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Interesting Conformational and Substitutional Disorder in the Crystal Structures of Three Homologous Crowns

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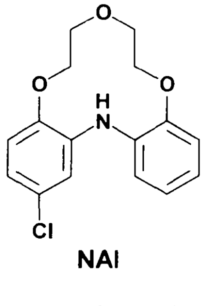
Abstract

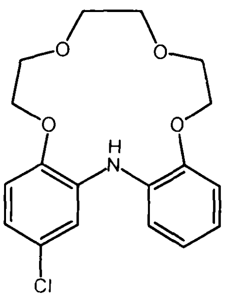
The structures of three members of a homologous family of diphenylamine-containing crowns, 2-chloro-6,7,9,10-tetrahydro-16*H*-dibenzo[*b*,*k*][1,4,7,10]monoazatrioxacyclododecine (NAI), 2-chloro-6,7,9,10,12,13-hexahydro-19*H*-dibenzo[*b*,*n*][1,4,7,10,13]monoazatetraoxacyclopentadecine (NAII), 2-chloro-6,7,9,10,12,13,15,16-octahydro-22*H*-dibenzo[*b*,*q*][1,4,7,10,13,16]monoazapentaoxacyclooctadecine] (NAIII), are reported, compared and trends are established. The largest crown (an 18-crown-6-type) presents an ability to form a molecular compound with water molecules spontaneously. The propeller-like conformational behaviour of the two phenyl rings leads to the presence of two chiral conformers in the unit cell of the crystals. Additionally, due to the conformationally non-equivalent role of the two phenyl rings, the chlorine substitution leads to two further species, resulting in four different conformers in each crystal structure. The presence of so many species in one crystal generates an interesting type of disorder in two of the three cases.

1. Introduction

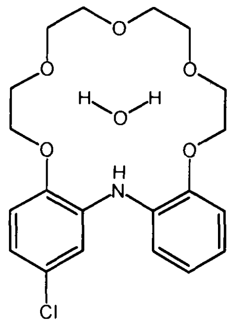
The synthesis and characterization of the type (I) compounds [with X = S, $N(CH_2)_mH$, m = 0, 1, 2, 3, 4 and n = 1, 2, 3, 4, R_1 = Cl, H and R_2 = Cl, H (Németh, 1993)] were initiated, since they share certain structural features with widely used central nervous system (CNS) drugs, such as chlorpromazine. The introduction of the crown-ether character was expected to increase the selectivity of the drug candidate as far as the given therapeutic field is related to ion transport.



NAI



NAII



NAIII

As a first step of the wider structural characterization of the family, we now present the X-ray structure and conformational analysis of three closely related compounds with n = 1, 2, 3, X = NH, R_1 = 2-Cl and R_2 = H.

2. Experimental

Crystals were obtained by dissolving the compounds in heptane followed by slow evaporation of the solvent. NAI gave, however, only very poor quality crystals. This is the reason for the data for that compound also being of poor quality. The final difference electron-density map of this structure contains one fairly high peak (1.079 e Å^{-3}; all the remaining peaks are less than half this height). From its position it is likely to be due to an unresolved disorder caused by a chlorine with very low occupancy.

All structures were solved by the *TEXSAN* package (Molecular Structure Corporation, 1989), but for the final refinement we used *SHELXL*93 (Sheldrick, 1993) so that we could restrain crystallographically independent molecules to having closely similar bond lengths and angles. Although the crystal structures of both NAII and NAIII can be solved and refined to a reasonably low R value in space group $P2_1/c$, the true space groups should be $P2_1$ and Pc, respectively, since in the former 61 out of the 378 collected *h*0*l* reflections with odd *l* are present, while in the latter 3 out of the 8 measured 0*k*0 reflections have very significant intensities. Therefore, we refined the NAII and NAIII structures in the lower symmetry space group using relatively strong restraints to keep bond lengths and angles of the pseudo-inversion

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Table 1. *Experimental details*

	NAI	NAII	NAIII
Crystal data			
Chemical formula	$C_{16}H_{16}ClNO_3$	$C_{18}H_{20}ClNO_4$	$C_{20}H_{24}ClNO_5.H_2O$
Chemical formula weight	305.75	349.80	411.87
Cell setting	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1$	Pc
a (Å)	13.922 (6)	11.146 (4)	12.477 (3)
b (Å)	6.951 (3)	12.343 (2)	12.646 (4)
c (Å)	30.173 (7)	13.737 (8)	13.4267 (11)
β (°)	93.04 (3)	107.92 (5)	102.747 (12)
V (Å^3)	2915.9 (20)	1798.3 (13)	2066.3 (9)
Z	8	4	4
D_x (Mg m^{-3})	1.393	1.292	1.324
Radiation type	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$
Wavelength (Å)	1.54180	1.54180	1.54180
No. of reflections for cell parameters	25	25	19
2θ range (°)	31.80–54.09	41.12–54.32	45.97–70.57
μ (mm^{-1})	2.407	2.060	1.946
Temperature (K)	298 (2)	298 (2)	293 (2)
Crystal form	Plate	Plate	Plate
Crystal size (mm)	0.40 × 0.20 × 0.08	0.40 × 0.20 × 0.15	0.40 × 0.20 × 0.15
Crystal colour	Transparent	Transparent	Transparent
Data collection			
Diffractometer	AFC-6*S*	AFC-6*S*	AFC-6*S*
Data collection method	ω–2θ scans	ω–2θ scans	ω–2θ scans
Absorption correction	None	Empirical	Empirical
$T_{\min}$	0.855	0.765	0.547
$T_{\max}$	1.000	0.999	1.000
No. of measured reflections	4542	9978	4220
No. of independent reflections	4323	6824	4220
No. of observed reflections	1110	3333	1612
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.0985	0.0931	–
$\theta_{\max}$ (°)	60.00	75.00	75.38
Range of h, k, l	$0 \rightarrow h \rightarrow 16$ $0 \rightarrow k \rightarrow 8$ $-37 \rightarrow l \rightarrow 37$	$-13 \rightarrow h \rightarrow 13$ $-15 \rightarrow k \rightarrow 15$ $-16 \rightarrow l \rightarrow 16$	$0 \rightarrow h \rightarrow 15$ $0 \rightarrow k \rightarrow 15$ $-16 \rightarrow l \rightarrow 16$
No. of standard reflections	3	3	3
Frequency of standard reflections	Every 150	Every 150	Every 150
Intensity decay (%)	0.79	0.52	0.48
Refinement			
Refinement on	F^2	F^2	F^2
$R[F > 4\sigma(F)]$	0.0748	0.0670	0.0652
$wR(F^2)$ (all data)	0.1907	0.1749	0.1745
S	1.308	1.049	1.126
No. of reflections used in refinement	4187	6795	4220
No. of parameters used	375	316	373
H-atom treatment	Only H-atom *U*'s refined	Only H-atom *U*'s refined	Only H-atom *U*'s refined
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1345P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1345P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1345P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.002	−0.172	0.346
$\Delta\rho_{\max}$ (e Å^{-3})	1.079	0.321	0.498
$\Delta\rho_{\min}$ (e Å^{-3})	−0.363	−0.243	−0.347
Extinction method	None	*SHELXL*93 (Sheldrick, 1993)	*SHELXL*93 (Sheldrick, 1993)
Extinction coefficient	–	0.0020 (4)	0.0006 (4)
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs			
Data collection	MSC/AFC Diffractometer Control	MSC/AFC Diffractometer Control	MSC/AFC Diffractometer Control
Cell refinement	MSC/AFC Diffractometer Control	MSC/AFC Diffractometer Control	MSC/AFC Diffractometer Control
Data reduction	*TEXSAN*: *PROCESS* (MSC, 1989)	*TEXSAN*: *PROCESS* (MSC, 1989)	*TEXSAN*: *PROCESS* (MSC, 1989)
Structure solution	*SHELXS*86 (Sheldrick, 1990)	*SHELXS*86 (Sheldrick, 1990)	*SHELXS*86 (Sheldrick, 1990)
Structure refinement	*SHELXL*93 (Sheldrick, 1993)	*SHELXL*93 (Sheldrick, 1993)	*SHELXL*93 (Sheldrick, 1993)
Preparation of material for publication	*TEXSAN*: *FINISH* (MSC, 1989)	*TEXSAN*: *FINISH* (MSC, 1989)	*TEXSAN*: *FINISH* (MSC, 1989)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for NAI*

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cl1	0.3414 (3)	−0.4028 (5)	1.33051 (12)	0.0761 (12)
C2	0.2560 (7)	−0.2212 (15)	1.3268 (4)	0.046 (3)
C3	0.2431 (8)	−0.0979 (15)	1.3619 (3)	0.047 (3)
C4	0.1741 (7)	0.0427 (16)	1.3598 (3)	0.049 (4)
C5	0.1147 (8)	0.0518 (16)	1.3209 (3)	0.048 (3)
C6	0.1286 (8)	−0.0704 (17)	1.2850 (3)	0.053 (4)
C7	0.2008 (8)	−0.2046 (17)	1.2880 (3)	0.050 (4)
N8	0.1537 (6)	0.1676 (12)	1.3934 (2)	0.052 (3)
C9	0.2200 (6)	0.2798 (13)	1.4199 (3)	0.044 (3)
C10	0.3196 (6)	0.2665 (16)	1.4175 (3)	0.053 (4)
C11	0.3789 (8)	0.3877 (18)	1.4430 (4)	0.063 (4)
C12	0.3405 (8)	0.5110 (18)	1.4723 (4)	0.067 (4)
C13	0.2430 (8)	0.5267 (17)	1.4762 (3)	0.059 (4)
C14	0.1844 (7)	0.4088 (16)	1.4505 (3)	0.044 (3)
O15	0.0833 (5)	0.4067 (12)	1.4527 (2)	0.057 (2)
C16	0.0353 (8)	0.5844 (18)	1.4427 (3)	0.063 (4)
C17	0.0355 (9)	0.6344 (16)	1.3954 (3)	0.060 (4)
O18	−0.0175 (5)	0.4921 (12)	1.3707 (2)	0.055 (2)
C19	−0.0110 (8)	0.4990 (16)	1.3240 (3)	0.057 (4)
C20	0.0650 (8)	0.3758 (16)	1.3072 (4)	0.062 (4)
O21	0.0386 (5)	0.1795 (11)	1.3172 (2)	0.052 (2)
Cl1′	0.4706 (3)	0.2414 (5)	0.99251 (11)	0.0769 (13)
C2′	0.4716 (8)	0.8998 (17)	1.1264 (4)	0.062 (4)
C3′	0.4034 (8)	0.7720 (16)	1.1093 (3)	0.053 (4)
C4′	0.3560 (8)	0.6488 (16)	1.1356 (3)	0.047 (3)
C5′	0.3764 (8)	0.6607 (16)	1.1815 (3)	0.055 (4)
C6′	0.4453 (8)	0.7895 (17)	1.1990 (3)	0.056 (4)
C7′	0.4934 (8)	0.9073 (17)	1.1712 (4)	0.068 (4)
N8′	0.2859 (4)	0.5181 (8)	1.1214 (2)	0.053 (3)
C9′	0.2944 (4)	0.3813 (8)	1.0870 (2)	0.046 (3)
C10′	0.3731 (4)	0.3760 (8)	1.0598 (2)	0.045 (3)
C11′	0.3735 (8)	0.2429 (17)	1.0260 (3)	0.051 (4)
C12′	0.3017 (9)	0.1120 (18)	1.0196 (3)	0.059 (4)
C13′	0.2237 (8)	0.1116 (16)	1.0458 (3)	0.054 (4)
C14′	0.2221 (7)	0.2455 (15)	1.0790 (3)	0.044 (3)
O15′	0.1447 (5)	0.2594 (12)	1.1077 (2)	0.060 (2)
C16′	0.1297 (8)	0.0922 (18)	1.1340 (3)	0.064 (4)
C17′	0.2042 (8)	0.0663 (16)	1.1695 (3)	0.060 (4)
O18′	0.2012 (5)	0.2217 (12)	1.2000 (3)	0.065 (3)
C19′	0.2818 (7)	0.2378 (16)	1.2306 (3)	0.058 (4)
C20′	0.3616 (8)	0.3507 (16)	1.2143 (4)	0.060 (4)
O21′	0.3273 (6)	0.5476 (12)	1.2102 (2)	0.062 (3)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for NAII*

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cl1	−0.0665 (17)	0.641 (3)	0.781 (3)	0.113 (13)
Cl2	0.0610 (3)	1.1229 (3)	1.0109 (3)	0.130 (2)
C2	0.0756 (8)	0.6874 (8)	0.7731 (7)	0.0802 (11)
C3	0.1547 (7)	0.7531 (7)	0.8496 (6)	0.0676 (9)
C4	0.2665 (7)	0.7908 (6)	0.8384 (5)	0.0552 (8)
C5	0.2991 (7)	0.7644 (6)	0.7526 (6)	0.0578 (8)
C6	0.2196 (8)	0.6979 (8)	0.6780 (6)	0.0757 (11)
C7	0.1094 (8)	0.6608 (9)	0.6897 (7)	0.0857 (13)
N8	0.3557 (6)	0.8509 (5)	0.9147 (5)	0.0659 (8)
C9	0.3331 (7)	0.9347 (6)	0.9732 (5)	0.0550 (8)
C10	0.2184 (7)	0.9816 (7)	0.9641 (6)	0.0654 (9)
C11	0.2078 (6)	1.0670 (8)	1.0275 (8)	0.0833 (12)
C12	0.3130 (8)	1.1087 (8)	1.0995 (7)	0.0898 (13)
C13	0.4291 (8)	1.0635 (7)	1.1081 (7)	0.0777 (11)
C14	0.4408 (6)	0.9792 (6)	1.0466 (6)	0.0592 (9)
O15	0.5509 (5)	0.9311 (5)	1.0474 (4)	0.0719 (7)
C16	0.6651 (7)	0.9897 (9)	1.0912 (7)	0.0835 (13)
C17	0.7616 (8)	0.9422 (10)	1.0517 (7)	0.0906 (13)
O18	0.7306 (6)	0.9590 (6)	0.9468 (5)	0.0927 (9)
C19	0.8149 (8)	0.9136 (10)	0.9004 (7)	0.102 (2)
C20	0.7568 (9)	0.9160 (8)	0.7877 (7)	0.0951 (14)
O21	0.6602 (5)	0.8354 (6)	0.7634 (5)	0.0870 (8)
C22	0.5647 (8)	0.8573 (9)	0.6722 (6)	0.0841 (12)
C23	0.4556 (7)	0.7869 (7)	0.6659 (5)	0.0760 (11)
O24	0.4097 (5)	0.8081 (5)	0.7483 (4)	0.0697 (7)
Cl1′	1.0542 (4)	1.3505 (6)	0.7098 (5)	0.096 (2)
Cl2′	0.9433 (4)	0.8714 (6)	0.4987 (7)	0.171 (4)
C2′	0.9172 (6)	1.3057 (8)	0.7292 (7)	0.0802 (11)
C3′	0.8425 (7)	1.2419 (7)	0.6520 (6)	0.0676 (9)
C4′	0.7306 (7)	1.2012 (6)	0.6606 (5)	0.0552 (8)
C5′	0.6969 (7)	1.2284 (6)	0.7477 (6)	0.0578 (8)
C6′	0.7694 (8)	1.2965 (8)	0.8216 (6)	0.0757 (11)
C7′	0.8826 (8)	1.3342 (9)	0.8110 (7)	0.0857 (13)
N8′	0.6432 (6)	1.1421 (5)	0.5853 (5)	0.0659 (8)
C9′	0.6673 (7)	1.0590 (6)	0.5265 (5)	0.0550 (8)
C10′	0.7843 (7)	1.0144 (7)	0.5383 (6)	0.0654 (9)
C11′	0.7960 (6)	0.9281 (7)	0.4768 (8)	0.0833 (12)
C12′	0.6931 (8)	0.8879 (8)	0.4025 (8)	0.0898 (13)
C13′	0.5761 (8)	0.9320 (7)	0.3903 (7)	0.0777 (11)
C14′	0.5614 (6)	1.0161 (6)	0.4504 (6)	0.0592 (9)
O15′	0.4498 (5)	1.0626 (5)	0.4480 (4)	0.0719 (7)
C16′	0.3341 (7)	1.0050 (9)	0.4006 (7)	0.0835 (13)
C17′	0.2359 (8)	1.0551 (10)	0.4375 (7)	0.0906 (13)
O18′	0.2644 (6)	1.0325 (6)	0.5432 (5)	0.0927 (9)
C19′	0.1810 (8)	1.0813 (10)	0.5903 (7)	0.102 (2)
C20′	0.2382 (9)	1.0824 (8)	0.7014 (7)	0.0951 (14)
O21′	0.3372 (5)	1.1569 (5)	0.7313 (5)	0.0870 (8)
C22′	0.4309 (8)	1.1350 (9)	0.8234 (6)	0.0841 (12)
C23′	0.5414 (4)	1.2095 (4)	0.8361 (4)	0.0760 (11)
O24′	0.5838 (4)	1.1848 (4)	0.7489 (4)	0.0697 (7)

symmetry-related molecules at closely similar values. The occupancies of the Cl atoms at positions 2 or 11 belonging to molecules which occupy one particular site were constrained to add up to one. In order to comply with the requirements for the data collection for non-centrosymmetric structures, following the referee's suggestion, we recollected the data for both NAII and NAIII with the inclusion of Friedel mates. For NAII a full data set was successfully collected. The refinement with the data set containing the Friedel mates converged to the same solution as the half data set concerning both occupancies and Flack x values. However, for NAIII both attempts to collect Friedel mates produced data sets which were inferior in quality to our first data set with no Friedel pairs. Therefore, we decided to use data from the first crystal. Our refinements in the non-centrosymmetric space groups for NAII and NAIII are also authenticated by the close agreement with the F_c values and the large F_o's for those reflections that would have been absent if the space group had been truly centrosymmetric ($P2_1/c$).*

Other experimental details are summarized in Table 1. Final atomic coordinates are given in Tables 2, 3 and 4.

3. Comments

The bond lengths, bond angles and torsion angles provided an opportunity for some general conclusions to

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* A list of observed and calculated structure factors has been deposited with the IUCr (Reference: KA0027). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for NAIII*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cl1	−0.2033 (5)	0.6359 (7)	0.2699 (8)	0.133 (4)
Cl2	−0.1880 (6)	0.1245 (9)	0.3840 (11)	0.090 (5)
Cl1′	0.8647 (7)	−0.1279 (10)	1.2066 (10)	0.114 (5)
Cl2′	0.8432 (5)	0.3730 (7)	1.1042 (8)	0.114 (4)
C2	−0.0808 (7)	0.5820 (11)	0.2588 (10)	0.102 (2)
C3	−0.0252 (8)	0.5096 (11)	0.3321 (8)	0.088 (2)
C4	0.0665 (6)	0.4586 (7)	0.3173 (5)	0.0732 (14)
C5	0.1054 (8)	0.4780 (10)	0.2255 (6)	0.073 (2)
C6	0.0520 (10)	0.5519 (11)	0.1586 (8)	0.099 (2)
C7	−0.0398 (10)	0.5996 (12)	0.1737 (9)	0.105 (2)
N8	0.1236 (5)	0.3872 (6)	0.3902 (5)	0.0738 (12)
C9	0.0757 (6)	0.2997 (7)	0.4245 (7)	0.0657 (14)
C10	−0.0285 (6)	0.2672 (8)	0.3845 (9)	0.075 (2)
C11	−0.0592 (5)	0.1761 (9)	0.4248 (11)	0.101 (2)
C12	−0.0042 (9)	0.1149 (9)	0.4960 (11)	0.105 (2)
C13	0.1023 (8)	0.1438 (9)	0.5325 (10)	0.093 (2)
C14	0.1441 (6)	0.2342 (7)	0.4975 (8)	0.0724 (15)
O15	0.2497 (5)	0.2679 (5)	0.5310 (6)	0.0810 (12)
C16	0.3251 (6)	0.2006 (8)	0.5991 (8)	0.087 (2)
C17	0.4343 (7)	0.2523 (9)	0.6235 (6)	0.098 (2)
O18	0.4754 (6)	0.2577 (9)	0.5340 (5)	0.0906 (12)
C19	0.5868 (8)	0.2885 (12)	0.5563 (6)	0.105 (2)
C20	0.6287 (9)	0.2812 (11)	0.4620 (8)	0.112 (2)
O21	0.5798 (10)	0.3626 (8)	0.3922 (6)	0.0989 (13)
C22	0.5855 (11)	0.3437 (11)	0.2911 (7)	0.109 (2)
C23	0.5450 (7)	0.4376 (10)	0.2305 (7)	0.102 (2)
O24	0.4303 (6)	0.4604 (8)	0.2249 (6)	0.0913 (12)
C25	0.3571 (7)	0.4052 (9)	0.1496 (7)	0.103 (2)
C26	0.2491 (7)	0.4547 (11)	0.1336 (6)	0.094 (2)
O27	0.2001 (7)	0.4312 (8)	0.2199 (6)	0.0835 (11)
O28	0.3565 (11)	0.4356 (9)	0.4271 (9)	0.0842 (12)
C2′	0.7482 (8)	−0.0687 (11)	1.2270 (10)	0.102 (2)
C3′	0.6902 (9)	0.0003 (11)	1.1516 (8)	0.088 (2)
C4′	0.5942 (6)	0.0456 (7)	1.1629 (6)	0.0732 (14)
C5′	0.5488 (8)	0.0173 (10)	1.2491 (6)	0.073 (2)
C6′	0.6085 (10)	−0.0482 (12)	1.3212 (8)	0.099 (2)
C7′	0.7022 (11)	−0.0934 (12)	1.3077 (9)	0.105 (2)
N8′	0.5358 (5)	0.1151 (6)	1.0888 (5)	0.0738 (12)
C9′	0.5813 (6)	0.2040 (7)	1.0545 (7)	0.0657 (14)
C10′	0.6868 (6)	0.2354 (8)	1.0898 (9)	0.075 (2)
C11′	0.7156 (6)	0.3263 (10)	1.0480 (10)	0.101 (2)
C12′	0.6570 (10)	0.3898 (10)	0.9811 (11)	0.105 (2)
C13′	0.5525 (9)	0.3564 (9)	0.9421 (10)	0.093 (2)
C14′	0.5139 (7)	0.2635 (7)	0.9755 (8)	0.0724 (15)
O15′	0.4090 (5)	0.2275 (5)	0.9422 (6)	0.0810 (12)
C16′	0.3316 (7)	0.2940 (8)	0.8752 (8)	0.087 (2)
C17′	0.2231 (6)	0.2410 (9)	0.8529 (6)	0.098 (2)
O18′	0.1794 (7)	0.2442 (8)	0.9410 (5)	0.0906 (12)
C19′	0.0700 (8)	0.2074 (11)	0.9201 (7)	0.105 (2)
C20′	0.0286 (9)	0.2130 (11)	1.0147 (9)	0.112 (2)
O21′	0.0854 (10)	0.1373 (8)	1.0870 (6)	0.0989 (13)
C22′	0.0682 (11)	0.1499 (11)	1.1855 (6)	0.109 (2)
C23′	0.1136 (8)	0.0578 (11)	1.2464 (7)	0.102 (2)
O24′	0.2290 (7)	0.0399 (8)	1.2507 (6)	0.0913 (12)
C25′	0.3004 (7)	0.0947 (9)	1.3276 (8)	0.103 (2)
C26′	0.4091 (7)	0.0465 (11)	1.3445 (6)	0.094 (2)
O27′	0.4581 (7)	0.0695 (8)	1.2582 (7)	0.0835 (11)
O28′	0.3058 (11)	0.0674 (9)	1.0587 (9)	0.0842 (12)

Table 5. *Selected geometric parameters (Å, °) for NAI*

Cl1—C2	1.733 (10)	C16—C17	1.467 (12)
C4—N8	1.376 (10)	C17—O18	1.421 (10)
C5—O21	1.382 (10)	O18—C19	1.418 (10)
N8—C9	1.420 (7)	C19—C20	1.471 (11)
C14—O15	1.413 (9)	C20—O21	1.448 (11)
O15—C16	1.429 (11)		
C3—C4—N8	126.1 (8)	O15—C16—C17	112.7 (9)
N8—C4—C5	116.9 (9)	O18—C17—C16	108.5 (9)
O21—C5—C4	120.9 (9)	C19—O18—C17	116.1 (8)
C4—N8—C9	127.4 (7)	O18—C19—C20	114.0 (8)
C14—C9—N8	118.7 (7)	O21—C20—C19	106.4 (8)
C9—C14—O15	114.5 (8)	C5—O21—C20	114.9 (8)
C14—O15—C16	115.9 (8)		
N8—C4—C5—O21	−0.7 (16)	O15—C16—C17—O18	63.6 (12)
C5—C4—N8—C9	−135.8 (11)	C16—C17—O18—C19	−169.5 (9)
C4—N8—C9—C14	175.6 (10)	C17—O18—C19—C20	93.1 (11)
N8—C9—C14—O15	2.4 (14)	O18—C19—C20—O21	64.1 (12)
C9—C14—O15—C16	−120.2 (10)	C4—C5—O21—C20	79.2 (13)
C14—O15—C16—C17	71.1 (11)	C19—C20—O21—C5	−155.0 (8)

Table 6. *Selected geometric parameters (Å, °) for NAII*

Cl1—C2	1.719 (5)	C17—O18	1.389 (10)
Cl2—C11	1.725 (4)	O18—C19	1.404 (10)
C4—N8	1.414 (8)	C19—C20	1.483 (11)
N8—C9	1.379 (8)	C20—O21	1.428 (9)
C14—O15	1.361 (7)	O21—C22	1.398 (9)
O15—C16	1.427 (9)	C22—C23	1.475 (10)
C16—C17	1.468 (10)	C23—O24	1.403 (7)
C5—C4—N8	116.7 (6)	C17—O18—C19	115.0 (7)
O24—C5—C4	115.1 (6)	O18—C19—C20	109.1 (8)
O24—C5—C6	125.4 (6)	O21—C20—C19	106.6 (8)
C9—N8—C4	127.8 (6)	C22—O21—C20	112.7 (7)
N8—C9—C14	116.0 (6)	O21—C22—C23	109.0 (7)
O15—C14—C9	113.6 (6)	O24—C23—C22	110.0 (6)
O15—C16—C17	107.6 (7)	C5—O24—C23	121.4 (5)
O18—C17—C16	110.3 (8)		
N8—C4—C5—O24	−5.4 (11)	C17—O18—C19—C20	167.5 (9)
C5—C4—N8—C9	140.5 (8)	O18—C19—C20—O21	−72.6 (11)
C4—N8—C9—C14	178.5 (8)	C19—C20—O21—C22	154.3 (8)
N8—C9—C14—O15	0.0 (11)	C20—O21—C22—C23	−166.2 (7)
C9—C14—O15—C16	159.5 (7)	O21—C22—C23—O24	60.9 (9)
C14—O15—C16—C17	−160.1 (8)	C4—C5—O24—C23	179.1 (6)
O15—C16—C17—O18	65.5 (11)	C22—C23—O24—C5	171.0 (8)
C16—C17—O18—C19	−178.0 (8)		

be drawn. It is generally valid for the three compounds that the C(aromatic)—O bond lengths are shorter [between 1.339 (7) and 1.382 (10) Å] than the C—O bond lengths with O atoms not directly connected to any of the aromatic rings [between 1.389 (10) and 1.454 (6) Å], which is due to the partial delocalization of the lone pair on the oxygen towards the aromatic ring (see Tables 5, 6 and 7). The only exception from this trend is the C14—O15 bond of the conformationally most strained molecule (NAI). This bond is quite long [1.413 (9) Å], whereby the strain present in the smallest macrocycle can be somewhat relieved. Other C(aliphatic)—O bond lengths are similar to those found in other crown ethers (Garrell, Smyth, Fronczek & Gandour, 1988). The C—C bonds are also somewhat shorter than those in aliphatic hydrocarbons. As far as the bond angles are concerned it is worth mentioning that the angles around oxygens resemble sp^2 values, while those around C atoms are characteristic of sp^3, as expected.

In all three crystal structures we detected the presence of four different species. In the case of the smallest crown (NAI) there are two crystallographically independent molecules (Fig. 1) with similar crown conformations differing only in the location of the Cl

Table 7. *Selected geometric parameters (Å, °) for NAIII*

Cl1—C2	1.7091 (8)	O18—C19	1.411 (8)
Cl2—C11	1.7094 (8)	C19—C20	1.475 (9)
C4—N8	1.405 (6)	C20—O21	1.435 (8)
C5—O27	1.339 (7)	O21—C22	1.395 (7)
N8—C9	1.384 (6)	C22—C23	1.465 (9)
C14—O15	1.364 (6)	C23—O24	1.445 (7)
O15—C16	1.437 (6)	O24—C25	1.391 (7)
C16—C17	1.480 (9)	C25—C26	1.458 (9)
C17—O18	1.408 (7)	C26—O27	1.454 (6)
C9—N8—C4	123.8 (5)	O21—C20—C19	109.6 (6)
N8—C9—C14	117.4 (5)	C22—O21—C20	114.1 (5)
O15—C14—C9	115.9 (5)	O21—C22—C23	108.4 (6)
C14—O15—C16	118.3 (4)	O24—C23—C22	114.0 (6)
O15—C16—C17	108.7 (5)	C25—O24—C23	114.9 (5)
O18—C17—C16	108.9 (5)	O24—C25—C26	109.2 (6)
C17—O18—C19	111.1 (5)	O27—C26—C25	109.4 (5)
O18—C19—C20	108.7 (6)	C5—O27—C26	119.1 (5)
N8—C4—C5—O27	−5.0 (17)	O18—C19—C20—O21	70.0 (13)
C5—C4—N8—C9	−123.4 (12)	C19—C20—O21—C22	−160.9 (11)
C4—N8—C9—C10	6.9 (16)	C20—O21—C22—C23	−173.3 (11)
C10—C9—C14—O15	176.6 (13)	O21—C22—C23—O24	−64.4 (12)
N8—C9—C14—O15	3.7 (16)	C22—C23—O24—C25	−84.2 (12)
C9—C14—O15—C16	−175.3 (11)	C23—O24—C25—C26	−164.9 (7)
C14—O15—C16—C17	179.0 (9)	O24—C25—C26—O27	−72.9 (12)
O15—C16—C17—O18	−66.0 (11)	C4—C5—O27—C26	−174.6 (11)
C16—C17—O18—C19	−169.4 (10)	C25—C26—O27—C5	173.3 (11)
C17—O18—C19—C20	173.7 (9)		

atom (attached to either C2 or C11). These two chiral molecules assume chiral shape and a centre of symmetry transforms them into their counterparts. For the two other crowns (NAII and NAIII; Figs 2 and 3) the two chirally unrelated species (differing only in the location of the Cl atom attached to either one or the other phenyl ring) occupy the same position in an alternative manner. We believe that the reason for the crystal structures of NAII and NAIII being somewhat similar but different from NAI could be that the alternative positions occupied by the Cl atom are empty in half the cases. This will result in a decrease in the degree of the close packing. Since NAI has the lowest molecular weight and molecular volume, the unoccupied volume needed for a Cl atom has the largest relative effect on its structure. The packing could become so loose that the given structure is no longer stable. Therefore, the formation of a different structure ($P2_1/a$, $Z = 8$) will occur. The relative compactness of the NAI structure is demonstrated well by the enhanced density (1.393 Mg m^{-3}) compared with that of NAIII (1.292 Mg m^{-3}).

For NAII and NAIII an interesting type of disorder leads to formally dichlorinated compounds in the crystal structures. The pseudo-centrosymmetric arrangement of the molecules is fairly well maintained. Essentially it is only the occupancies of the chlorine substituents that break the rule. In NAIII the occupancies of the four species are: Cl: 0.66, Cl2: 0.34, Cl1′: 0.42, Cl2′: 0.58; for NAII: Cl1: 0.09, Cl2: 0.91, Cl1′: 0.44, Cl2′: 0.56. In order to further assess the reliability of the disordered structures the Cl···Cl contacts less than 3.4 Å have been calculated. There are no contacts of this type in the ordered structure of NAI. In NAIII one intermolecular contact of this type exists: Cl1···Cl1′ ($x-1, y+1, z-1$) 3.27 (2) Å. In NAIII there are two Cl···Cl repulsions: Cl1···Cl2 ($-x$, $y-\frac{1}{2}$, $2-z$) 2.85 (4) and Cl1′···Cl2′ ($2-x$, $y+\frac{1}{2}$, $1-z$) 2.88 (1) Å, indicating local order in the adjacent layers along the twofold screw axis (Haller, Rae, Heerdegen, Hockless & Welberry, 1995).

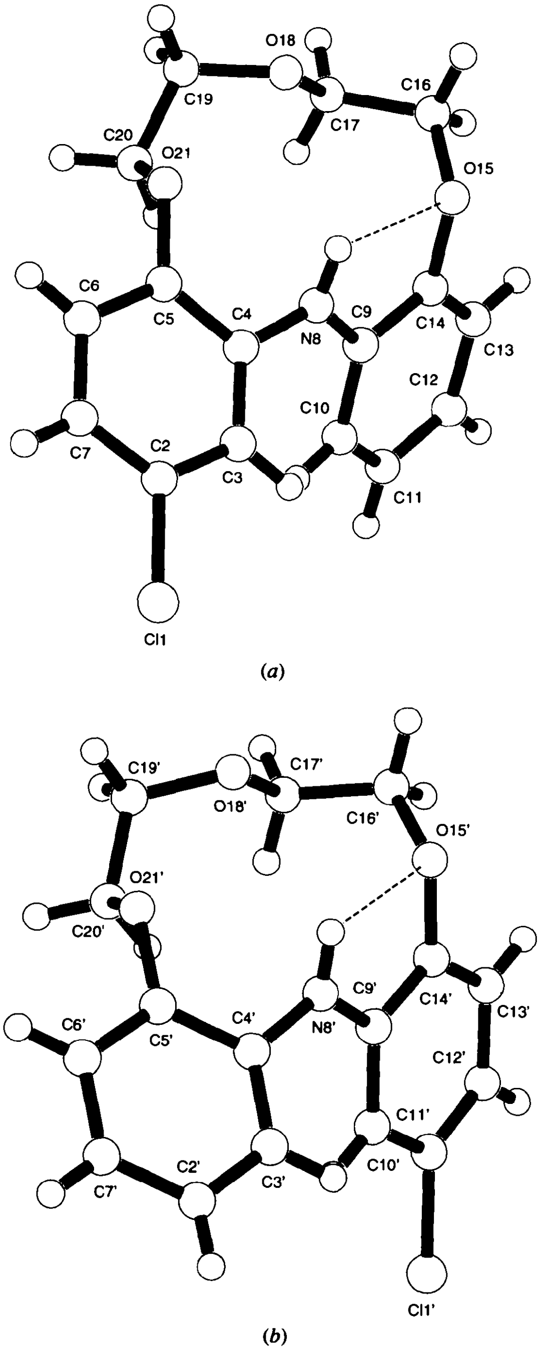

Fig. 1. The two independent molecules of NAI in the asymmetric unit.

The two phenyl rings of all three compounds will become distinguishable since the NH group prefers to be coplanar with one of the rings and not with the other. The lone pair on the nitrogen atom will become delocalized towards both of the phenyl rings, resulting in a shortening of the corresponding C—N bonds and a C—N—C bond angle characteristic of sp^2 atoms (see Tables 5, 6 and 7).

The conformational behaviour of propeller-like substituents of a central atom, *i.e.* the isomerization in compounds displaying restricted rotation of aryl groups, has been extensively studied by several groups, both for the general open-chain-type situation (Gust & Mislow, 1973) as well as for the more specific case of the crown ethers (Lockhart, McDonnell & Tyson, 1983; Clegg, Lockhart & McDonnell, 1985).

In this context it seems to be worth analysing the torsion angles along the crowns of the three compounds (Tables 5, 6 and 7). The C—C bonds are all synclinal (Klyne & Prelog, 1960) with relatively small deviations from the expected values of 60 and −60°. In contrast, the C—O bonds are antiperiplanar with substantial (~20°) deviations from 180°, which are possibly due to the absence of H atoms on the oxygens as opposed to carbons. As expected, NAI seems to be the conformationally most strained molecule of the three. The C9—O14—C15—C16 torsion angle (and similarly C9′—O14′—C15′—C16′) of NAI is, for example, in an anticlinal conformation [−120 (1) and −119.5 (9)°, respectively].

Table 8. *Selected intermolecular contacts (Å) for NAIII*

D—H···*A*	H···*A*	*D*—*A*	*D*—H···*A*
N8—H8···O28^{i}	1.95 (1)	2.90 (1)	171.9 (4)
N8′—H8′···O28′^{i}	1.90 (1)	2.87 (1)	169.5 (4)
O28—H28*A*···O24^{i}	2.07 (2)	3.07 (1)	176.6 (4)
O28—H28*B*···O18^{i}	1.89 (2)	2.90 (2)	174.7 (4)
O28′—H28*C*···O24′^{i}	1.98 (2)	2.96 (1)	178.3 (5)
O28′—H28*D*···O18′^{i}	2.04 (2)	2.98 (2)	156.5 (4)

Symmetry code: (i) *x*, *y*, *z*.

It is also worth noting that the interplanar angles of the two phenyl rings are similar in all three structures, although the different ring sizes could lead to quite different values [NAIII 57.8 (3) and 57.1 (3)°, NAII 44.1 (3) and 44.9 (2)°, NAI 44.8 (3) and 44.6 (3)° for all molecules].

As is well known (Goldberg, 1984), crown-ether-type molecules tend to form inclusion complexes with a number of ligands. The crystal structure determination revealed a spontaneous formation of such a complex of NAIII with water, the source of which is unknown, although it is likely to be the atmosphere. The affinity of NAIII to water is not surprising if we notice the optimal hydrogen-bonding donor and acceptor abilities of NAIII to water molecules (Fig. 3 and Table 8).

A systematic study of the complex-forming ability of the members of this series will be undertaken in the future.

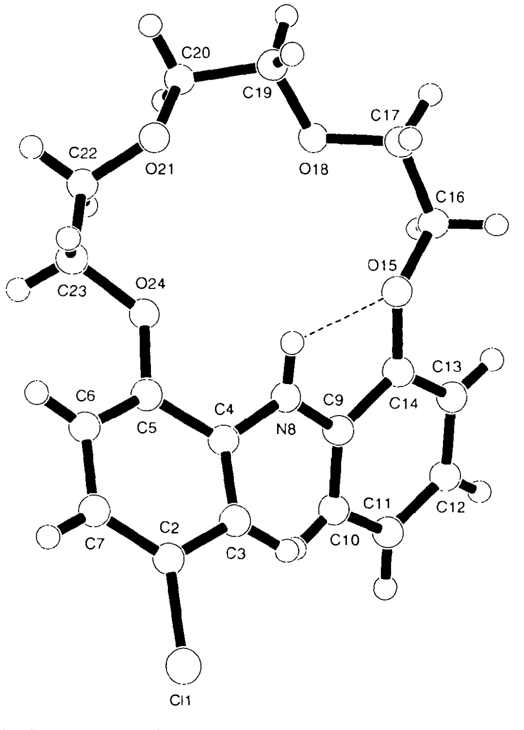

Fig. 2. The structure of the molecule NAII.

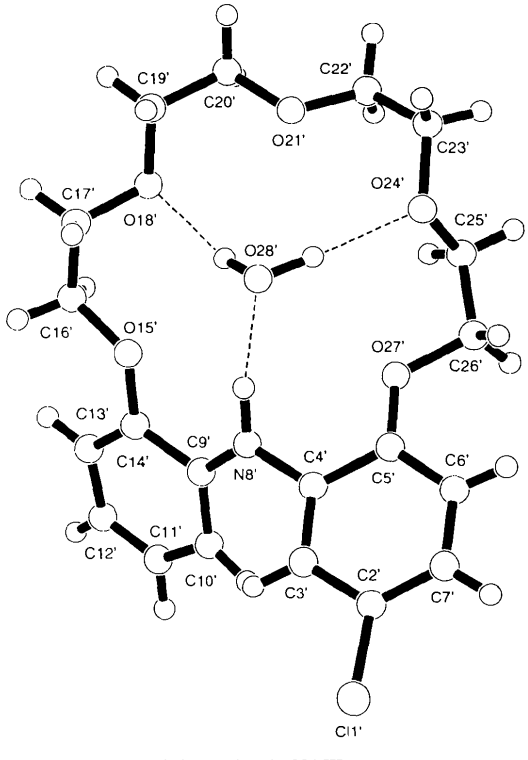

Fig. 3. The structure of the molecule NAIII.

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