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Crystal Structures and Solution Conformations of the *meso*-Forms of 2,3,11,12-Tetraphenyl-[18]crown-6

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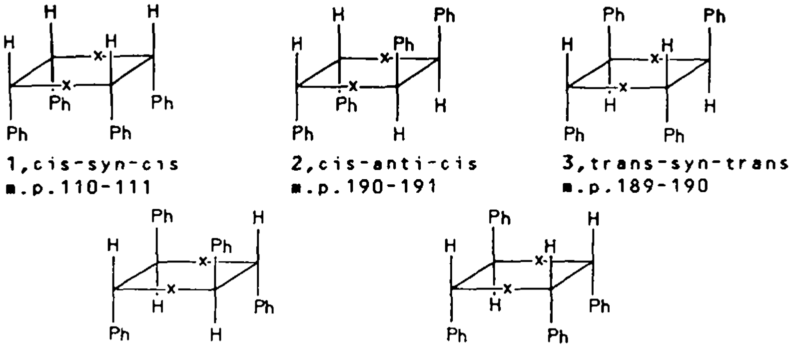
Abstract: The X-ray crystal stuctures of the achiral *cis-anti-cis* and *trans-syn-trans* diastereoisomers of 2,3,11,12-tetraphenyl-[18]-crown-6 and their sodium iodide 1:1 complexes are presented. In the free ligands, the vicinal phenyl groups assume a diaxial- antiperiplanar orientation in the *cis-anti-cis* isomer and a diequatorial-synclinal one in the *trans-syn-trans* isomer. The vicinal coupling constants of the benzylic protons in the diphenylethanediyl groups in the three *meso*-forms, derived from ^{13}C satellites, suggest similar conformations in the solid state and in deuteriotrichloromethane solution. Conformational changes of the crown ethers from the free ligand to their complexes are discussed in the context of previously determined complex association constants.

Introduction

Complex association constants of crown ethers with metal and ammonium ions are largely determined by the conformational differences of the crown in its free and bound forms which are influenced by substituents on the periphery of the ring.
2,3,11,12-Tetraphenyl-[18]crown-6 represents a structure with four chiral centres, giving rise to the same type of stereoisomers as described for the dodecahydro-2,3,11,12-dibenzo-[18]crown-6 system ("dicyclohexano-[18]crown-6") [1], namely three meso forms 1-3 and two pairs of enantiomers, 4 and 5 (Scheme 1; this graphic representation indicates only the relative configurations at the various chiral centers, *not* the extended conformations of the molecules). 1-5 are readily accessible and well characterised [2]. The syntheses of the enantiomers of 4 [3] and 5 [4] have also been achieved.
This series of stereoisomers is thus well suited for the study of configurational and conformational influences on the complexing behaviour of crown ethers.

Association constants of 1-5 with alkali metal and ammonium cations [2] show remarkable differences depending on the configuration of the diphenylethanediyl units. 3 and 4 which contain only *trans*-connected phenyl groups are much better ligands than 1 and 2, the corresponding *cis* structures. In the series of the dicyclohexano-crowns, the isomers with

Scheme 1



1,cis-syn-cis
m.p.110-111

2,cis-anti-cis
m.p.190-191

3,trans-syn-trans
m.p.189-190

4,trans-anti-trans
m.p.152-153(racemic)

5,trans-cis
m.p.95-96(racemic)

$X = -O-CH_2-CH_2-O-CH_2-CH_2-O-$

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cis-fused cyclohexane rings are the better ligands [1]. Apparently, in this case, the conformations depend on both the cyclohexane and the crown ether rings whereas in the tetraphenyl crowns the phenyl substituents can be more easily adapted to the requirements of the crown ether ring in the free state and in complexes; in particular, diaxial conformations should also be possible here . In order to obtain more detailed information, we have determined the crystal structures of the free ligands 2 and 3 and their sodium iodide complexes, 2a and 3a. We have also performed an ^{1}H-NMR study using the chemical shifts and vicinal coupling constants of the benzylic protons of the crown ethers as a means of estimating the conformations of the free ligands and complexes in solution. We report, in this communication, our results on the three *meso*-forms. The two chiral crown ethers will be dealt with in a separate paper with special emphasis on the chiral recognition properties.

Experimental Section

Materials

The crown ethers 1-3 were obtained as described previously [2]; samples which were highly purified by repeated recrystallisation from 2-methoxyethanol had melting points as given in Scheme 1.
Crown ether complexes with NaI, KBr, KSCN and NH$_4$SCN were made by stirring a dichloromethane solution of the ligand overnight with excess powdered salt. After filtration, the complexes were precipitated with pentane. Dissolution in dichloromethane and precipitation with pentane was repeated until well crystallised materials with sharp melting points (Table 1) were obtained. The yields are generally high (> 80%). Elementary analyses indicate 1:1 complexes in all cases although not very accurate owing to inclusion of solvent in the crystals.

Table 1: Melting Points (°C) of the Crown Ether Complexes Prepared

Ligand	1	2	3
NaI	245-47	222-24	275-76
KBr	128-33	196-98	204-06
KSCN	197-200	194-96	213-17
NH$_4$SCN	249-52	258-60	260-68

^{1}H-NMR spectra

The spectra of 0.1 M CDCl$_3$ solutions were obtained with a Bruker WH 90 PTF NMR spectrometer; chemical shifts are given with respect to TMS as internal standard. ^{13}C satellites were resolved from 300 to 1440 scan spectra. Chiral interactions with optically active 1-phenylethyl ammonium bromides were studied in CDCl$_3$ solutions 0.1 M in both ligand and salt [2]. Maximum induced chemical shifts and coupling constants for the ligands are observed under these conditions.

X-Ray crystal structures

Single crystals of the ligands 2 and 3 and the NaI complexes 2a and 3a were grown from dichloromethane/pentane solutions. Data were collected on an automated four circle diffractometer with monochromated MoK$_\alpha$ radiation [λ = 0.71069 Å] in a profile fitting mode [3]. The structures of 2 and 3 were solved by multisolution direct methods, those of 2a and 3a from Patterson and subsequent Fourier syntheses. Non-hydrogen atoms (except the carbon of CH$_2$Cl$_2$ in 2a) were refined anisotropically, idealised aromatic nuclei in 2a were refined as "rigid groups". Ligand H atoms were included in calculated positions (C-H = 0.96 Å) as "riding atoms" with $U(H_i) = 1.2\ U_{eq}(C_i)$; three water hydrogen atoms in 2a located from a difference map were also treated as "riding atoms". Partial conformational disorder along the aliphatic chain in 2a is indicated by high anisotropic movement of C(6) to C(9)[4]. Crystal data and details of the data collection procedures are given in Table 2, atom parameters are listed in Table 3; further information is available from G.W. on request.

Results and Discussion

Crystal structures

The crystal structures of the *cis-anti-cis* isomer 2, the *trans-syn-trans* isomer 3, and their sodium iodide complexes 2a and 3a are represented in Fig.1 in top and side views. Significant structural data are compiled in Table 4. Unfortunately, no suitable single crystals could be grown of 1 and 1a.

Table 2: Crystallographic and Diffraction Data

	2	**2a**	**3**	**3a**
formula unit	$C_{36}H_{40}O_6$	$C_{36}H_{40}O_6$ $xNaIx2H_2O$ xCH_2Cl_2	$C_{36}H_{40}O_6$	$C_{36}H_{40}O_6$ $xNaI$
M.W.	568.72	839.57	568.72	718.61
crystal size[mm]	0.6x0.15 x0.15	0.4x0.15 x0.1	0.7x0.2 x0.2	0.75x0.65 x0.6
crystal habit	colourless needles	yellowish needles	colourless prisms	yellowish prisms
space group	monoclinic $P2_1/n$	monoclinic $P2_1/c$	monoclinic $P2_1/c$	triclinic $P\bar{1}$
a[Å]	8.193(3)	19.498(6)	12.546(4)	8.986(2)
b[Å]	20.021(7)	19.662(6)	22.724(6)	12.414(4)
c[Å]	19.102(6)	10.714(3)	11.684(3)	16.059(5)
α[°]	90	90	90	89.58(2)
β[°]	95.12(2)	100.28(2)	108.57(4)	78.76(1)
γ[°]	90	90	90	82.24(2)
Z	4*	4*	4*	2
D_x [Mgm^{-3}]	1.210	1.380	1.196	1.371
μ[mm^{-1}]	0.075	0.970	0.075	0.960
max. 2θ[°]	45	45	47	50
number of unique data collected	4068	5269	4641	6099
number of $F>n\sigma(F)$	2353	3481	3013	5453
n	3	3	4	4
number of L.S.parameters	331	440	379	397
R	0.095	0.072	0.055	0.043
R_w	0.069	0.063	0.053	0.050
g	$2.0x10^{-4}$	$3.4x10^{-4}$	$5.7x10^{-4}$	$2.0x10^{-4}$

*two independent halves per asymmetric unit

It is well known that free crown ether ligands and other macrocycles have a remarkable tendency to "fill their own cavity" by assuming appropriate conformations [7], unless they are constructed as rigid molecules (spherands [8], cavitands [9]). In [18]-crown-6 derivatives the cavity filling is achieved by twisting two opposite ethylenedioxy units from the synclinal (sc) into the anti-periplanar (ap) conformation of the vicinal oxygen atoms; this behaviour has been found for unsubstituted [18]crown-6 [10] as well as the dibenzo-[11] and dicyclohexano [12] derivatives. In these conformations the crown ethers assume roughly rectangular structures with the (ap) portions on the longer side as it is also found for the tetraphenyl crowns in this paper. Surprisingly, the topologically *cis*-oriented phenyl groups in 2 are located at the (ap) ethylene groups and do thus appear in the axial-axial positions with respect to the crown ether ring. One hydrogen of each diphenylethanediyl unit points inwards and one oxygen outwards with respect to the ring. Two ortho hydrogens of the phenyl rings also help to fill the crown ether cavity, forming a rather compact structure of rhomboid shape, which is also reflected in the unusual large diagonal distance of the "outward" O(1) and O(1A) oxygen atoms.

Table 3: Atomic Coordinates (x10⁴) and isotropic thermal parameters (Å² x10³) of 2,2a,3 and 3a.

2

	x	y	z	U
O(1)	11345(5)	1844(2)	5156(2)	55(2)*
C(2)	10694(6)	1327(3)	4690(3)	54(2)*
C(3)	8884(6)	1261(3)	4759(2)	47(2)*
O(4)	8383(4)	689(2)	4367(2)	45(1)*
C(5)	6669(6)	598(3)	4255(3)	59(2)*
C(6)	6335(7)	-57(3)	3892(3)	64(3)*
O(7)	6698(5)	-580(2)	4373(2)	59(2)*
C(8)	6695(8)	-1229(4)	4050(3)	68(3)*
C(9)	6985(8)	-1759(3)	4589(3)	64(3)*
C(10)	11087(5)	1478(2)	3948(2)	50(2)*
C(11)	12228	1075	3650	62(3)*
C(12)	12652	1206	2973	76(3)*
C(13)	11934	1742	2592	81(4)*
C(14)	10793	2146	2890	77(3)*
C(15)	10369	2014	3567	59(3)*
C(16)	8600(5)	1200(3)	5537(2)	47(2)*
C(17)	7955	1736	5889	68(3)*
C(18)	7747	1685	6604	100(4)*
C(19)	8183	1098	6967	102(4)*
C(20)	8828	562	6615	86(3)*
C(21)	9036	613	5900	65(3)*
O(51)	5382(4)	1008(2)	-326(2)	44(1)*
C(52)	4629(7)	1362(3)	203(3)	44(2)*
C(53)	2848(7)	1141(3)	109(2)	47(2)*
O(54)	2084(4)	1290(2)	731(2)	51(1)*
C(55)	733(6)	860(3)	830(3)	55(2)*
C(56)	1227(7)	215(3)	1196(3)	58(2)*
O(57)	1910(4)	-222(2)	714(2)	49(2)*
C(58)	2425(7)	-838(3)	1031(3)	52(3)*
C(59)	3096(6)	-1284(3)	496(3)	50(2)*
C(60)	5473(4)	1223(3)	927(2)	42(2)*
C(61)	6014	1763	1346	59(3)*
C(62)	6866	1654	2001	67(3)*
C(63)	7178	1003	2237	66(3)*
C(64)	6638	462	1818	62(3)*
C(65)	5785	572	1163	58(3)*
C(66)	1991(5)	1485(2)	-536(2)	42(2)*
C(67)	2323	1276	-1205	58(3)*
C(68)	1597	1602	-1799	69(3)*
C(69)	539	2138	-1723	67(3)*
C(70)	207	2348	-1054	63(3)*
C(71)	933	2021	-460	55(3)*

2a

	x	y	z	U
C	2212(12)	2234(10)	401(20)	278(9)
Cl(1)	1392(3)	2308(3)	-358(7)	294(4)*
Cl(2)	2111(4)	2333(4)	2037(7)	369(5)*
Ow(2)	988(3)	606(3)	-379(4)	86(2)*
Hw(2a)	954	1031	-847	100
Hw(2b)	1406	338	-100	100
Ow(1)	5993(3)	5380(3)	1303(6)	109(3)*
Hw(1a)	5790	5222	2110	133
I	2873(1)	197(1)	796(1)	88(1)*
Na(1)	5000	5000	0	85(2)*
Na(2)	0	0	0	75(2)*
O(1)	5841(2)	3753(2)	-99(4)	64(2)*
C(2)	6072(4)	3482(4)	1141(7)	61(3)*
C(3)	5634(4)	3404(4)	1761(6)	61(3)*
O(4)	5157(3)	4058(3)	1870(4)	63(2)*
C(5)	4685(4)	4082(4)	2741(7)	77(4)*
C(6)	4529(4)	4818(5)	2963(7)	78(4)*
O(7)	4239(3)	5108(2)	1778(5)	68(2)*
C(8)	3885(4)	5714(4)	1937(8)	81(4)*
C(9)	3595(4)	6016(4)	669(8)	72(4)*
C(10)	6466(4)	2827(4)	1135(7)	59(3)*
C(11)	6266(4)	2330(5)	235(8)	76(4)*
C(12)	6606(5)	1715(5)	253(9)	79(4)*
C(13)	7153(5)	1595(6)	1190(12)	92(5)*
C(14)	7374(5)	2052(7)	2112(11)	98(5)*
C(15)	7025(4)	2684(5)	2081(8)	82(4)*
C(16)	4887(4)	2894(4)	1129(6)	55(3)*
C(17)	4819(4)	2271(4)	1683(8)	78(4)*
C(18)	4331(5)	1808(4)	1112(8)	99(4)*
C(19)	3916(5)	1964(4)	8(8)	100(4)*
C(20)	3981(5)	2572(5)	-559(8)	105(4)*
C(21)	4457(4)	3045(4)	1(7)	78(4)*
O(51)	1103(2)	-591(2)	1320(4)	55(2)*
C(52)	1345(4)	-549(4)	2667(6)	55(3)*
C(53)	1273(4)	188(4)	3015(6)	60(3)*
O(54)	555(3)	356(3)	2732(4)	66(2)*
C(55)	463(5)	1081(4)	2761(8)	86(4)*
C(56)	-249(5)	1247(4)	2301(7)	97(4)*
O(57)	-443(3)	1088(2)	988(4)	69(2)*
C(58)	-1167(4)	1166(4)	603(7)	69(3)*
C(59)	-1323(4)	1200(4)	-801(6)	67(3)*
C(60)	992(4)	-1071(4)	3363(6)	54(3)*
C(61)	1384(5)	-1478(4)	4281(8)	78(4)*
C(62)	1062(7)	-1968(5)	4914(8)	95(5)*
C(63)	352(7)	-2057(5)	4621(10)	92(5)*
C(64)	-33(5)	-1655(5)	3720(9)	94(4)*
C(65)	288(4)	-1167(4)	3099(7)	79(4)*
C(66)	1610(4)	341(4)	4359(6)	61(3)*
C(67)	1253(4)	210(4)	5365(7)	84(4)*
C(68)	1579(5)	336(4)	6611(7)	108(5)*
C(69)	2241(6)	555(6)	6853(10)	137(6)*
C(70)	2579(6)	682(7)	5854(13)	142(6)*
C(71)	2268(5)	585(5)	4623(9)	103(5)*

3

	x	y	z	U
O(1)	781(2)	3699(1)	4851(2)	55(1)*
C(2)	1558(2)	3661(1)	4188(3)	50(1)*
C(3)	2254(2)	4221(1)	4424(3)	51(1)*
O(4)	1487(2)	4699(1)	4073(2)	55(1)*
C(5)	1995(2)	5252(1)	4461(3)	57(1)*
C(6)	1084(2)	5685(1)	4383(3)	61(1)*
O(7)	1596(2)	6220(1)	4876(2)	68(1)*
C(8)	841(3)	6698(1)	4760(3)	64(1)*
C(9)	158(2)	6683(1)	5603(3)	58(1)*
C(10)	2295(2)	3116(1)	4545(2)	46(1)*
C(11)	2487(3)	2744(1)	3718(3)	67(1)*
C(12)	3205(3)	2265(2)	4084(3)	77(2)*
C(13)	3716(3)	2151(2)	5269(3)	67(2)*
C(14)	3533(3)	2518(2)	6105(3)	74(2)*
C(15)	2812(3)	2996(2)	5742(3)	66(1)*
C(16)	3117(2)	4228(1)	3771(3)	50(1)*
C(17)	2791(3)	4326(1)	2546(3)	72(2)*
C(18)	3555(4)	4326(2)	1926(4)	99(2)*
C(19)	4666(4)	4219(2)	2523(4)	111(2)*
C(20)	5019(3)	4126(2)	3752(4)	100(2)*
C(21)	4246(3)	4127(1)	4376(4)	73(2)*
O(51)	2316(1)	5355(1)	-883(2)	51(1)*
C(52)	2307(2)	5940(1)	-459(2)	45(1)*
C(53)	3210(2)	5977(1)	773(2)	45(1)*
O(54)	4255(1)	5838(1)	603(2)	52(1)*
C(55)	5134(2)	5763(1)	1720(2)	52(1)*
C(56)	6125(2)	5515(1)	1438(3)	52(1)*
O(57)	6951(2)	5410(1)	2574(2)	58(1)*
C(58)	8059(2)	5310(1)	2549(3)	59(1)*
C(59)	8255(2)	4707(1)	2148(3)	60(1)*
C(60)	1174(2)	6109(1)	-368(2)	48(1)*
C(61)	645(3)	5737(2)	207(3)	75(2)*
C(62)	-351(4)	5903(2)	376(4)	110(2)*
C(63)	-831(3)	6436(2)	-43(5)	120(2)*
C(64)	-325(3)	6802(2)	-623(4)	99(2)*
C(65)	677(3)	6640(1)	-796(3)	67(1)*
C(66)	3239(2)	6583(1)	1332(3)	46(1)*
C(67)	2828(3)	6680(2)	2274(3)	69(2)*
C(68)	2846(3)	7237(2)	2747(4)	94(2)*
C(69)	3276(3)	7701(2)	2300(4)	94(2)*
C(70)	3694(3)	7609(2)	1371(4)	79(2)*
C(71)	3677(3)	7055(1)	892(3)	59(1)*

3a

	x	y	z	U
I	2238(1)	780(1)	2273(1)	74(1)*
Na	4719(2)	801(1)	7648(1)	59(1)*
O(1)	5752(2)	2630(2)	8016(1)	58(1)*
C(2)	7211(4)	2625(3)	7459(2)	54(1)*
C(3)	6847(4)	2731(2)	6569(2)	54(1)*
O(4)	5940(3)	1905(2)	6463(1)	68(1)*
C(5)	5017(6)	2168(4)	5842(3)	97(2)*
C(6)	3438(6)	2470(4)	6288(4)	128(3)*
O(7)	2852(3)	1665(2)	6844(3)	127(2)*
C(8)	1906(7)	975(4)	6660(5)	178(4)*
C(9)	2602(8)	-115(4)	6378(4)	136(3)*
O(10)	3438(3)	-566(2)	6977(2)	73(1)*
C(11)	2826(4)	-1451(3)	7435(2)	57(1)*
C(12)	3315(4)	-1481(2)	8292(2)	53(1)*
O(13)	2723(3)	-446(2)	8672(1)	61(1)*
C(14)	3000(5)	-287(3)	9496(2)	69(1)*
C(15)	2804(4)	919(3)	9677(2)	64(1)*
O(16)	4043(3)	1328(2)	9130(1)	66(1)*
C(17)	4316(4)	2360(3)	9366(2)	64(1)*
C(18)	5839(4)	2547(3)	8889(2)	68(1)*
C(19)	8057(4)	3524(3)	7666(2)	64(1)*
C(20)	7361(6)	4596(3)	7723(3)	83(2)*
C(21)	8145(8)	5431(4)	7881(3)	112(2)*
C(22)	9602(9)	5212(6)	7999(3)	128(3)*
C(23)	10318(7)	4169(7)	7954(3)	122(3)*
C(24)	9532(5)	3289(4)	7795(3)	90(2)*
C(25)	8254(4)	2644(3)	5862(2)	55(1)*
C(26)	8975(5)	3545(3)	5624(3)	80(1)*
C(27)	10217(6)	3461(4)	4941(3)	103(2)*
C(28)	10706(5)	2506(4)	4493(3)	94(2)*
C(29)	10022(5)	1609(4)	4744(3)	81(2)*
C(30)	8803(4)	1677(3)	5431(2)	70(1)*
C(31)	3371(4)	-2501(3)	6924(2)	58(1)*
C(32)	4908(5)	-2802(3)	6614(2)	78(1)*
C(33)	5391(7)	-3778(4)	6177(3)	105(2)*
C(34)	4391(9)	-4439(4)	6047(3)	107(3)*
C(35)	2873(9)	-4144(4)	6342(3)	112(3)*
C(36)	2335(5)	-3157(3)	6781(2)	78(2)*
C(37)	2774(4)	-2423(2)	8816(2)	52(1)*
C(38)	3805(4)	-3336(3)	8889(2)	64(1)*
C(39)	3304(6)	-4215(3)	9355(3)	83(2)*
C(40)	1802(6)	-4164(4)	9757(3)	91(2)*
C(41)	804(6)	-3271(4)	9685(3)	95(2)*
C(42)	1264(4)	-2405(3)	9220(3)	75(1)*

*Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table. 4: Selected Atomic Distances and Torsion Angles of 2,2a,3 and 3a.

	2	2a	3	3a
bond lengths [Å]				
Ph-C-C-Ph	1.505(7)	1.519(11)	1.518(4)	1.528(4) [C(2)-C(3)]
				1.522(5) [C(11)-C(12)]
av.$C-C_{aliph.}$	1.491	1.501	1.493	1.454 [O(7)-chain]
				1.494 [O(16)-chain]
O(1)-C(2)	1.437(6)	1.429(9)	1.427(4)	1.435(3)
O(10)-C(11)				1.431(4)
O(4)-C(3)	1.408(6)	1.409(9)	1.422(3)	1.424(4)
O(13)-C(12)				1.413(3)
av.$C-O_{chain}$	1.407	1.415	1.418	1.389 [O(7)-chain]
				1.416 [O(16)-chain]
torsion angles [°] at the stilbene units				
H-C-C-H	171.8(0)	63.4(2)	176.8(0)	170.7(0) [C(2)-C(3)]
				177.0(0) [C(11)-C(12)]
Ph-C-C-Ph	172.6(4)	60.7(8)	57.4(3)	62.6(3) [C(2)-C(3)]
				56.3(3) [C(11)-C(12)]
O-C-C-O	171.9(4)	62.9(6)	57.2(3)	52.7(3) [C(2)-C(3)]
				58.1(3) [C(11)-C(12)]
interatomic distances [Å]				
O(1)-O(1A)	7.713	5.923	6.274	4.973 [O(1)-O(13)]
O(4)-O(4A)	4.397	5.410	5.062	4.031 [O(4)-O(10)]
O(7)-O(7A)	6.173	5.246	6.899	4.023 [O(7)-O(16)]
O(1)-O(4)	3.585(ap)	2.756(sc)	2.698(sc)	2.624 [O(1)-O(4)]
				2.672 [O(10)-O(13)]
O(4)-O(7)	2.893(sc)	2.721(sc)	3.573(ap)	2.780
				2.804 [O(13)-O(16)]
				2.762 [O(7)-O(10)]
				2.781 [O(1)-O(16)]
Na-O(1)		2.962		2.677
Na-O(4)		2.705		2.502
Na-O(7)		2.623		2.444
Na-O(10)				2.531
Na-O(13)				2.807
Na-O(16)				2.410

On the other hand, in the trans-syn-trans isomer, 3, the phenyl groups are located at (sc) ethylene groups and thus appear synclinal and bis-equatorial. Structure 3 is more rectangular in shape and less compact than structure 2 as can be seen from the transannular O-O distances (Table 4). Thus, the structure 3 quite closely resembles those of [18]crown-6 and the known structures of dicyclohexano crowns whereas the structure of 3 is unprecedented and completely different from the cyclohexano crown isomer with the same substitution pattern [12].

The two crown ethers form different types of complexes with sodium iodide. 2a is a "normal" crown complex with the sodium ion in the centre of the plane of six oxygen atoms and the phenyl groups in axial-equatorial positions. The sodium ion is further coordinated to two water molecules on either face of the ring. In the lattice, such complexes with 8-coordinated sodium are bridged to one another by the iodide counter-ion. Additionally, the crystals contain dichloromethane solvent molecules in a regular array. This type of complex is closely related to the sodium bromide complex of *cis-anti-cis*-dicyclohexano-[18]crown-6 [13]. The complex 2a lies on an inversion centre, but the H_2O-Na-H_2O axis is not perpendicular to the ring plane so as to avoid steric interaction with the axial phenyl groups. As a result of this distortion, the Na-O distances to the oxygens next to the *equatorial* phenyl group are substantially longer than to the other oxygens. This is contrary to the observations on the corresponding complexes of dicyclohexano-[18]-crown-6 [13,14].

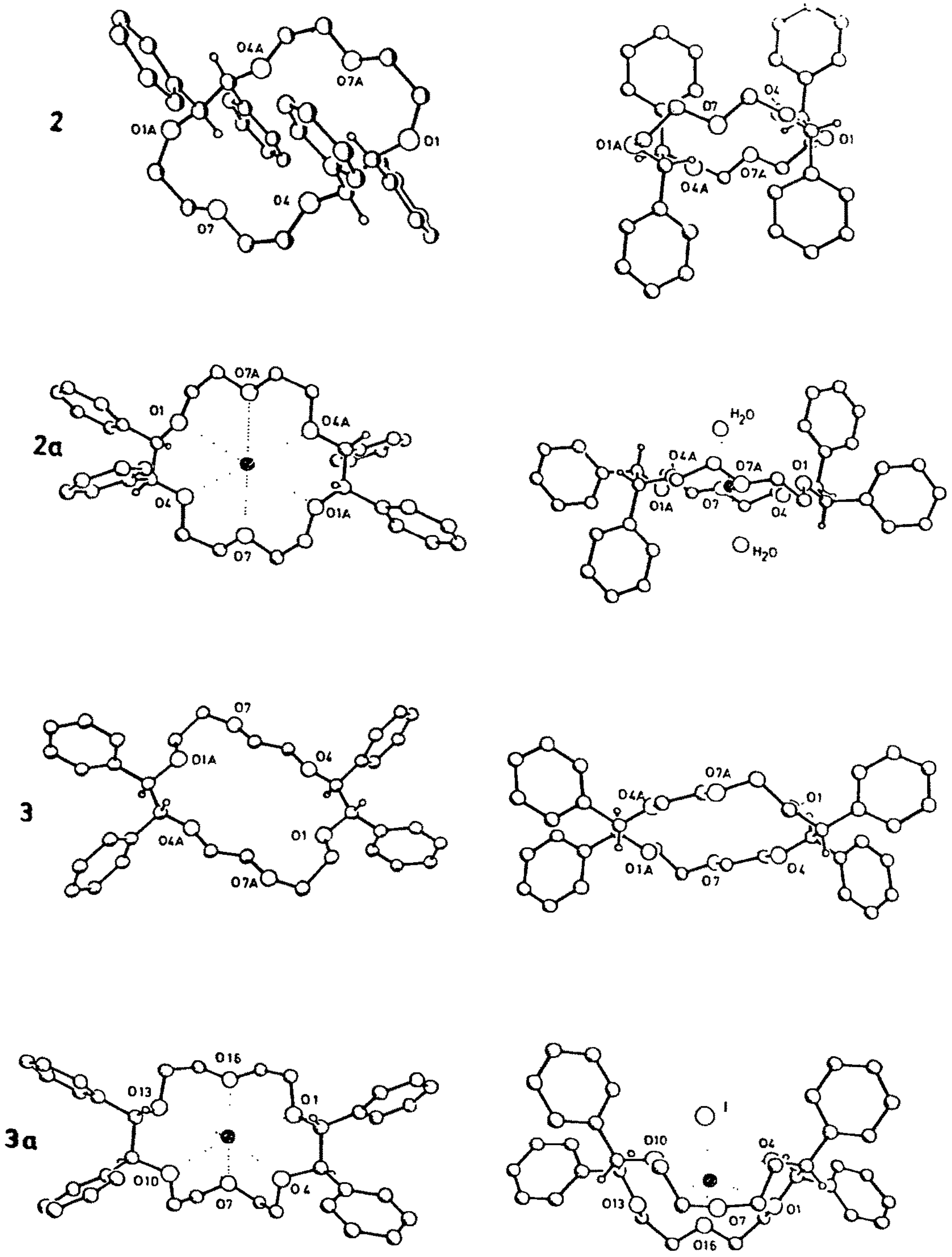

Fig. 1: Molecular Structures of the crown ethers 2 and 3 and their sodium iodide complexes 2a and 3a. Hydrogen atoms are omitted except in the benzylic positions.

The structure of 2a shows a 7-coordinated sodium ion. The ligand is strongly bent with five oxygens approximately in plane with the sodium ion and the sixth oxygen beneath this plane. The seventh coordination site above the plane is provided by the counter-ion, the distance of 3.166 Å indicating close ion pair contact. The complex is asymmetric but it may be approximately described with a symmetry plane through I, Na, O7 and O16. The structure may be compared with the NaSCN complex of [18]crown-6; in this complex, however, the thiocyanate ion is bridged to the sodium ion by a water molecule [15].
Only minor conformational changes are necessary from the free ligand 3 to the complex 3a whereas the phenyl groups in 2 have to be rotated towards each other by a dihedral angle of 120 ° to reach the conformation of the complex 2a. This finding is consistent with the observed 20-fold higher association constant of 3 for sodium ions[2].

^{1}H-NMR spectroscopy

The conformations of organic molecules are not necessarily the same in the solid state and in solution. We therefore sought for information on the solution conformations of 1,2 and 3, and their alkali metal and ammonium complexes. The conformational behaviour of free and complexed crowns has been studied theoretically by molecular mechanics calculations[16,17] and experimentally by ir[18,19] and nmr[20,21,22] spectroscopy. Thus, the conformation of unsubstituted [18]crown-6 was found to be the same in the solid state[10] and in less polar solvents[18] and does also correspond to one of the minimum energy conformations evaluated by molecular mechanics calculations[17]. On the other hand, the crystal structure of dibenzo-[18]crown-6[11] shows an elongated conformation similar to those of 2 and 3 in this paper whereas no indication of the presence of antiperiplanar -O-CH_2-CH_2-O- groups was found in ^{1}H-nmr studies in several solvents[20].
The isomers of 2,3,11,12-tetraphenyl-[18]crown-6 are particularly well suited for ^{1}H-nmr studies because the benzylic protons in the 2,3,11, and 12 positions appear separated from the other aliphatic protons in the nmr spectra[2]. These signals have different chemical shifts for each isomer and thus contain information on the conformation of the diphenylethanediyl units.
In 1 and 2, the protons of each diphenylethanediyl group are enantiotopic (see Scheme 1) and thus appear as singlets. In the chiral environment provided by complexing with 1-phenylethyl ammonium bromide, the two protons become distereotopic and appear as an AB spectrum[2,23]. The vicinal H,H-couplings thus become visible. Only one AB spectrum is observed because in both crown ethers the two diphenylethanediyl groups are homotopic due to the presence of C_2 axes by which they are interconvertible. In isomer 3, the two diphenylethanediyl groups are enantiotopic but the protons within each group are homotopic, giving rise to the observation of one singlet in the free ligand and two singlets in the complex with the optically active ammonium salt, for the benzylic protons. The vicinal H-H coupling is not obtained in the latter case.
Fortunately, however, the vicinal ^{1}H-^{1}H-coupling constants for all free ligands and complexes are accessible from ^{13}C satellite spectra. The low field parts of the satellites appear in a region of the spectrum which is unperturbed by other resonances. The identification of the ^{13}C satellites is confirmed by the observed one-bond ^{13}C-^{1}H coupling constants in the range of 142-146 Hz which is in good agreement with the values found for e.g. 1,4-dioxane. In the following, the solution conformations of the crown ethers and their complexes with Na, K and ammonium ions are discussed on the basis of nmr data given in Table 5.
Narrow resonances are found in all nmr spectra indicating rapid conformational and/or ligand exchange equilibria. Chemical shifts and coupling constants have thus to be taken as *average* values.
The influences operating on the chemical shifts of the benzylic protons can be divided into three main factors:

i. Complexation of cations will lead to a decrease in electron density of the crown ether oxygens and to a downfield shift of the proton resonances. This is found in all complexes with sodium cations as compared with the free ligands; smaller or no effects are found with potassium ions.
ii. In the relative position of the protons (axial or equatorial) with respect to the plane of the crown ether ring, equatorial protons may be expected to be less shielded and thus to appear shifted more downfield than axial protons[25]. This effect may be responsible for the higher δ values of 1 and 2 as compared to 3.
iii. The relative position of the protons with respect to the anisotro-

pic regions of the phenyl groups in the crown ethers or in the complexands may have major influences; this effect may be responsible for the upfield shift of the benzylic resonances in the complexes with 1-phenylethylammonium bromide.

The latter two influences are likely to be quite sensitive to conformational changes. However, their rigorous interpretation would require calculations based on optimized geometries which are not available at present.
More concise information is expected from the vicinal coupling constants since these depend directly on the dihedral angle of the coupling nuclei[26]. According to the findings in the 1,4-dioxane system[27], one can expect coupling constants in the range of 3 Hz for the synclinal position and in the range of 10 Hz for the antiperiplanar position of the vicinal protons.
Thus, the small coupling constants in crown ether **1** and its complexes suggest a synclinal orientation of the benzylic protons. This would correspond to axial/equatorial positions with respect to the crown ether ring, similar to the geometry found in the crystal structure of **2a**.
The relatively high coupling constant in the free ligand **2**, however indicates a significant contribution of the antiperiplanar conformation of the vicinal hydrogens, as found in the crystal molecular structure. Furthermore, on complexation, the coupling constant decreases considerably, with the exception of the potassium bromide complex where the effect is still significant, but small. This finding completely matches the conformational changes from **2** to **2a** observed in the crystal structures.

Finally, high coupling constants troughout are found for crown ether **3** and its complexes which indicates a predominant antiperiplanar orientation of the vicinal benzylic protons as it is found in the crystal structures of both the free ligand **3** and its sodium iodide complex **3a**.

In conclusion, the combined results of the crystal structure and proton nmr studies on the crown ethers and crown ether complexes in this paper suggest that the solid state and solution conformations are quite similar. This finding is consistent with the previously determined order of complexing ability: 3>1>2.

Table 5: ^{1}H nmr chemical shifts and coupling constants of the benzylic protons of **1**, **2**, and **3** and some of their complexes*

compound	δ	$^3J_{H-H}$	$^1J_{C-H}$
	1 (cis-syn-cis)		
free ligand	4.81	3.3	142.2
NaI	4.96	3.1	142.9
KBr	4.83	2.7	143.5
KSCN	4.85		
NH_4SCN	4.80	2.8	143.0
$\underset{NH_3Br}{PhCH}CH_3$	4.52	2.9	
	2 (cis-anti-cis)		
free ligand	4.88	6.2	143.5
NaI	4.96	3.9	143.0
KBr	4.88	5.1	144.0
KSCN	4.83		
NH_4SCN	4.82	2.8	142.6
$\underset{NH_3Br}{PhCH}CH_3$	4.84	4.9	
	3 (trans-syn-trans)		
free ligand	4.52	8.0	143.7
NaI	4.76	9.5	146.3
KBr	4.70	8.9	145.5
KSCN	4.67		
NH_4SCN	4.64	8.8	145.6
$\underset{NH_3Br}{PhCH}CH_3$	4.39		

* chemical shifts in ppm vs. TMS; coupling constants in Hz

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References

1) Burden,I.J.;Coxon,A.C.;Stoddart, J.F.;Wheatley,C.M., *J.Chem.Soc., Perkin Trans.1*,1977,220.

2) Merz,A.;Eichner,M.;Tomahogh,R., *Liebigs Ann.Chem.* 1981,1774.

3) Dietl,F.;Merz,A.;Tomahogh,R., *Tetrahedron Lett.* 1982,5255.

4) Merz,A.;Haunschild,J.,unpublished.

5) Clegg, W.,*Acta Cryst.* 1981,*A37*,22.

6) Such disorder is not unusual,even in complexed ligands, e.g.:Larson, S.B.;Dalley,N.K.,*Acta Cryst.* 1982,*B38*, 1309.

7) Cram,D.J.;Trueblood,K.N.,*Top.Curr. Chem.*1981,*98*,43.

8) Cram,D.J.;Dicker,I.B.;Knobler,C.B. Trueblood,K.N.,*J.Amer.Chem.Soc.* 1982,*104*,6828.

9) Gabard,J.;Collet,A.,*J.Chem.Soc., Chem.Comm.* 1981,1137; Moran,J.R.;Karbach,S.;Cram,D.J., *J.Amer.Chem.Soc.* 1982,*104*,5826.

10) Maverick,E.M.;Seiler,P;Schweizer,W.B.;Dunitz,J.D.,*Acta Cryst.* 1980,*B36*,615.

11) Bright,D.;Truter,M.R., *J.Chem. Soc.(B)* 1970,1544.

12) Dalley,N.K.;Smith,J.S.;Larson,S.B. Christensen,J.;Izatt,R.M.,*J.Chem. Soc.,Chem.Comm.* 1975,43.

13) Mercer,M.;Truter,M.R.,*J.Chem.Soc., Dalton Trans.* 1973,2215.

14) Hughes,D.L.;Truter,M.R.,*J.Chem. Soc.,Chem.Comm.* 1982,727.

15) Dobler,M.;Dunitz,J.D.;Seiler,P., *Acta Cryst.* 1974,*B30*,2741.

16) Bovill,M.J.;Chadwick,D.J.;Sutherland,I.O,*J.Chem.Soc.,Perkin Trans.* 1980,1529.

17) Wipff,G.;Weiner,P.;Kollmann,J., *J.Amer.Chem.Soc.*1982,*104*,3249.

18) Dale,J.;Kristiansen,P.O.,*Acta Chem.Scand.* 1972,*26*,1471.

19) Tsatas,A.T.;Stearns,R.W.;Risen, W.M.,jr.,*J.Amer.Chem.Soc.* 1972, *94*,5247.

20) Live,D.;Chan,S.I.,*J.Amer.Chem.Soc.* 1976,*98*,3769.

21) Shchori,E.;Jagur-Grodzinski,J.; Shporer,M.,*J.Amer.Chem.Soc.* 1973, *95*,3842.

22) Grandjean,J.;Laszlo,P.;Offermann, W.;Rinaldi,P.L.,*J.Amer.Chem.Soc.* 1981,*103*,1300.

23) Pirkle,W.;Beare,S.D.,*J.Amer.Chem. Soc.*1969,*91*,5150;Mannschreck,A., *Nachr.Chem.Techn.*1975,*23*,294.

24) Lippert,E.;Prigge,H.,*Ber.Bunsenges.Phys.Chem.*1963,*67*,415.

25) This effect is well-known in cyclohexane derivatives: Pople,J.A.; Schneider,W.G.;Bernstein,H.J, *"High-resolution Nuclear Magnetic Resonance"*,McGraw-Hill, New York, 1959; Chapter 14. cM

26) Karplus,M.,*J.Chem.Phys.* 1959,*30*, 11;*J.Amer.Chem.Soc.* 1963,*85*,2870.

27) Gatti,G.;Segre,A.L.;Morandi,C., *Tetrahedron* 1967,*23*,4385; Abraham,R.J.;Gatti,G.,*J.Chem.Soc. (B)* 1969, 961.