Proton-Template Synthesis, Structure, and Characterization of a Robson-Type Macrocycle with a Totally π-Conjugated System

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π-Conjugated (**1**−**4**) and partially reduced (**5**) macrocyclic Schiff bases have been obtained by proton-template condensation of 2,6-diformyl-4-R_1-phenol (R_1 = Me, *t*-Bu) with 1,2-diamino-4,5-R_2-benzene (R_2 = H, Me). The macrocyclic ligands have been characterized by elemental analysis, by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy, and by electron impact mass spectrometry. Also, the X-ray crystal structures of **1** and **2** were solved. The crystals were all grown from formic acid. Crystal **1** is triclinic, space group $P\bar{1}$ with a = 867.1(5), b = 916.3(4), and c = 1087.2(3) pm and α = 69.62(2), β = 87.57(3), and γ = 63.72(4)° for Z = 1. Crystal **2** is monoclinic, space group $P2_1/n$ with a = 632.0(1), b = 1661.5(3), and c = 1658.0(3) and β = 99.87(3)° for Z = 2. Both of the molecules are planar with centers of symmetry. They are protonated twice while being neutralized by two negatively charged perchlorate ions.

Introduction

Binuclear macrocyclic complexes of the Robson type are of interest as models of biomolecules. Since the1970s they have been prepared and widely studied.[1−23] Because of the methodology of the template route, the complexes are restricted mainly to those metal ions that can be employed as the template reagents, although sometimes such complexes can also be obtained by metal−metal exchange.[24]

Recently we reported the proton-template synthesis of a metal-free macrocyclic ligand **1** composed of a totally π-conjugated system, and from this ligand the binuclear Ni(II)- and Cu(II)-complexes were successfully produced.[25] It was earlier shown by Brychcy et al. that only the binuclear Cu(II)-complex of **2** can be synthesized by the metal template route. When other metals are employed as the template ions, they lead only to the mononuclear complexes and in some cases the partially reduced metal-free macrocycle is produced.[26−28] If rare earth metals are employed as template ions, the mononuclear sandwich-like complexes result.[29] From the metal-free ligands, some other binuclear complexes, for example, the mixed valence Co(II)−Co(III)-complexes[30] can be obtained. Because of the π-conjugated system of these ligands, their complexes have shown extraordinary behaviors comparable to those of other Robson-type macrocycles. In this paper, we report a serial synthesis of the π-conjugated macrocycles **1**−**4** as well as partially reduced macrocycle **5,** and their characterization by IR, UV, and NMR spectroscopic and X-ray crystal structure analysis.

Results and Discussion

Synthesis and Characterization of the Macrocycles. The preparation of **1** was first attempted by the

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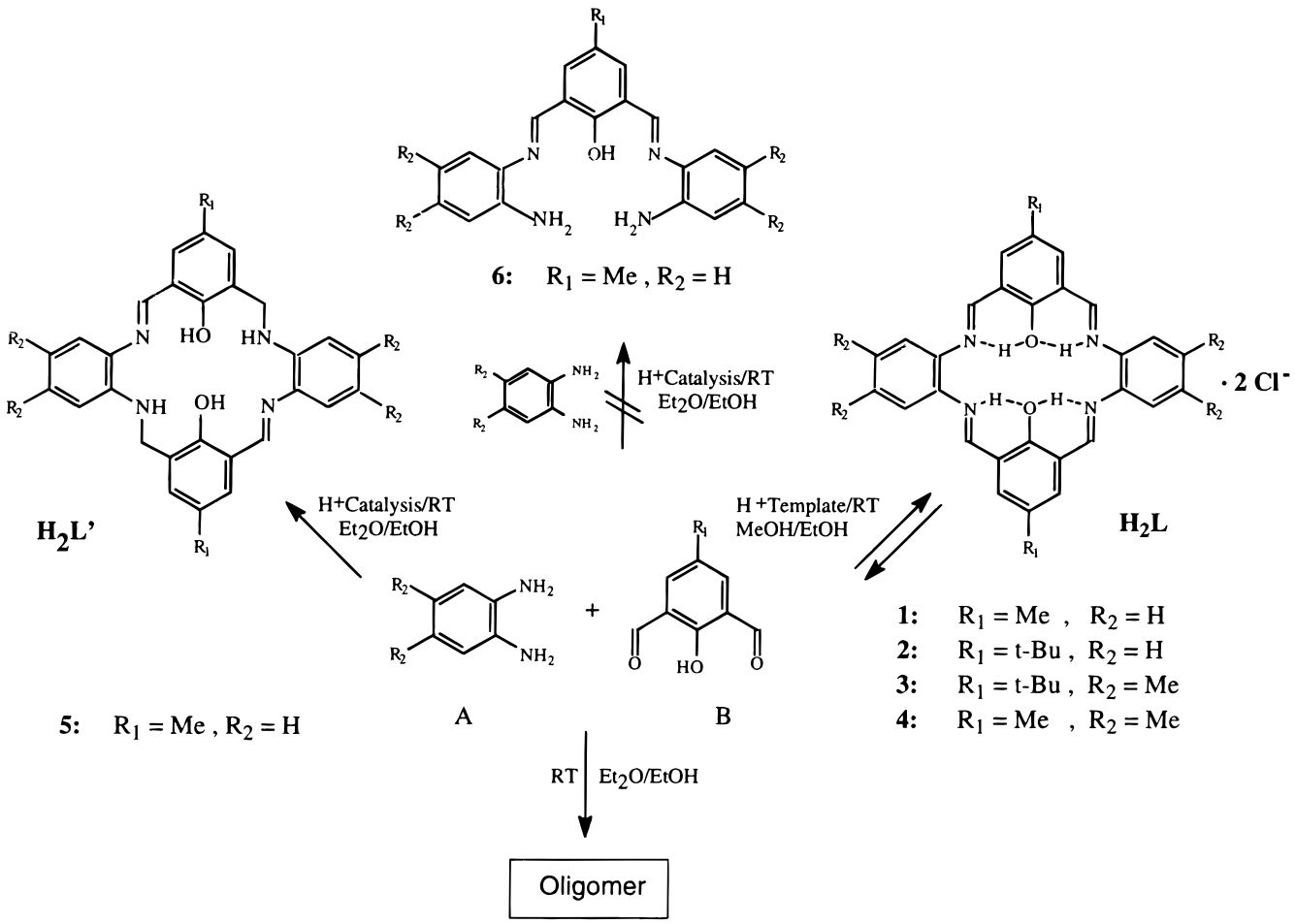
Scheme 1



Schiff base condensation of 2,6-diformylphenol and *o*-phenylenediamine at room temperature, but this led to an oligomer, the terminal groups of which were identified from IR spectra ($\nu_{C=O}$1680 cm^{-1} and ν_{NH} 3420 cm^{-1}). If a drop of concentrated hydrochloric acid was used as catalyst, the macrocycle **5** was produced, which had been prepared in another way by Vigato et al.[30] When twice the amount of *o*-phenylenediamine was employed, the product was the same as before rather than the [1 +2] product **6**. It is clear that the phenylenediamine functions not only as a component of **5** but also as the reducing reagent. It seems that the driving force for the construction of the macrocycle lies in the formation of hydrogen bonds. If a small number of protons are provided, the macrocycle most likely to result is the partially reduced product **2**, which positions the amino H to form a hydrogen bond with the phenolic oxygen. In the meantime, the phenylenediamine can act as a reducing reagent for the imido groups of the macrocycle. However such reductions to our knowledge have never been reported. Only when an equivalent amount of protons is provided and the mixed solvent of ethanol and methanol is employed is the totally π-conjugated macrocycle **1** formed as its dihydrochloride. In this case the phenylenediamine does not serve a reducing function. In this way, the macrocycles **2**−**4** were produced.

Our results show that the concentrated hydrochloric acid is a suitable proton source that brings relatively few molecules water into the reaction system and has no oxidative function. Therefore it is alternatively feasible to use *o*-phenylenediamine dihydrochloride and keep the reaction system isolated from air.

Another important aspect of this macrocycle preparation is that the reaction must be carried out at room temperature or lower, since the thermodynamics of higher temperature do not permit the formation of the hydrogen bonds that drive the reactant molecules to assemble into the macrocycle.

The electron impact (EI) mass spectra of the macrocycles show peaks resulting from both molecular ions and fragmentation products consistent with the structures proposed in Scheme 1. The strong IR absorptions of the C═N groups appear at about 1620 cm^{-1}, and absorptions for C═O and NH are absent. Since we found no suitable solvent for recrystallization, adequate microanalyses for the products H_2L·2HCl were not obtainable. Suitable microanalytical results were obtained for **1**−**3** as H_2L·$2HClO_4$, which recrystallize from warm formic acid (99−100%).

In the UV/vis spectra of H_2L·$2HClO_4$, absorption bands appear at about 300, 380, and 530 nm, which are assigned to π−π* transitions (Table 1). Because of the four methyl groups on the macrocyclic ring of **3** and **4**, all of the absorption bands are red-shifted about 5−15 nm.

Of the products **1**−**3**, which are suitable for combustion analysis, only **2** was characterized by NMR spectroscopy, as permitted by its reasonable solubility in DMSO. Due to the symmetry of the macrocycle, ^{1}H NMR spectroscopy reveals three singlets corresponding to the 18 methyl

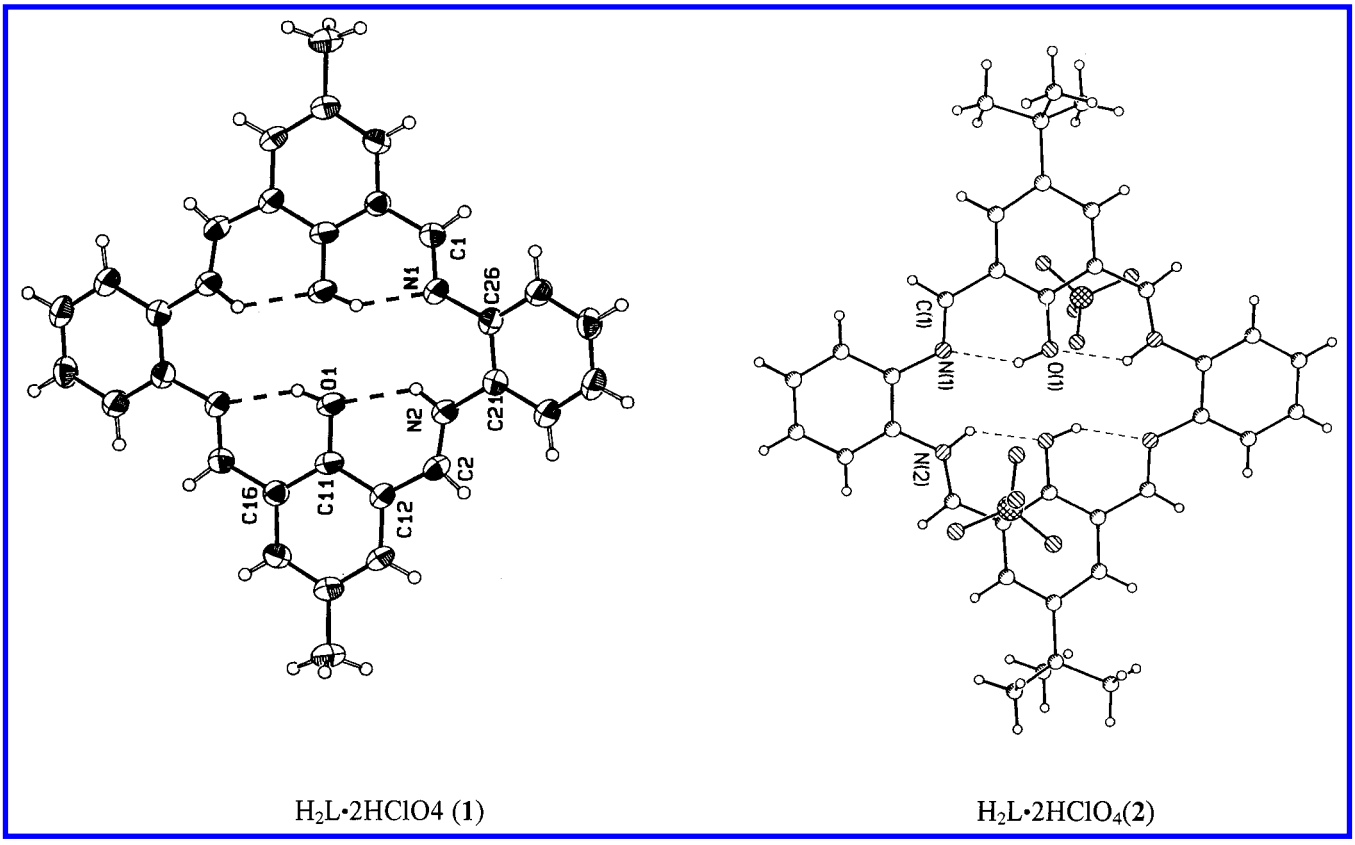


Figure 1. Crystal structure of the macrocyclic ligands.

Table 1. IR and UV Bands of the Macrocyclic Compounds

	IR (cm^{-1})		UV− vis (nm)	
	$\nu_{C=N}$	ν_{phenyl}	$\pi \rightarrow \pi^*$	λ_{max} (log)
1	1631	1618, 1525	285 (4.6)	370 (4.4), 530 (4.1)
2	1635	1616, 1537	290 (4.7)	375 (4.6), 530 (4.3)
3	1635	1603, 1538	305 (5.0)	390 (4.6), 535 (4.6)
4	1635	1605, 1516	305 (4.7)	390 (4.6), 540 (4.4)

protons (δ 1.33) and signals for the four aromatic protons of the 4-*tert*-butylphenol rings (δ 7.91) and for the four protons of the imido groups (δ 9.19), respectively, as well as a pair of four aromatic-proton multiplets (δ 7.40 and 7.79). However, the ^{13}C NMR spectra display only 8 carbon signals for the 10 different carbons, which may result from the relatively low concentration of the sample. The two missing carbon signals belong to Cqu and to CH.

Structure of the Macrocyclic Ligands. Of the compounds **1**−**4**, only the perchlorates of **1** and **2** can be prepared as suitable single crystals for X-ray structural analysis. They are obtained by recrystallization from warm formic acid. Both crystallize in the centrosymmetric space group with the center of symmetry in the macrocycle. As indicated by the carbon−nitrogen bond parameters of the two compounds (Table 2), the molecules are totally π-conjugated, in that all of the nitrogen and carbon atoms (except those of the methyl and *tert*-butyl groups) exhibit typical sp^2 hybridization, and the imido C=N bond lengths are also typical. Therefore both of the molecules can be regarded as planar, although **2** shows a small deviation from the plane.

Molecule **1** has a N_4O_2 plane which is coplanar with the phenyl ring C(21)−C(26) but has a 2.97° dihedral angle with the phenyl ring C(11)−C(16). The molecule **2** has a N_4 plane that is coplanar with the phenyl ring C(21)−C(26) but forms a dihedral angle of 15.9° with the phenyl ring C(11)−C(16) and the phenolic oxygen atoms depart from the N_4 plane about ±41 pm. If half of the diagonal length of the tetragon N_2O_2 is taken to be radius of the binucleating cavity, the average value is 184 pm for **1** and 196 pm for **2**. Between the six donor atoms of N_4O_2, the two phenolic hydrogens and two guest protons act as template ions linking the coordinate atoms with hydrogen bonds. Of these the bonds O-H---N and H-O---H make the greatest contributions to the stabilization of the macrocycles: they measure 186.3 and 196.7 pm for **1** and 190.3 and 201.9 pm for **2**, respectively. This

Table 2. Selected Bond Lengths [pm] and Angles [deg]

compound **1**		compound **2**	
N(2)−C(2)	128.2(4)	N(1)−C(1)	128.7(3)
N(2)−C(21)	142.2(4)	N(1)−C(11)	145.1(3)
N(1)−C(1)	128.1(4)	N(2)−C(2)	129.3(3)
N(1)−C(26)	142.5(4)	C(2)−C(12)[a]	142.9(3)
C(2)−C(12)	142.6(5)	C(11)−C(12)[a]	140.7(3)
C(1)−C(16)[a]	144.1(4)	O(1)−C(11)	134.3(2)
C(21)−C(26)	139.5(4)	N(1)−C(21)	142.2(3)
C(11)−C(12)	140.8(4)	N(2)−C(26)	142.0(3)
C(11)−C(16)	140.1(5)	C(11)−C(16)	140.3(3)
C(11)−O(1)	132.8(4)	C(21)−C(26)	140.5(3)
C(2)N(2)C(21)	128.0(3)	N(1)C(1)C(16)	122.79(19)
C(1)N(1)C(26)	121.1(3)	N(2)C(2)C(12)[a]	125.1(2)
N(2)C(2)C(12)	125.8(3)	O(1)C(11)C(12)	119.07(19)
N(1)C(1)(C16)[a]	123.5(3)	C(11)C(12)C(2)[a]	123.01(19)
N(2)C(21)C(26)	117.8(3)	C(11)C(16)C(1)	121.75(19)
C(21)C(26)N(1)	118.5(3)	C(21)C(26)N(2)	117.43(19)
C(11)C(12)C(2)	122.3(3)	C(2)N(2)C(26)	126.48(19)
C(11)C(16)C(1)[a]	121.6(3)	C(1)N(1)C(21)	119.53(18)
O(1)C(11)C(16)	120.8(3)	O(1)C(11)C(16)	121.75(19)
O(1)C(11)C(12)	119.1(3)	C(26)C(21)N(1)	117.37(18)

[a] Symmetry transformations used to generate equivalent atoms: $-X + 1, -Y, -Z$.

Table 3. Summary of Crystal Data Intensity Collection and Structure Refinement Parameters

	1	2
formula	$C_{30}H_{26}Cl_2N_4O_{10}$	$C_{36}H_{38}Cl_2N_4O_{10}$
M_r	673.45	757.60
T (K)	193(2)	133(2)
crystal system	triclinic	monoclinic
space group	$P-1$	$P2_1/n$
λ (pm)	71.073	71.073
a (pm)	867.1(5)	632.0(1)
b (pm)	916.3(4)	1661.5(3)
c (pm)	1087.2(3)	1658.0(3)
α (deg)	69.62(2)	90
β (deg)	87.57(3)	99.87(3)
γ (deg)	63.72(4)	90
V (nm^3)	0.7196(6)	1.7152(5)
Z	1	2
D_e (Mg/m^3)	1.554	1.467
μ (Mo Kα, mm^{-1})	0.295	0.256
2θ (deg)	4.04−43.98	4.90−55.18
F(000)	348	792
measd refln	2101	25705
unique refln	1756	3967
final R_1[a]	0.0424	0.053
wR_2[b]	0.2145	0.1085

[a] $R_1 = \sum(F_o - F_c)/\sum F_o$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

Table 4. Relevant Hydrogen Bonds Parameters [Bond (ppm), Angle (deg)]

compound **1**		compound **2**	
N(1)···H(1)	186.3	N(1)···H(1)	1.903
O(1)−H(1)	84.0	O(1)−H(1)	84.3
N(2)···H(2)	88.0	N(2)···H(2)	86.2
O(1b)···H(2)	196.7	O(1a)···H(2)	201.9
N(1)···H(2)	233.9	N(1)···H(2)	230.5
N(1)H(1)O(1)	148.42	N(1)H(1)O(1)	147.19
N(2)H(2)O(1b)	132.91	N(2)H(2)O(1a)	131.20

explains why **2** in a proton-accepting solvent is more unstable than **1**. The relevant hydrogen bond parameters are shown in Table 4.

Conclusion

The fully π-conjugated metal-free macrocycles derived from *o*-phenylendiamine and 2,6-diformyl-4-alkylphenol can be prepared by the proton template method. (i) If a stoichiometric amount of protons is supplied, the desired macrocycle is produced. (ii) If the protons are provided in a trace amount as a catalyst, the product is obtained in the partially reduced form. (iii) In generating the fully π-conjugated macrocycles, the formation of hydrogen bonds between the donor atoms plays an important role. Therefore stabilization of the hydrogen bonds must be considered in choosing feasible conditions. (iv) The fully π-conjugated macrocyclic compounds are structurally planar and centrosymmetric molecules with two nucleating cavities of ca. 1.90 pm radius.

Experimental Section

Materials. All reagents and solvents were purchased from commercial sources and used without further purification unless otherwise described.

2,6-Diformyl-4-methylphenol was prepared according to literature procedures.[2] For the preparation of 2,6-diformyl-4-*tert*-butyl-phenol, the method was modified as follows: 4-*tert*-Butylphenol (20 g) and hexamethylenetetraamine (40 g) were mixed in a mortar. The pulverized mixture was added to polyphosphoric acid (300 g) at 110 °C under vigorous stirring. After 10 min reaction the mixture was cooled and hydrolyzed with water and the product was isolated by steam distillation (yield 6.5%).

Synthesis of $H_2L\cdot 2HCl$. The *o*-phenylenediamine (2 mmol) was dissolved in 4 mL of absolute methanol. To the solution was added 0.2 mL of concentrated hydrochloric acid and under stirring an ethanol solution (50 mL) of 2,6-diformyl-4-alkylphenol (2 mmol) was slowly dropwise added. The reaction mixture was then stirred at room temperature for 6 h. The formed red microcrystals or powder products were filtrated, washed with ethanol and ether, and dried in a vacuum (yield ca. 70%). Mass, *m*/*z* (%): **1**, 472 (82) [M^+], 455 (19) [$M^+ - OH$]; **2**, 556 (80) [M^+], 541(30) [$M^+ - CH_3$]; **3**, 612 (100) [M^+], 597 (70) [$M^+ - CH_3$]; **4**, 528 (100) [M^+].

Synthesis of 5. *o*-Phenylenediamine (2 mmol) was dissolved in 30 mL of absolute ether. To the solution was added a drop of concentrated hydrochloric acid, and then an ethanol solution of 2,6-diformyl-4-methylphenol (2 mmol in 50 mL of absolute ethanol) was slowly added. The formed product was separated as orange microcrystals by filtration, washed with ether, and dried in a vacuum (yield ca. 60%). Mass [*m*/*z* (%)]: 476 (50) [M^+], 459 (5) [$M^+ - OH$]. Anal. Calcd for $C_{30}H_{28}N_4O_2$: C 75.61, H 5.92, N 11.76. Found: C 75.00, H 6.19, N 11.47.

Preparation of $H_2L\cdot 2HClO_4$. $H_2L\cdot 2HCl$ (1 mmol) was dissolved in 120 mL of formic acid (99−100%), and to the solution was added $Mn(ClO_4)_2\cdot 4H_2O$. After ca. 1 min of stirring, the microcrystals of $H_2L\cdot 2ClO_4$were precipited. The mixture was heated in a water bath to a transparent solution and then slowly cooled to room temperature. The formed red crystals were collected by filtration and washed with ether, yield (30−40%).

1·$2HClO_4$. Anal. Calcd for $C_{30}H_{26}N_4O_{10}Cl_2$: C 53.50, H 3.86, N 8.32. Found: C 53.29, H 4.11, N 8.58. **2**·$2HClO_4$. Anal. Calcd for $C_{36}H_{38}N_4O_{10}Cl_2$: C 57.07, H 5.02, N 7.40. Found: C 57.25, H 4.98, N 7.39. ^1H NMR (400.04 MHz, DMSO-d_6, 297 K) δ: 1.33 (s,18H), 7.40 (m,4H), 7.79 (m,4H), 7.91 (s,4H), 9.19 (s,-4H). ^{13}C NMR (100.50 MHz, DMSO-*d*, 298 K) δ: 30.8 (CH_3), 33.7 (Cqu), 117.3 (CH), 119.2 (Cqu), 128.8 (CH), 135.3 (Cqu), 138.9 (Cqu), 160.0 (CH). **3**·$2HClO_4$. Anal. Calcd for $C_{40}H_{46}N_4O_{10}$-Cl_2: C 59.05, H 3.66, N 6.89. Found: C 59.26, H 3.54, N 6.90.

Crystal Structure Analysis. The crystal data intensity collection and structure refinement parameters are given in Table 3 for compounds **1** and **2**.

The data intensity collection for **1** was carried out on a four-circle diffractometer (Enraf-Nonius CAD4) by using graphite-monochromated Mo Kα radiation at 80 °C, ω-scan mode. A semiempirical absorption correction (ψ-scan) was carried out leading to a transmission in the region of 0.99 and 0.94. The structure was solved by direct methods[31] and subjected to full matrix least-squares refinement based on F^2 values,[32] with anisotropic displacement factors for all heavier atoms (data/parameter: 2/1). The hydrogen atoms were included at idealized positions with fixed temperature factors using a Riding model.[33] Final reliability factors: $R_1 = 0.042$ for 1388 reflections with $I > 2\sigma(I)$, $wR_2 = 0.125$($w = 1/[\sigma^2(F_o)^2 + (0.0738P)^2 + 0.4487P]$, with $P = [F_o^2 + 2F_c^2]/3$) for all data.

The intensities of the crystal for **2** were collected on a Stoe-Siemens-Huber four-circle diffractometer with Siemens CCD area detector by using φ-scans on a shock cooled crystal in an oil drop.[34] Data integration was performed with the program SAINT. A semiempirical absorption correction was applied. The structure was solved by direct methods (SHELXS-97).[35] Refinement of F^2 was accomplished by the least-squares methods (SHELXL-97).[36] All non-hydrogen atoms were refined

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anisotropically. For the hydrogen atoms the Riding model was used. The hydrogen atoms bonded to oxygen and nitrogen were refined free.

Crystallographic data (excluding structure factors) for the structures of **1** and **2** reported in this paper have been deposited with the Cambridge Crystallographic Data Center.

Safety Note. Perchlorate salts of organic compounds are potentially explosive. In our preparations, only very small amounts of samples have been handled and our procedures proved to be safe as described. Nevertheless, protective measures must be used.

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