

The Number of Ideal Rings on the Diamond Lattice; Application to Crown Ethers

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Three independent computing methods are described for the calculation of the number of different conformations of rings of up to 26 atoms, superimposable on the diamond lattice. Our computations extend results published earlier and show them to be partly incorrect. As an application, the number of different conformations for 'ideal' crown ethers has been calculated (6-crown-2, 12-crown-4, 18-crown-6, and partly, 24-crown-8) and a comparison has been made with structures determined by X-ray crystallography.

Since Pedersen synthesized the first crown ether in 1967 and proposed a still-used nomenclature for it,¹ crown ethers have become increasingly more important, for instance as selective complexing agents for ions^{2,3} and even neutral molecules.⁴ Although at first sight medium and large crown ethers seem to be very flexible, the number of essentially different conformations of crown ethers found by X-ray crystallographic structure determinations is still very limited.^{5,6} Although a number of papers exist that deal with the conformations of crown ethers,^{4,7-9} there seems to exist hitherto no complete and detailed analysis of the conformational possibilities for crown ethers.

In order to get an insight into the number of different conformations possible for crown ethers and especially for 18-crown-6, we developed a computer program to calculate all ideal crown ether rings. We made the following assumptions: all C-C and C-O bond lengths are equal, all bond angles are exactly tetrahedral (109.471°) and all torsion angles can adopt only the values for perfectly staggered conformations, *i.e.*, 60° (*gauche*, g^+), 180° (*anti*, a) or 300° = -60° (*gauche*, g^-). That these assumptions are not far from reality is shown by the following bonding parameters, averaged over ten independent structure determinations involving 18-crown-6: C-O bond length 1.42 Å, C-C bond length 1.495 Å, \widehat{OCC} bond angle 109.5°, and \widehat{COC} bond angle 112.6° (see also Dunitz *et al.*¹²). Deviations from these mean values are generally not more than 0.03 Å for bond lengths and 2° for bond angles. Torsion angles show larger deviations of up to 30° from the ideal values. With these assumptions the rings fit on the diamond lattice.

We first calculated the number of polymethylene rings for comparison with earlier published results¹³⁻¹⁵ and derived from this, in a second stage, the number of ideal crown ether rings.

Results and Discussion

Part A. Polymethylene Rings on the Diamond Lattice.—Method (a). We used the method, developed by Saunders,¹³ to calculate all ideal polymethylene conformations for rings containing 6, 8 . . . 22 atoms (only even-membered rings fit on the diamond lattice, the six-ring being the smallest one).

† The shortening of the C-C bonds, compared with the normal $C_{sp^3}-C_{sp^3}$ alkane bond length¹⁰ (1.541 Å) is not only found in crown ethers, but also in, for instance, 1,2-dimethoxyethane¹¹ (1.492 Å).

In his notation Saunders used the numbers 1-4 to denote the four directions that exist in the diamond lattice. To a chain on the diamond lattice a number is assigned consisting of the successive direction codes. For chains with N atoms ($N - 1$) direction codes are needed, for N -rings one needs one direction code more, denoting the direction from atom N to atom 1. The first two directions of a ring may arbitrarily be chosen as 1 and 2. We will not go into a detailed description of Saunders' method (see ref. 13), but will only describe two improvements we have applied to speed up the calculations.

As Saunders showed, it is always possible to start with a g^+ torsion angle (starting directions chosen as 123). An alternative method is the following: if we assume that a conformation has no *anti* torsion angle, there must be at least one g^+g^- sequence to form a ring (a sequence of all g^+ or all g^- torsion angles forms a helix). As the sequences $g^+g^-g^+$ and $g^-g^+g^-$ form six-rings (not allowed sub-rings for N -rings with $N > 6$), the g^+g^- sequence has to be part of a $g^+g^+g^-g^-$ sequence for rings with more than six atoms and without *anti* torsion angles. The alternative is a ring with at least one *anti* torsion angle. As a sequence of all *anti* torsion angles cannot form a ring (but instead forms an all-extended zigzag chain), there must be at least one ag^+ sequence in the ring (or ag^- , yielding the mirror images). If this sequence is extended with two further torsion angles, there are nine sets left, of which the $ag^+g^-g^+$ set may be dropped immediately for rings containing more than six atoms (sub-ring of size six). The $ag^+g^+g^-$ set can also be omitted, because if the fifth torsion angle is g^+ , we have again the six-ring, if it is g^- or a , all conformations starting with these sets will also be found with the starting sets $g^+g^+g^-g^-$ (in which case further torsion angles may be *anti*) or $ag^+g^-g^-$. Finally the two sets ag^+ag^+ and ag^+ag^- may be dropped, because further torsion angles will either result in conformations containing at least one of the six remaining sets, or in conformations of the form $agagag . . .$ (where the *gauche* torsion angles may be of the g^+ or g^- type), which do not form rings.

So from the 81 possible combinations for the first four torsion angles only six are needed to generate all possibilities. Although we used the torsion notation above (g^+ , g^- , and a), this part of the calculations was actually performed using the direction code as Saunders did. In this notation the six remaining starting sets are (with the corresponding torsion code in parentheses): 123421 ($g^+g^+g^-g^-$), 121342 ($ag^+g^+g^+$), 121343 (ag^+g^+a), 121313 (ag^+aa), 121323 (ag^+g^-a), and 121324 ($ag^+g^-g^-$). It is possible to go even one or more steps further in this *a priori* elimination process, but this seemed to result in little more acceleration of the calculations.

The second improvement we applied deals with the process of eliminating rings that are identical with, or mirror images of, previous ones. If this process is applied to the direction codes, this will result in $48N$ permutations to be performed for each N -ring (namely N cyclic permutations around the ring, a factor two for the reversal of the direction around the ring and a factor 24 for the permutations of the four directions). We converted the direction notation for a given ring into the torsion notation (Table 1), resulting in only $4N$ necessary permutations to perform the same elimination process as described above, because the 24 permutations of the four directions are replaced by two permutations in the torsion notation $[(g^+, a, g^-) \rightarrow (g^+, a, g^-)$, the identity, and $(g^+, a, g^-) \rightarrow (g^-, a, g^+)$, converting a conformation into its mirror image].

We also calculated the number of possible conformations without overlap¹³ (the situation that two atoms not bound to a common atom occupy positions separated by one lattice point, resulting in serious steric hindrance when attached hydrogen atoms are considered). In this case three more starting sets may be omitted, because they contain an overlap situation (in all three sets a g^+g^- sequence).

The results obtained with this method are listed in Table 2, second column. Our results for the rings consisting of 16, 18, and 20 atoms including overlap do not agree with the earlier published results of Saunders¹³ (Table 2, last column). In order to resolve this disagreement, two of us (F. G. and H. N.) have written another computer program [method (b)], independent and with a set-up totally different from method (a).

Method (b). This method is divided into two sections. First a computer representation of a part of the diamond lattice is constructed and, secondly, this representation is used in a step-by-step search for rings.

In the first section the unit cell of diamond is used (Figure 1).

Table 1. Conversion from the 'direction code' into the 'torsion code.' The left column indicates the first direction, starting from an odd-numbered atom; the upper row, the second and third. 123 is arbitrarily chosen as g^+ . Triplets of directions starting from even-numbered atoms give the opposite of the corresponding torsion codes in this table ($g^+ \rightarrow g^-, a \rightarrow a, g^- \rightarrow g^+$). +, 0, -, and \times mean g^+ , a, g^- , and *not allowed*, respectively

	12	13	14	21	23	24	31	32	34	41	42	43
1	\times	\times	\times	0	+	-	0	-	+	0	+	-
2	0	-	+	\times	\times	\times	+	0	-	-	0	+
3	+	0	-	-	0	+	\times	\times	\times	+	-	0
4	-	+	0	+	-	0	-	+	0	\times	\times	\times

Because the unit cell is cubic, the cell axes can also be used as an (orthonormal) Cartesian reference system. When the unit cell edge is given length four, all atoms can be described with integer co-ordinates. The positions of the 18 atoms from Figure 1 are collected in Table 3, together with an indication of their neighbours. (The C-C bond length in this system is $\sqrt{3}$, but this is merely a scaling factor.) The first three atoms of a chain may be fixed $[(0,0,0), (1,1,1), \text{ and } (2,2,0)]$ and the first torsion angle may be chosen as $+60^\circ$ [which fixes atom four at $(1,3,-1)$]. A larger part of the diamond lattice is generated by applying a number of unit-cell translations. The minimum number of steps to cross a unit cell from one face to the opposing face is four. As we only wanted to calculate rings with at most 18 members, one can easily recognize, taking the start directions into account, that the maximum numbers of unit cells needed in the x -, \bar{x} -, y -, \bar{y} -, z -, and \bar{z} -directions are 3, 2, 3, 2, 2, and 2 respectively. So a sub-lattice of 100 unit cells suffices for all N -rings with $N \leq 18$. For every point in this sub-lattice the minimum number of steps to reach the point starting from the origin is calculated. Points with a minimum number of greater than nine are eliminated from the list, because they can never be part of an N -ring with $N \leq 18$. The remaining points (614) are stored, together with for each

Table 2. The number of different conformations for N -rings, superimposable on the diamond lattice ($N = 6, 26$), by three different methods (see text for explanation) and comparison with earlier published results. The numbers between brackets denote the number of rings without overlap; — means not calculated

Ring size	Method			Earlier results	
	(a)	(b) *	(c) *	Smith ^{14,15}	Saunders ¹³
6	1 (1)	1	1	— (1)	1 (1)
8	1 (0)	1	1	— (0)	1 (0)
10	1 (0)	1	1	— (0)	1 (0)
12	4 (0)	4	4	— (0)	4 (0)
14	13 (1)	13	13	— (1)	13 (1)
16	51 (1)	51	51	— (1)	56 (1)
18	239 (11)	239	239	— (11)	238 (11)
20	1 204 (19)	—	1 204	— (—)	1 202 (19)
22	6 750 (120)	—	6 750	— (—)	— (120)
24	— (419)	—	—	— (—)	— (419)
26	— (2 290)	—	—	— (—)	— (—)

* The number of rings without overlap was not explicitly determined, but because all rings (including the ones without overlap) agreed fully with all rings determined with method (a), the number of rings without overlap is equal to that in method (a).

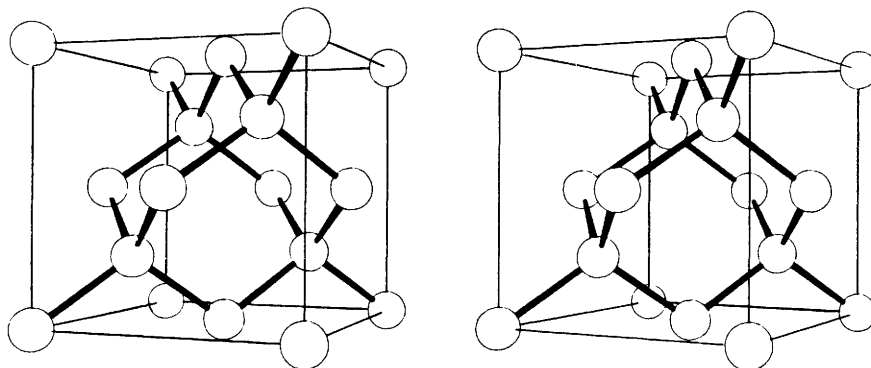


Figure 1. Stereoview of the cubic unit cell of diamond (space group $Fd\bar{3}m$). C-atoms at $(0,0,0; \frac{1}{4}, \frac{1}{4}, \frac{1}{4}) + (0,0,0; 0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, 0)$; the others obtained by unit-cell translations. Point symmetry $\bar{4}3m$ ¹⁶

Table 3. Co-ordinates of the 18 atoms in the diamond unit cell (with the edge chosen as having length 4). Connected atoms are indicated by an \times

X	Y	Z	X	Y	Z	X	Y	Z	X	Y	Z	X	Y	Z	X	Y	Z			
0	0	0	0	4	0	0	4	4	0	4	2	2	0	4	2	2	1	3	3	1
4	0	0	0	0	4	0	4	0	4	4	2	0	2	2	4	2	1	3	1	3
0	4	0	0	0	0	4	0	4	4	4	0	2	2	2	2	4	1	3	1	3
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4	2	2																		
2	4	2																		
2	2	4																		
1	1	1																		
3	3	1																		
3	1	3																		
1	3	3																		

point an index, its co-ordinates, and the indices of its neighbours.

In the second section a recursive procedure is used to determine all possible rings within the sub-lattice defined above. The outline of this procedure is as follows: at the start an index of 0 is attributed to each point in the input list. In travelling through the lattice, for each point reached the indices of its neighbours are augmented with 1. The next point of the string must be a neighbour with index 1. Therefore the string can never 'double back' on itself, because the lattice point it came from already has an index of 2. Also there is no possibility of getting a sub-ring, because the index of a point determining a sub-ring will be 2 before reaching it (namely 0 at the start, 1 when the string passes along it, and 2 at the last step performed before it could be reached again). As a second condition, a point is only used in the string if the minimum number of steps to reach the origin from that point is less than $N + 1 - n$ (where N is the number of atoms in the ring and n the number of performed steps). As the procedure is recursive, when the last step has been performed (determining a ring or not) or when a point is reached without any possibility to proceed, the procedure returns to one level lower, resetting the indices for the last step. With this method all rings for a given N are easily found and the only remaining problem is the reduction of all conformations, including mirror images and regardless of orientation, to unique structures. This is carried out by determining the N torsion angles for every four connected atoms in the ring and by eliminating conformations encountered previously by an analogous process as described in method (a).

The results have been listed in the third column of Table 2 and agree fully with the results of method (a).

Method (c). As a final test we programmed a third method. We chose a special co-ordinate system within the diamond lattice. If the four atoms, surrounding an arbitrarily chosen atom, are denoted by A, B, C, and D (forming a regular tetrahedron), we have chosen atom A as being positioned in the origin, the x -axis lying along AB, the y -axis parallel to CD, and the z -axis orthogonal to the xy -plane. If the half length of AB is chosen as the unit length of the x - and y -axes and $\frac{1}{4}\sqrt{2}AB$ as the unit length of the z -axis, it can be proven that all lattice points have integer co-ordinates. [This coor-

dinate system is related to the one in method (b) by a rotation of 45° around the z -axis and a re-scaling of the x - and y -unit lengths (not z) by a factor $\sqrt{2}$ to retain integer co-ordinates.] Projected on to the xy -plane every chain within the diamond lattice forms a path on a square grid, and therefore can be represented by a two-dimensional figure consisting of orthogonal line segments of equal length. It is possible to calculate all z -co-ordinates of an arbitrary chain within the diamond lattice from the projection on to the xy -plane, if the z -co-ordinates of two neighbouring atoms n and $(n - 1)$ are known, because if $z_n = z_{n-1} \pm 1$, then $z_{n+1} = z_n \mp 1$ if the projection of the atoms $(n - 1)$, n , $(n + 1)$ on to the xy -plane forms a straight line, and $z_{n+1} = z_n \pm 1$ if it forms a corner (either left or right). Every linear part in the xy -projection of a chain therefore has alternating z -co-ordinates, whereas every part without linearity has constant increasing or decreasing z -co-ordinates.

To obtain all N -rings we first constructed the xy -projections of all N -chains in this co-ordinate system. If we use the characters s , l , and r for a 'straight,' 'left corner,' or 'right corner' projection part, all possible projections of N -chains can be obtained by constructing all possible strings of length $(N - 1)$ consisting of these three characters. As in method (a) it is possible to limit the calculations by using the same six starting sets. If the first two atoms are positioned at $(0,0,0)$ and $(1,0,1)$, these are (in projection code, the torsion codes in parentheses): $slsls(g^+g^+g^-g^-)$, $ssrlr(ag^+aa)$, $ssrsl(ag^+g^+g^+)$, $ssrss(ag^+g^+a)$, $ssrrl(ag^+g^-a)$, and $ssrrr(ag^+g^-g^-)$. The first s in every starting set arbitrarily positions atom 3 at $(2,0,0)$. The x - and y -co-ordinates of all points in a chain are easily calculated. All not-closed projections are rejected (which means: $|x_N - x_1| + |y_N - y_1| \neq 1$). For the remaining projections the z -co-ordinates of all atoms are calculated as shown above. The projections with $|z_N - z_1| \neq 1$ are rejected, the remaining conformations being closed. Rings with sub-rings are rejected by comparing all other pairs (i,j) of non-neighbouring atoms (sub-ring if $|x_i - x_j| + |y_i - y_j| = 1$ and $|z_i - z_j| = 1$), the remaining rings being acceptable. Finally the torsion code for each ring is determined and only unique rings are selected by a procedure analogous to the one used in methods (a) and (b).

The results of these calculations have been collected in

column 4 of Table 2 and are identical with the results of the previous two methods.

Two advantages of this method are its easy visualization (on squared graph paper) and, secondly, the fact that the calculations are much faster than when using a 'normal' co-ordinate system (atom 1 in the origin, atom 2 along the x -axis, atom 3 in the xy -plane), roughly by a factor 200 as shown in an early stage of programming, mainly a result of the use of integer co-ordinates and the dispensation of goniometric functions, which are usually needed for the co-ordinate calculations.

As can be seen from Table 2 the three independent methods we employed for the calculation of N -membered 'diamond-rings' are fully in agreement with one another. Therefore it seems probable that the small disagreement between our results and those of Saunders¹³ for the 16-, 18-, and 20-membered rings, including overlap, has arisen from an error in the latter.

All different conformations for the 6—12-membered rings (including overlap) are collected in Table 4, whereas for the 14-, 16-, and 18-rings the conformations without overlap are collected in Table 5.

Part B. Application to Crown Ethers.—As an application we determined the number of conformations for crown ethers, $\text{CH}_2\text{OCH}_2(\text{CH}_2\text{OCH}_2)_n\text{CH}_2\text{OCH}_2$. All different conformations were derived from the ideal polymethylene rings by taking into account the difference in atoms (C—O—C instead of

C—C—C). In principle there are therefore three times as many different ideal crown ether rings as 'diamond-rings,' which we can obtain from the polymethylene rings by a cyclic permutation of the O-atoms by 0, 1, and 2 positions. However, some of the resulting conformations will be identical. In our model we used C—C and C—H bonding distances of 1.5 and 1.0 Å, respectively.

As the repeating unit in crown ethers is the $-\text{CH}_2-\text{O}-\text{CH}_2-$ group, the number of heavy atoms in crown ethers is always a treble. Therefore ideal crown ethers always consist of a six-fold number of atoms, because only even-membered rings can be ideal. We will use the popular nomenclature proposed by Pedersen.¹

For comparison we have checked all X -ray structure determinations of crown ethers that have an entry in the Cambridge Crystallographic Data Base (CCDB).¹⁷ We selected all essentially independent crown ether rings, by which we mean that two or more crown ether rings in an asymmetric unit with different surroundings are treated separately, but different determinations of the same crystal structure or crystallographically different crowns with comparable surroundings are treated as one. Moreover, we searched the recent literature for X -ray structure determinations of crown ethers not yet incorporated in the CCDB, without, however, claiming an exhaustive search. All crown ether rings that cannot be ideal in the sense discussed above were discarded (for instance, crown ethers with double or triple bonds, with keto- or benzo-groups), just as were crown ethers with very bulky side-groups, which will restrict the ring too much to treat it as an, in principle, flexible crown ether. The remaining structures were compared with the calculated conformations. Values of experimental torsion angles were rounded to the nearest value of 60, 180, or 300° (g^+ , a , or g^-). Large deviations from these are mentioned and discussed in the text.

As a result of the occurrence of two different types of heavy atoms in crown ethers, three kinds of overlap can be distinguished, that is $\text{CH}\cdots\text{HC}$ overlap (as discussed in the previous section), $\text{CH}\cdots\text{O}$ overlap, and $\text{O}\cdots\text{O}$ overlap. $\text{CH}\cdots\text{HC}$ overlap is physically unrealistic and will occur only when accompanied by large deviations from the ideal conformation in order to release the $\text{H}\cdots\text{H}$ repulsion. (Methylene van der Waals radius 2.0 Å,¹⁸ $\text{C}\cdots\text{C}$ and $\text{H}\cdots\text{H}$ overlap distances in the model 2.45 and 0.82 Å).

The $\text{O}\cdots\text{O}$ overlap has a different character, because there are no atoms attached to the oxygens that interact, and can be considered as a relatively weak van der Waals repulsion

Table 4. All different conformations of N -rings for $N = 6, 8, 10,$ and 12 in both torsion and direction code and the number of overlaps for each. The first torsion code indicates the torsion angle defined by atom 1, 2, 3, and 4, and so on. The first direction is from atom N to 1, the next from atom 1 to 2, and so on. Every triplet in the direction code (position $n, n + 1, n + 2$) defines a torsion code (position n) (see Table 1 for conversion). +, 0, and - stand for g^+ , a , and g^- respectively

Ring size	Conformation		Overlaps
	Torsion code	Direction code	
6	+ - + - + -	123123	0
8	+ + - - + + - -	12342143	2
10	+ + 0 + + - - 0 - -	1234312343	2
12	+ + 0 + + 0 + + - 0 0 -	123431214313	2
	+ 0 0 - + 0 0 - + 0 0 -	123231212313	3
	+ + 0 + - 0 - - + 0 0 -	123431412313	3
	+ + 0 0 - - + + 0 0 - -	123434214343	3

Table 5. The different conformations of N -rings without overlap for $N = 14, 16,$ and 18 in both torsion and direction code (see Table 4 for further explanation)

Ring size	Conformation	
	Torsion code	Direction code
14	+ + 0 + + 0 0 - - 0 - - 0 0	12343121234312
16	+ + 0 0 - - 0 0 + + 0 0 - - 0 0	1234342121434312
18	+ + + 0 + + 0 0 + + 0 0 - - 0 - 0	123414232321414232
	+ + + 0 + + 0 + 0 - - 0 - - 0 - 0	123414232123414232
	+ + + 0 + + 0 0 0 + + 0 + + 0 + 0	123414232321413242
	+ + + 0 + 0 0 + 0 + + 0 0 - 0 0 + 0	123414242321414242
	+ + + 0 + 0 0 - 0 - - 0 - 0 0 + 0	123414242123414242
	+ + 0 + 0 0 - 0 - - 0 0 + 0 0 - 0 0	123431314123231312
	+ + 0 + 0 0 + 0 0 - - 0 - 0 0 - 0 0	123431312123431312
	+ + 0 + + 0 + 0 0 + + 0 + + 0 + 0	123431214143231412
	+ + 0 + + 0 0 0 - - 0 - - 0 0 0	123431212123431212
	+ + 0 0 0 + + 0 0 - - 0 0 0 - - 0 0	123434312123434312
	+ 0 0 - 0 0 + 0 0 - 0 0 + 0 0 - 0 0	123231312123231312

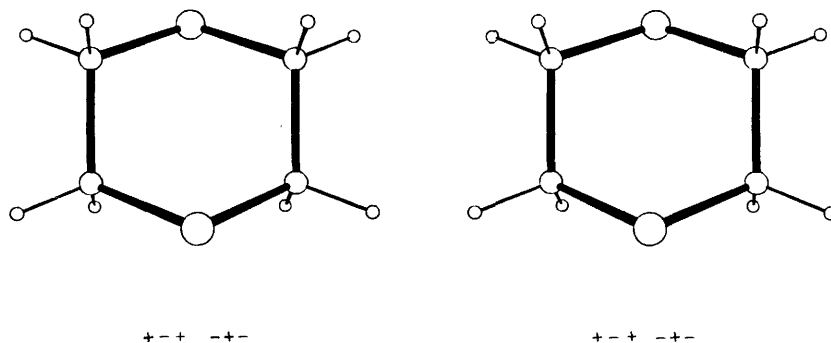


Figure 2. Stereoview of the ideal conformation of 6-crown-2

between oxygen atoms (oxygen van der Waals radius 1.40 Å,¹⁸ O...O overlap distance in the model 2.45 Å), augmented with an electrostatic (lone pair-lone pair) repulsion. This type of overlap does not occur frequently, because the most frequent cause of overlap is the occurrence of a g^+g^- sequence, which gives rise to overlap between one atom and a second one four positions further in the ring, which can consequently give only CH...HC or CH...O overlap.

CH...O overlap is far less severe than CH...HC overlap, because the van der Waals repulsion between the H and O atoms is opposed by an electrostatic attraction between them. CH...O overlap can be regarded as a non-linear intramolecular hydrogen bonding, although some authors prefer to describe it as an intramolecular dipolar interaction.¹⁹ In a recent review by Taylor and Kennard²⁰ it is concluded that short C-H...O interactions are likely to be more attractive than repulsive and can reasonably be described as hydrogen bonds. Most of the *intermolecular* C...O distances reported lie in the range 3.1–3.4 Å.^{21–23} However, Sutor²⁴ showed almost 20 years ago that *intramolecular* C-H...O bonding gives distances that are considerably shorter (C...O distances of 2.7–3.3 Å) and she also pointed out that in intramolecular H-bonding the deviations from linearity are rather common, especially when CH₂ is the donor group, and that the hydrogen atom is most probably directed towards the lone-pair orbital of the acceptor atom. (Calculated C...O and H...O distances in the model 2.45 and 1.73 Å, C-H...O angle 125.3°.)

Podo *et al.*¹⁹ made a theoretical analysis of the possible conformations of 1,2-dimethoxyethane and found that both the (C-C)_{anti} and the (C-O)_{anti} torsion angles were favoured over the *gauche* torsion angles by 0.1 and 1.1 kcal mol⁻¹, respectively. For a 1,5-CH...O interaction they calculated a destabilization of 0.3–0.5 kcal mol⁻¹. Other reported values are: (C-C)_{anti}-(C-C)_{gauche} 0.15–0.50 kcal mol⁻¹;²⁵ (C-O)_{anti}-(C-O)_{gauche} -1.1 kcal mol⁻¹;²⁶ (C-C)_{anti}-(C-C)_{gauche} -0.4 kcal mol⁻¹, (C-O)_{anti}-(C-O)_{gauche} -0.9 kcal mol⁻¹, and 1,5-CH...O overlap interaction 0.3 kcal mol⁻¹ destabilization.²⁷ It is clear that there is a much greater accordance with respect to the difference between a *gauche* and an *anti* C-O torsion angle than between a *gauche* and an *anti* C-C torsion angle, but all agree that C-O bonds have a very strong tendency to form an *anti* arrangement, whereas the preference for a *gauche* or *anti* C-C bond is far less striking.

We have used the energy values of Podo *et al.*¹⁹ (as they are intermediate) to make a very rough calculation of the conformational energies (CE) of all possible ideal crown ether conformations relative to an imaginary crown ether with all torsion angles *anti* and without overlap. (This was also used by Byström and Månsson²⁸ in their calculations of the so-called reduced apparent strain energies in some non-ideal crown ethers.) Since we are not aware of a reliable value for the

CH...HC overlap interaction destabilization energy, we have chosen, arbitrarily, a high value of 100.0 kcal mol⁻¹ for easy comparison of the CE of different conformations, together with the immediate recognition of the number of CH...HC overlaps from the CE-value. O...O overlap repulsion is completely neglected.*

All figures have been made with ORTEP.²⁹ All hydrogen atoms have been added (in the ideal as well as in the non-ideal crown ethers) at C-H distances of 1.0 Å with \widehat{CCH} and \widehat{OCH} angles of 109.471°. For the ideal crown ethers all atoms have been projected on to the least-squares plane; the experimentally found conformations have been rotated such that easy comparison with the appropriate ideal crown ether is possible.

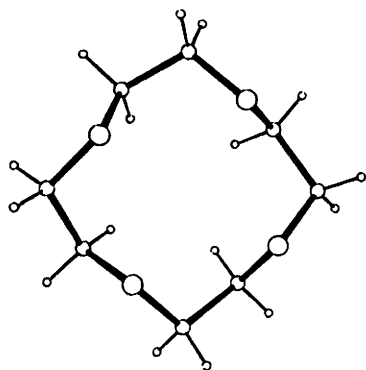
6-Crown-2. The smallest member of the crown ethers, 6-crown-2, better known as 1,4-dioxane, can exist only in one ideal conformation, the well-known chair conformation $g^+g^-g^+g^-g^+g^-$ (Figure 2) without overlap. Because there is only one ideal conformation and because it is known that the crown ether ring in complexes with 1,4-dioxane and in 1,4-dioxane derivatives never deviates much from this (see for instance Alcock and Sawyer³⁰), we did not perform an exhaustive search in the CCDB or in more recent literature.

12-Crown-4. For the more flexible 12-crown-4 molecule there exist seven possible ideal conformations (Figure 3a–g, Table 6), derived from four different ‘diamond-rings.’ There is only one 12-crown-4 conformation without CH...HC overlap, with six *gauche* C-O torsion angles and two CH...O overlaps. All other ideal conformations have at least one CH...HC overlap and are therefore very unlikely to occur.

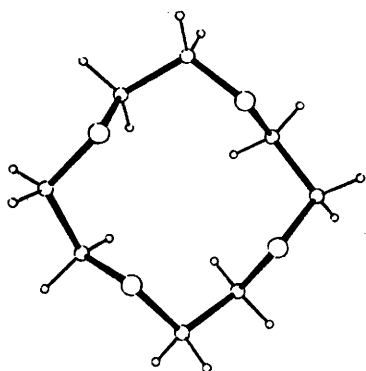
In the CCDB and the more recent literature we encountered only ten 12-crown-4 units which fulfil the conditions outlined above. None of these has an essentially ideal conformation. This is not surprising if we recognize that the only ideal conformation without CH...HC overlap has three of the four oxygen atoms directed out of the ring (Figure 3a), which is unfavourable for complex formation and crystal packings.

The ten found 12-crown-4 units fall apart into three different conformations, namely seven with approximate C₄ symmetry ($g^+g^+g^+g^+g^+g^+g^+g^+g^+g^+g^+g^+$ or the mirror image), *i.e.* one in the Na(12-crown-4)₂Cl·5H₂O complex³¹ (the two crown units are related by a C₂-axis), one in the Ca(12-crown-4)Cl₂·8H₂O complex,³² one in the Co(12-crown-4)(NO₃)₂ complex,³³ two crown units in the Na(12-crown-4)₂OH·8H₂O complex,³⁴ and

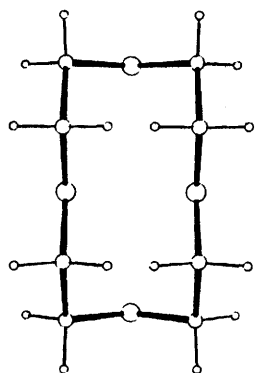
* It should be stressed that the CEs, computed in this way, have limited value, owing to the neglect of a large number of interactions; they are only a rough estimate of the relative energies of the different conformations. Small differences in CE are therefore not significant. Inclusion of, for instance, the effects of electrostatic interactions, complex formation, and crystal packing will certainly influence the relative stabilities of conformations with approximately the same CE.



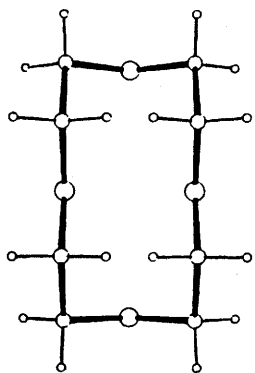
3h



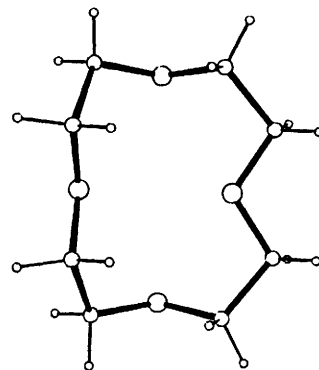
3i



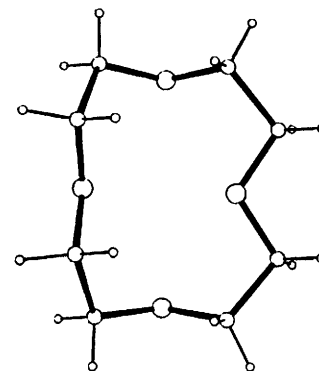
++0 0-- ++0 0--



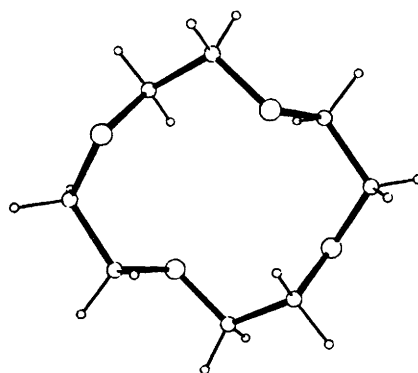
++0 0-- ++0 0--



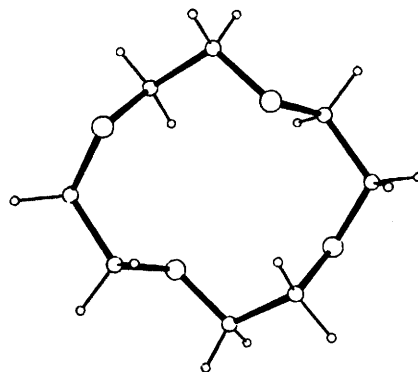
3k



3l



3m



3n

Figure 3. Stereoviews of the seven ideal conformations of 12-crown-4 (3a—3g with ascending CE) and of three non-ideal conformations of 12-crown-4 (3h—3j; positions of the heavy atoms taken from refs. 31, 36, and 38, respectively)

Table 6. All different ideal conformations for 12-crown-4 in both torsion and direction code (see Table 4 for further explanation). The atom numbering is always O(1), C(2), C(3), O(4) etc. Columns 3–6 give the conformational energy (CE) and the number of CH...HC, O...O, and CH...O overlaps (see text for explanation). The character in the last column indicates the plot of the conformation in Figure 3

Conformation						CE/ kcal mol ⁻¹	Overlaps				
Torsion code			Direction code				CC	OO	CO		
+ 0 +	+ 0 +	+ - 0	0 - +			123241432424	7.6	0	0	2	A
+ 0 0	- + 0	0 - +	0 0 -			123231212313	105.4	1	0	2	B
++ 0	++ 0	++ -	0 0 -			123431214313	106.2	1	0	1	C
++ 0	+ - 0	- - +	0 0 -			123431412313	106.6	1	0	2	D
+ 0 +	+ - 0	0 + -	- 0 -			123241212413	107.6	1	0	2	E
++ -	- 0 0	++ -	- 0 0			123421214312	107.6	1	0	2	F
++ 0	0 - -	++ 0	0 - -			123434214343	204.8	2	1	0	G

Table 7. The different ideal conformations for 18-crown-6 with CE ≤ 5.0 kcal mol⁻¹ in both torsion and direction code (see Tables 4 and 6 for further explanation). The character in the last column indicates the plot of the conformation in Figure 4. An * after the torsion code indicates that the conformation was experimentally encountered

Conformation						CE/ kcal mol ⁻¹	Overlaps				
Torsion code			Direction code				CC	OO	CO		
0 + 0	0 - 0	0 + 0	0 - 0	0 + 0	0 - 0 *	121313232121313232	0.6	0	0	0	A
++ 0	0 - 0	0 - 0	- - 0	0 + 0	0 + 0 *	123434242123434242	2.8	0	0	0	B
+ + 0	0 - 0	0 + 0	0 - -	0 - 0	0 + 0 *	123434242323414242	2.8	0	0	0	C
+ - 0	0 + 0	0 0 0	- + 0	0 - 0	0 0 0 *	123131212123131212	3.4	0	0	2	D
+ - 0	0 + 0	0 - 0	0 + 0	0 - +	0 - 0	123131212323131232	3.6	0	0	2	
++ +	0 + 0	0 + 0	+ + 0	0 - 0	0 + 0	123414242321414242	3.9	0	0	0	
+ + 0	0 - -	0 + 0	+ - 0	0 + 0	0 + 0	123434212423434242	4.3	0	0	1	
++ 0	0 0 0	- + 0	0 - 0	0 - 0	- + 0	123434342323434142	4.6	0	0	2	
++ 0	0 - 0	0 + 0	0 - +	0 + 0	- + 0	123434242323424142	4.7	0	0	2	
++ 0	+ + 0	0 0 0	- - 0	- - 0	0 0 0	123431212123431212	4.8	0	0	0	F
+ + 0	0 - -	0 0 0	- - 0	0 + +	0 0 0	123434212123434212	4.8	0	0	0	
+ - 0	0 0 0	+ - 0	0 0 0	+ - 0	0 0 0	123131312323231212	4.8	0	0	3	
++ +	0 + 0	0 - 0	- - -	0 - 0	0 + 0 *	123414242123414242	5.0	0	0	0	E
++ 0	+ + 0	0 + 0	+ + 0	+ + 0	0 + 0	123431212423134242	5.0	0	0	0	

two in the Na(12-crown-4)₂ClO₄ complex,³⁵ two with exact *C_i* symmetry (*g⁺g⁺a g⁺g⁻a g⁻g⁻a g⁻g⁺a*) in the Mg(H₂O)₆Cl₂·(12-crown-4) complex³⁶ and in the crystalline state of the uncomplexed polyether,³⁷ and one with approximate *C_s* symmetry (*g⁺g⁺a a g⁻g⁻ a g⁻a a g⁺a*) in the Cu(12-crown-4)Cl₂ complex.³⁸ Of course in all these 12-crown-4 units there must be some torsion angles that deviate substantially from the ideal values, because the three torsion codes are not in agreement with ideal ring structures. For all three symmetries one 12-crown-4 unit is depicted in Figure 3.

If we keep in mind that for ideal *N*-rings *N* - 3 subsequent torsion angles define the ring (and that the remaining three are totally defined by the others), it is clear that the macro-ring with *C₄* symmetry can be viewed as derived from the ideal conformation *g⁺g⁺a g⁺g⁺a g⁺g⁺g⁻ aag⁻* (compare Figures 3c and 3h). The main difference is the folding out of the CH₂-group, which points inwards in the ideal conformation, thereby avoiding the CH...HC and CH...O overlap of the latter. Further, all four oxygen atoms become directed further inward and all to the same side of the ring, whereas all hydrogens become directed further outward and to the other side of the ring. The resultant conformation looks very suitable for complex formation with cations or molecules with an electropositive part. (Torsion angles in Figure 3h: 83, 59, -164, 78, 59, -165, 81, 60, -165, 79, 56, and -164°.)

Likewise the macro-ring with *C_i* symmetry (Figure 3i) can be viewed as being derived from the ideal crown conformation *g⁺g⁺a g⁺g⁻a g⁻g⁻g⁺ aag⁻* (Figure 3d). Here the same pattern becomes obvious: the CH₂-group, which points inwards in the ideal conformation, is turned outwards, thereby

avoiding a CH...HC and a CH...O overlap. The second CH...O overlap in the ideal ring has also been weakened by turning the CH₂-group involved a little outwards. The resultant conformation is quite different from the previous one. Two oxygen atoms are directed to one side of the cyclomer, the other two to the other side. Therefore this conformation seems more suited for complexation with ligands at both sides of the ring [as actually happens in the Mg(H₂O)₆Cl₂(12-crown-4) complex³⁶]. The deviations from ideal torsion angles is on average greater than in the previous *C₄* conformations, probably because there are three overlaps to be diminished instead of two. (Torsion angles in the centrosymmetric conformation of Figure 3i: 71, 91, -167, 83, -98, and 147°.)

Finally the *C_s* conformation of the macro-ring in the Cu(12-crown-4)Cl₂ complex³⁸ (Figure 3j) looks at first sight like being far more distorted from any ideal conformation. Compared, however, with the ideal conformation *g⁺g⁺a ag⁻g⁻ g⁺g⁺a ag⁻g⁻* (Figure 3g), it can be seen that the only difference is the turning of the lower straight part of the ring by (drastically) changing the torsion angles that cause the two sharp corners in the lower part of the ideal conformation (*g⁺g⁺ → ag⁻* and *g⁻g⁻ → g⁺a*). Both severe CH...HC overlaps of the ideal conformation are thereby eliminated. All O-atoms are directed to the same side of the ring, but to a less extent than in the *C₄* conformation. (Torsion angles in Figure 3j: 71, 56, -170, 170, -57, -70, 136, -51, -169, 170, 49, -133°.)

18-Crown-6. The number of ideal conformations for 12-crown-4 is rather limited, for 18-crown-6 this is drastically raised to 675 ideal 18-crown-6 conformations from the 239

Table 8. The different ideal conformations for 24-crown-8 with CE ≤ 5.0 kcal mol⁻¹ and without any overlap in both torsion and direction notation (see Tables 4 and 6 for further explanation). The first conformation is depicted in Figure 5

Conformation								CE/ kcal mol ⁻¹	
Torsion code				Direction code					
0 + 0	0 + 0	0 - 0	0 - 0	0 + 0	0 + 0	0 - 0	0 - 0	121313434141212424343232	0.8
+ 0 0	0 0 -	0 0 +	0 0 0	0 - 0	0 + 0	0 0 0	- 0 0	123232313121212323131312	4.6
+ + 0	+ 0 0	0 0 -	0 - -	0 0 0	0 + 0	0 - 0	0 0 0	123431313141232323131212	4.8
+ 0 0	0 + 0	0 + 0	0 - 0	0 - 0	0 0 -	0 - 0	0 0 +	123232424141212323241414	4.8
+ + 0	0 0 +	+ 0 0	0 0 0	+ + 0	0 - 0	0 - 0	0 0 0	123434312121214343131212	4.8
+ + 0	0 - -	0 0 0	0 0 0	+ + 0	0 - -	0 0 0	0 0 0	123434212121214343121212	4.8
+ + 0	0 0 0	- - 0	0 0 0	+ + 0	0 0 0	- - 0	0 0 0	123434342121214343431212	4.8
+ + 0	0 0 0	0 + +	0 + 0	0 + 0	0 + 0	0 + 0	- 0 0	123434343121414343231312	4.9
+ + 0	0 0 +	+ 0 0	0 + 0	0 + 0	0 - 0	0 + 0	+ 0 0	123434312121414343131412	4.9
+ + 0	0 + 0	0 0 +	+ 0 0	0 + +	0 0 0	0 - 0	0 + 0	123434141423232141414242	4.9
+ + 0	0 + 0	0 - -	0 0 0	0 + +	0 0 0	0 - -	0 - 0	123434141323232141414232	5.0
+ + 0	0 - 0	+ + 0	0 - 0	0 + 0	0 + 0	+ 0 0	- 0 0	123434243131414343231312	5.0
+ + 0	0 - 0	0 - 0	0 0 0	+ + 0	0 - -	0 0 -	0 + 0	123434242121214343121242	5.0
+ + 0	0 - 0	- 0 0	- - 0	0 + +	0 0 0	0 - 0	0 + 0	123434241413232141414242	5.0
+ + 0	0 - -	0 0 -	0 - 0	0 + 0	0 - 0	0 + 0	+ 0 0	123434212131414343131412	5.0

different 'diamond-ring' conformations. While there is no ideal conformation without any overlap for 12-crown-4, there are 27 overlap-free 18-crown-6 ideal conformations. The 14 conformations with lowest CE (≤ 5.0 kcal mol⁻¹) are collected in Table 7.

In the CCDB and more recent literature we found a total of 50 18-crown-6 units that fulfil the above outlined restrictions. Of these, 35 [for example, the macro-ring in the 18-crown-6: *S*-*tert*-butylthiouronium (1:2) complex³⁹] have approximately the lowest CE (0.6 kcal mol⁻¹) ideal conformation with D_{3d} symmetry ($ag^+a ag^-a ag^+a ag^-a ag^+a ag^-a$; Figure 4a). The second most common conformation appears to be the ideal one with second lowest CE (2.8 kcal mol⁻¹), encountered six times, namely in the 5:1 complex of urea with 18-crown-6,⁴⁰ in the (18-crown-6)·benzenesulphonamide (1:2) complex,⁴¹ in the $UO_2(NO_3)_2(H_2O)_2$ (18-crown-6) complex,⁴² in the 2:1 complex between guanidinium nitrate and 18-crown-6,⁴³ in the 2:1 complex of 2,4-dinitroaniline and 18-crown-6,⁴⁴ and in the 2:1 complex of 4-nitro-1,2-benzenediamine and 18-crown-6⁴⁵ (all $g^+g^+a ag^-a ag^-a g^-g^-a ag^+a ag^+a$; Figure 4b). The other ideal conformation with a CE of 2.8 kcal mol⁻¹ ($g^+g^+a ag^-a ag^+a ag^-g^- ag^-a ag^+a$, Figure 4c) is encountered twice, namely in the (18-crown-6)·(LiSCN)₂·2H₂O complex⁴⁶ and in the (18-crown-6)·(*n*-butylisouronium picrate) complex.⁴⁷ There are two more ideal conformations encountered, each only once: the $g^+g^-a ag^+a aaa g^-g^+a ag^-a aaa$ conformation with CE = 3.4 kcal mol⁻¹ (Figure 4d) in the crystal structure of the free 18-crown-6⁴⁸ and the $g^+g^+g^+ ag^+a ag^-a g^-g^-g^- ag^-a ag^+a$ conformation with a CE of 5.0 kcal mol⁻¹ (Figure 4e) in the $Co(H_2O)_6 \cdot CoCl_4 \cdot acetone$ (18-crown-6) complex.⁴⁹ In view of the many approximations involved in our CE-calculations, the relation between the CE-values and the frequency of occurrence of the different conformations may be fortuitous.

The ideal conformation $g^+g^+a g^+g^+a aaa g^-g^-a g^-g^-a aaa$ (Figure 4f), which is adopted by the corresponding hydrocarbon, cyclo-octadecane, in the crystalline state,⁵⁰ is, however, not found for 18-crown-6 units.

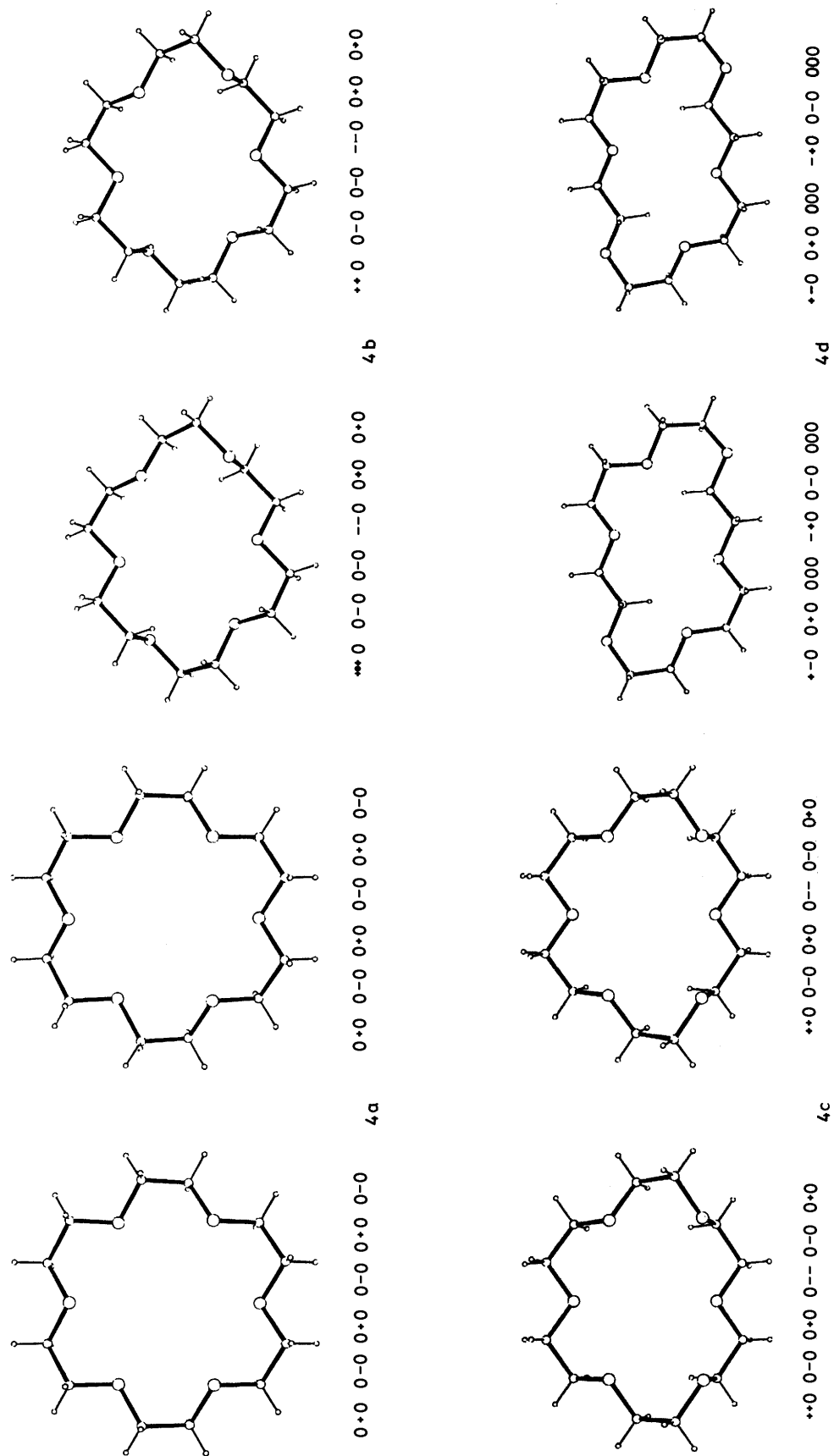
We have found five 18-crown-6 units with conformations that cannot be viewed as ideal. The first one is encountered in the $NaCNS \cdot H_2O$ ·(18-crown-6) complex⁵¹ (Figure 4g) with a torsion sequence of $g^+g^+a ag^-a ag^+a ag^-g^-g^+g^+ ag^+a$. This conformation can be viewed as directly derivable from the ideal conformation $g^+g^+a ag^-a ag^+a ag^-g^- ag^-a ag^+a$ (Figure 4c), because 15 subsequent torsion angle codes (which in the ideal case define fully the 18-ring) are equal in both

conformations. Therefore the difference in the three remaining torsion codes must be a result of rather large deviations from the ideal torsion angle values (which actually is the case, see below). If Figures 4c and 4g are compared, it can be seen that the most pronounced effect is the 'pinching together' of the two C-C bonds most left and most right, with the result that five oxygens form a more regular pentagon, whereas the sixth oxygen atom moves a little deeper below the ring and more to the middle, thereby forming the apex of a (distorted) pentagonal pyramid. It is supposed that this rather unusual conformation is a result of the co-ordination properties of the sodium ion. (Torsion angles in Figure 4g: 70, 52, -174, -173, -59, -177, -171, 61, 173, 167, -59, -74, 115(!), 47, 77, -176, 63, and -172°.)

The other four non-ideal 18-crown-6 units, found in the 1:1 complexes of 18-crown-6 with uronium nitrate⁵² (Figure 4h), uronium picrate,⁴⁷ neodymium nitrate,^{53,54} and lanthanum nitrate,⁵⁵ all have quite the same conformation with torsion code $g^+g^+a ag^-a ag^+a g^+g^+a ag^-a ag^+a$. The same reasoning as above shows that this conformation can also be viewed as being directly derived from an ideal one, and moreover from the same $g^+g^+a ag^-a ag^+a ag^-g^- ag^-a ag^+a$ conformation. If one compares Figures 4c and 4h the most pronounced difference is that the two C-C bonds most left and right, which are exactly parallel in the ideal crown, are twisted in the non-ideal crown ether ring, mainly because of two C-O torsion angles of 83°. (Torsion angles in Figure 4h: 83, 62, 176, 179, -74, -175, -177, 75, -178, 83, 62, 174, 178, -73, -173, -175, 73, and -176°.)

A very interesting feature appears in the conformation of the macro-ring in the already mentioned (18-crown-6)·(*n*-butylisouronium picrate) complex.⁴⁷ In an initial state of refinement part of the ring was found to be disordered. It was possible to describe this disorder by attributing two (partly occupied) different positions to five atoms of the polyether ring, thereby forming two different conformations, namely the ideal $g^+g^+a ag^-a ag^+a ag^-g^- ag^-a ag^+a$ (occupation: 72.1%) and the non-ideal $g^+g^+a ag^-a ag^+a g^+g^+a ag^-a ag^+a$ (occupation: 27.9%) conformation. It therefore seems probable that this non-ideal conformation is not only 'theoretically' derivable from the ideal one, but that this conformational change is also possible 'in practice'.

24-Crown-8. For 24-crown-8 we calculated only the conformations without any overlap. Out of the 419 different 'diamond-ring' conformations without overlap follow 1 212 different 24-crown-8 conformations. The 15 conformations



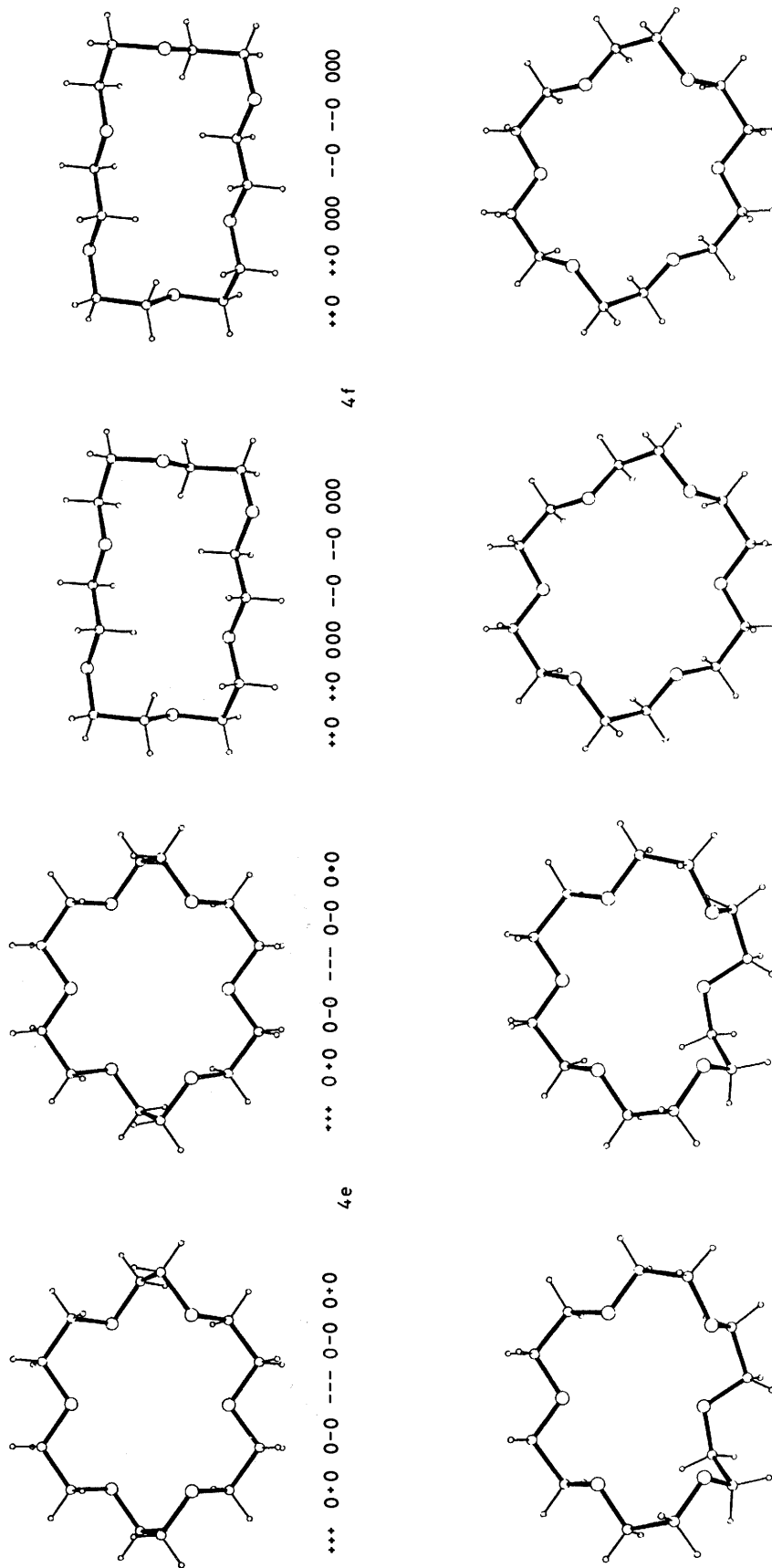


Figure 4. Stereoviews of six ideal conformations of 18-crown-6 (4a—4f) and of two non-ideal conformations (4g, 4h; positions of the heavy atoms taken from ref. 51 and 52 respectively)

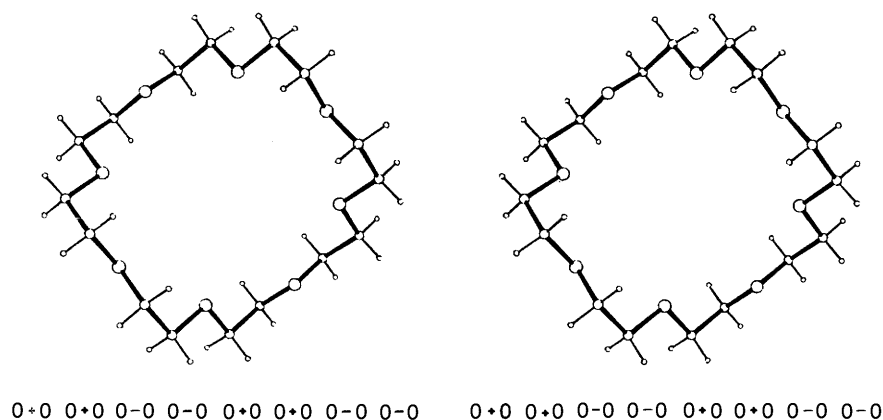


Figure 5. Stereoview of the ideal conformation of 24-crown-8 with lowest CE ($0.8 \text{ kcal mol}^{-1}$)

with lowest CE ($\leq 5.0 \text{ kcal mol}^{-1}$) are collected in Table 8. The lowest CE ($0.8 \text{ kcal mol}^{-1}$) ideal conformation $ag^+a ag^+a ag^-a ag^-a ag^+a ag^+a ag^-a ag^-a$ with D_{2d} symmetry is depicted in Figure 5. It can be proved that this conformation has indeed the lowest CE of all 24-crown-8 conformations (including the ones with overlap): every overlap means the existence of an 'almost sub-ring' (but one position). The largest 'almost sub-ring' to be considered in a 24-ring is of size 14 (because an 'almost sub-ring' of size >14 will always be accompanied by a second one with size <14) and the smallest, of course, of size six. As a complete sub-ring is defined by $N - 3$ subsequent torsion angles (with N being the number of members in the sub-ring), an 'almost sub-ring' will be by $N - 4$. For instance, the most simple overlap (1,5-interaction) is defined by two subsequent torsion angles from the six-ring, necessarily g^+g^- . By inspection of all N -rings for $N = 6-14$ with all possibilities of eliminating a sequence of four torsion angles from them, it appears that each remaining part contains at least one g^+g^+ , g^-g^- , or g^+g^- section, which means that always one C-O and one C-C or two C-O torsion angles must be *gauche*, giving a CE of at least $1.2 \text{ kcal mol}^{-1}$.

In our search in the CCDB and more recent literature we encountered no 24-crown-8 unit that fulfils the conditions, so no comparison can be made with ideal conformations.

Conclusions

It appears that the model of ideal crown ether conformations works pretty well. For the 12-crown-4 unit without any reasonable ideal conformation the structures found can be described as being derived from ideal ones with the removal of the most severe hindrances (CH...HC overlap mostly). For 18-crown-6 with far more possibilities the encountered conformations agree very well with the ideal ones, and (perhaps most surprising) the very simple model for calculating CEs gives a very good prediction of the most probable, favourable conformations. For the 24-crown-8 unit the $ag^+a ag^+a ag^-a ag^-a ag^+a ag^+a ag^-a ag^-a$ conformation will probably prove to be a low-energy conformation.

Although some more precise molecular mechanics calculations of the conformational energies of some crown ethers^{8,9} have been reported, it seems very useful to extend this sort of calculations to more conformations to get a better insight into

the conformational flexibility of crown ethers and in their complexation possibilities. In the meantime we are performing such calculations, results of which will be published soon.

All calculations were performed on a DEC-1080 computer. Methods (a) and (c) were programmed in FORTRAN 10 and method (b) in PASCAL. Typical CPU-times used for the calculation of the number of ideal conformations for the 18-membered polymethylene ring with methods (a), (b), and (c) were 5, 40, and 18 s, respectively.

Complete lists of the conformations of 'diamond-rings' with 14-22 members including overlap and with 20-26 members without overlap and of the ideal conformations of 18-crown-6 including overlap and 24-crown-8 without overlap have been deposited as Supplementary Publication No. SUP 23716 (204 pp.).*

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References

- 1 C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 7017.
- 2 M. R. Truter, 'Metal-Ligand Interactions in Organic Chemistry and Biochemistry, Part 1,' ed. B. Pullman and N. Goldblum, Reidel, Dordrecht-Holland, 1977, pp. 317-335.
- 3 R. M. Izatt, L. D. Hansen, D. J. Eatough, J. S. Bradshaw, and J. J. Christensen, 'Metal-Ligand Interactions in Organic Chemistry and Biochemistry, Part 1,' ed. B. Pullman and N. Goldblum, Reidel, Dordrecht-Holland, 1977, pp. 337-361.
- 4 J. Dale, *Isr. J. Chem.*, 1980, **20**, 3.
- 5 N. K. Dalley, 'Synthetic Multidentate Macrocyclic Compounds,' ed. R. M. Izatt and J. J. Christensen, Academic Press, London, 1978, pp. 207-243.
- 6 I. Goldberg, 'The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and their Sulphur Analogues,' ed. S. Patai, Wiley, Chichester, 1980, Suppl. E, pp. 175-214.
- 7 J. Dale, *J. Chem. Soc.*, 1963, 93.
- 8 M. J. Bovill, D. J. Chadwick, I. O. Sutherland, and D. Watkin, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1529.
- 9 G. Wipff, P. Weiner, and P. Kollman, *J. Am. Chem. Soc.*, 1982, **104**, 3249.
- 10 O. Kennard, 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. III, p. 276.
- 11 A. R. Claggett, W. H. Ilesley, T. J. Anderson, M. D. Glick, and J. P. Oliver, *J. Am. Chem. Soc.*, 1977, **99**, 1797.
- 12 J. D. Dunitz, M. Dobler, P. Seiler, and R. P. Phizackerley, *Acta Crystallogr.*, 1974, **B30**, 2733.

* For details of the Supplementary Publication Scheme see Instructions to Authors (1983), *J. Chem. Soc., Perkin Trans. 2*, 1983, Issue 1.

- 13 M. Saunders, *Tetrahedron*, 1967, **23**, 2105.
- 14 R. P. Smith, *J. Chem. Phys.*, 1965, **42**, 1162.
- 15 R. P. Smith, *J. Chem. Phys.*, 1963, **38**, 1463.
- 16 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1965, vol. I, p. 340.
- 17 'Cambridge Crystallographic Data Base,' version March 1982, supplied by the Cambridge Crystallographic Data Centre, Cambridge, 1982.
- 18 'Handbook of Chemistry and Physics,' The Chemical Rubber Co., Ohio, 1962, 46th edn., p. D92.
- 19 F. Podo, G. Némethy, P. L. Indovina, L. Radics, and V. Viti, *Mol. Phys.*, 1974, **27**, 521.
- 20 R. Taylor and O. Kennard, *J. Am. Chem. Soc.*, 1982, **104**, 5063.
- 21 K. S. Luk, M. P. Sammes, and R. L. Harlow, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1166.
- 22 P. Anderson and T. Thurmann-Moe, *Acta Chem. Scand.*, 1964, **18**, 433.
- 23 E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc. A*, 1970, 406.
- 24 D. J. Sutor, *J. Chem. Soc.*, 1963, 1105.
- 25 K. Matsuzaki and H. Ito, *J. Polym. Sci., Polym. Phys. Ed.*, 1974, **12**, 2507.
- 26 H. Wieser, W. G. Laidlaw, P. J. Krueger, and H. Fuhrer, *Spectrochim. Acta, Part A*, 1968, **24**, 1055.
- 27 J. E. Mark and P. J. Flory, *J. Am. Chem. Soc.*, 1966, **88**, 3702.
- 28 K. Byström and M. Månsson, *J. Chem. Soc., Perkin Trans. 2*, 1982, 565.
- 29 C. K. Johnson, ORTEP, Report ORNL-3794, 1965, Oak Ridge National Laboratory, Tennessee.
- 30 N. W. Alcock and J. F. Sawyer, *J. Chem. Soc., Dalton Trans.*, 1980, 115.
- 31 F. P. van Remoortere and F. P. Boer, *Inorg. Chem.*, 1974, **13**, 2071.
- 32 P. P. North, E. C. Steiner, F. P. van Remoortere, and F. P. Boer, *Acta Crystallogr.*, 1976, **B32**, 370.
- 33 E. M. Holt, N. W. Alcock, R. R. Hendrixson, G. D. Malpass Jr., R. G. Ghirardelli, and R. A. Palmer, *Acta Crystallogr.*, 1981, **B37**, 1080.
- 34 F. P. Boer, M. A. Neuman, F. P. van Remoortere, and E. C. Steiner, *Inorg. Chem.*, 1974, **13**, 2826.
- 35 E. Mason and H. A. Eick, *Acta Crystallogr.*, 1982, **B38**, 1821.
- 36 M. A. Neuman, E. C. Steiner, F. P. van Remoortere, and F. P. Boer, *Inorg. Chem.*, 1975, **14**, 734.
- 37 P. Groth, *Acta Chem. Scand., Ser. A*, 1978, **32**, 279.
- 38 F. P. van Remoortere, F. P. Boer, and E. C. Steiner, *Acta Crystallogr.*, 1975, **B31**, 1420.
- 39 J. W. H. M. Uiterwijk, S. Harkema, G. J. van Hummel, J. GeEVERS, and D. N. Reinhoudt, *Acta Crystallogr.*, 1982, **B38**, 1862.
- 40 S. Harkema, G. J. van Hummel, K. Daasvatn, and D. N. Reinhoudt, *J. Chem. Soc., Chem. Commun.*, 1981, 368.
- 41 A. Knöchel, J. Kopf, J. Oehler, and G. Rudolph, *J. Chem. Soc., Chem. Commun.*, 1978, 595.
- 42 G. Bombieri, G. de Paoli, and A. Immirzi, *J. Inorg. Nucl. Chem.*, 1978, **40**, 799.
- 43 J. A. Bandy, M. R. Truter, J. N. Wingfield, and J. D. Lamb, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1025.
- 44 G. Weber and G. M. Sheldrick, *Acta Crystallogr.*, 1981, **B37**, 2108.
- 45 G. Weber, *Acta Crystallogr.*, 1982, **B38**, 629.
- 46 P. Groth, *Acta Chem. Scand., Ser. A*, 1982, **36**, 109.
- 47 J. W. H. M. Uiterwijk, G. J. van Hummel, S. Harkema, J. A. A. de Boer, K. Daasvatn, J. GeEVERS, H. J. den Hertog Jr., E. Kaufmann, and D. N. Reinhoudt, to be published.
- 48 E. Maverick, P. Seiler, W. B. Schweizer, and J. D. Dunitz, *Acta Crystallogr.*, 1980, **B36**, 615.
- 49 T. B. Vance Jr., E. M. Holt, C. G. Pierpont, and S. L. Holt, *Acta Crystallogr.*, 1980, **B36**, 150.
- 50 J. Dale, *Angew. Chem., Int. Ed. Engl.*, 1966, **5**, 1000.
- 51 M. Dobler, J. D. Dunitz, and P. Seiler, *Acta Crystallogr.*, 1974, **B30**, 2741.
- 52 J. W. H. M. Uiterwijk, S. Harkema, D. N. Reinhoudt, K. Daasvatn, H. J. den Hertog Jr., and J. GeEVERS, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 450.
- 53 J.-C. G. Bünzli, B. Klein, and D. Wessner, *Inorg. Chim. Acta*, 1980, **44**, L147.
- 54 G. Bombieri, G. de Paoli, F. Benetollo, and A. Cassol, *J. Inorg. Nucl. Chem.*, 1980, **42**, 1417.
- 55 J. D. J. Backer-Dirks, J. E. Cooke, A. M. R. Galas, J. S. Ghotra, C. J. Gray, F. A. Hart, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1980, 2191.

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