. Eberlin et al. discovered and elucidated

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[**] This work was supported by the National Science Foundation and the U.S. Department of Energy, Office of Basic Energy Science.

  1433-7851/99/3803-0386 $ 17.50+.50/0