

Crystal Structure Analyses of 1,4,7,10,13,16-Hexaoxacyclooctadecane and its Complexes with Alkali Thiocyanates

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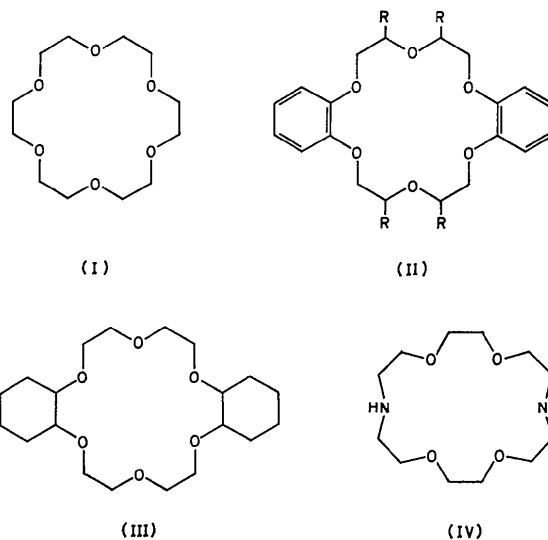
The results of crystal structure analyses of 1,4,7,10,13,16-hexaoxacyclooctadecane $(\text{CH}_2\text{CH}_2\text{O})_6$ and its complexes with NaNCS , KNCS , RbNCS , CsNCS [and $\text{Ca}(\text{NCS})_2$] are discussed. In the K^+ , Rb^+ , Cs^+ and Ca^{2+} complexes the unsubstituted hexaether adopts a conformation with virtual D_{3d} symmetry although the larger Rb^+ and Cs^+ ions are displaced by more than 1 Å from the mean plane of the ligand. In the Na^+ complex, the ring is strongly distorted from its symmetrical conformation to accommodate the smaller cation. The uncomplexed hexaether has a centrosymmetric conformation containing three different types of monomeric subunit. The shortening of the C–C bonds found in these and related complexes is discussed and judged to be mainly an artificial effect arising from inadequate treatment of curvilinear vibrations.

Introduction

Interest in alkali and alkaline earth complexes with organic ligands arose from the discovery (Moore & Pressman, 1964) that the biological effects of certain antibiotic substances depended on the presence or absence of specific alkali metal cations in the medium. The suggestion that these substances acted as ion-carriers (ionophores) across membranes with different specificities for different ions was soon confirmed and elaborated (Stefanac & Simon, 1966; Mueller & Rudin, 1967). Since the determination of the structure of the K^+ -nonactin complex (Kilbourn, Dunitz, Pioda & Simon, 1967) much detailed structural information about the coordination of cations with many antibiotics and synthetic model compounds has been obtained [see Truter (1973) for a review]. In general, the coordination observed in complexes with neutral macrocyclic compounds (e.g. nonactin, enniatin, valinomycin, 'crown' ethers) deviates only slightly from an ideal high-symmetry type, whereas the coordination in complexes with negatively charged ligands (monensin, nigericin, etc.) is often highly irregular.

Among the many factors that may affect the cation specificity of a given ligand, the spatial arrangement of the ligating atoms (usually oxygen) is expected to have a decisive influence. However, unless unusually strong geometric constraints are present in the ligand, this arrangement is unlikely to remain invariant with change in cation radius. The ligand conformation may change from one complex to another, and the conformation of the free ligand may again be quite different from that in any of the complexes. Structure analyses of the same ligand, free and in complexes with different cations, are therefore desirable and have been carried out in several

cases. The most complete series available so far is for the macrobicyclic [2,2,2]cryptate and includes complexes with Na^+ , K^+ , Rb^+ , Cs^+ , Tl^+ , Ca^{2+} , Ba^{2+} as well as the free ligand (Moras & Weiss, 1973; Moras, Metz & Weiss, 1973; Metz, Moras & Weiss, 1973), but extensive information is also available for actins and their Na^+ , K^+ and Rb^+ complexes (Dobler, Dunitz & Kilbourn, 1969; Dobler, 1972; Iitaka, Sabamaki & Nawata, 1972; Dobler & Phizackerley, 1974a) and for a variety of macrocyclic ethers (Truter, 1973).



The recent improved synthesis of macrocyclic ethers $(\text{CH}_2\text{CH}_2\text{O})_n$, often known as 'crown' ethers, from ethylene oxide (Dale & Kristiansen, 1972), has made it possible to carry out similar comparative studies for the unsubstituted hexaether (I). Such studies, it was hoped, would be of interest in showing how this potentially

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highly symmetrical but flexible ligand adapts its conformation to the different steric requirements of alkali cations, and would also provide a basis for sizing up the influence of the various substituents present in the analogous complexes of (II) and (III). Infrared spectroscopic measurements (Dale & Kristiansen, 1972) showed that in its KBr complex the hexaether (I) adopts a conformation with exclusively *ap,sc,ap* monomeric units [see Klyne & Prelog (1960) for nomenclature], generally similar to the conformations observed in Na⁺ and Rb⁺ complexes of the 2,3,11,12-dibenzo compound (II) (Bright & Truter, 1970; Bush & Truter, 1971) and in a Na⁺ complex of the dicyclohexyl compound (III) (Mercer & Truter, 1973) but with the higher symmetry (D_{3d}) attainable for an unsubstituted ligand. Infrared measurements on the uncomplexed hexaether (I) indicated a conformation of much lower symmetry containing three types of monomeric unit. This was tentatively identified (Dale & Kristiansen, 1972) as the centrosymmetric compact rectangular 'diamond-like' conformation of the 18-membered ring (Dale, 1963), which would contain two different types of *sc,sc,ap* monomer and one type of *ap,ap,ap* monomer. A recent X-ray analysis (Groth, 1972) of the crystalline complex of (I) with potassium toluenesulphonate confirms the approximate D_{3d} symmetry of the ligand; however, the crystal structure is disordered, so that accurate structural parameters could not be obtained.

We have now carried out a series of X-ray analyses of the uncomplexed hexaether (I) and its crystalline complexes with sodium, potassium, rubidium, caesium and calcium thiocyanates, kindly provided by Professor J. Dale. Details of the individual analyses are given elsewhere, so we need only review the results briefly here and draw some general conclusions.

The D_{3d} conformation of complexed hexaether

The conformations of the hexaether found in the complexes with KNCS, RbNCS and CsNCS have approximate D_{3d} symmetry and are almost superimposable on one another (Seiler, Dobler & Dunitz, 1974; Dobler & Phizackerley, 1974b). All torsion angles

about C–C bonds are close to 65° (synclinal, *sc*), those about C–O bonds are close to 180° (antiplanar, *ap*), C–C–O bond angles are roughly tetrahedral, C–O–C angles a few degrees wider. In all three structures the six ligating oxygen atoms are alternately about 0.20 Å above and below their mean plane to form a nearly planar hexagon of side approximately 2.80 Å (K⁺ complex, 2.80–2.87 Å, average 2.82 Å; Rb⁺ complex, 2.75–2.86 Å, average, 2.81 Å; Cs⁺ complex, 2.78–2.88 Å, average, 2.83 Å). This is the value usually adopted as the van der Waals diameter of oxygen (Pauling, 1960), so it seems justified to regard neighbouring oxygen atoms as being in contact. Much the same conformation occurs in the disordered structures of the potassium toluene-*p*-sulphonate (Groth, 1972) and calcium thiocyanate (Dunitz & Seiler, 1974b) complexes.

Note that the geometry of an 18-membered ring depends on only five independent parameters if strict D_{3d} symmetry is assumed. For the hexaether, in internal coordinates, these may be taken as the C–C and C–O distances, the CCO and COC angles, and *one* additional parameter. Thus if the O···O distance *or* the C–C torsion angle *or* the C–O torsion angle is specified together with the bond distances and angles, the ring geometry is fixed. In other words, an energetically optimal value of one parameter may be incompatible with energetically optimal values of the others. It is a remarkable property of the hexaether that nearly optimal values of all the parameters can be attained simultaneously, which may go some way towards explaining the essential invariance of the observed ring conformation in these complexes, in spite of important differences in the interaction of the ring with the cation and the environment.

In the KNCS complex, the K⁺ ion sits exactly at the centre (here a crystallographic inversion centre) of the hexagon of ligating oxygen atoms (Fig. 1). The K⁺···O distances are not quite equal (2.77–2.83 Å, average 2.81 Å) (that is, the hexagon is not quite regular) and they are slightly longer than the sum of the corresponding ionic and van der Waals radii (2.73 Å

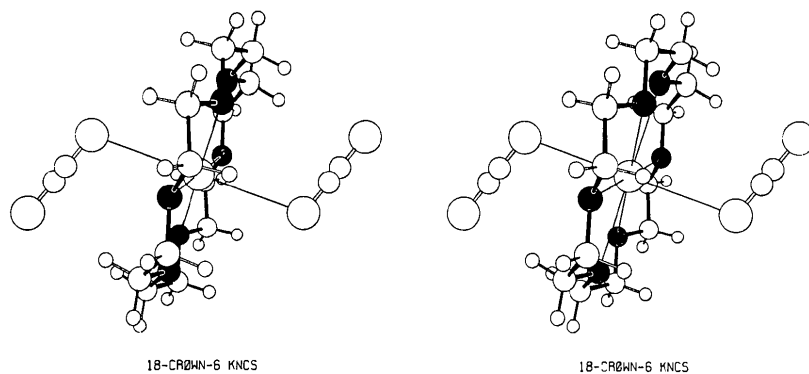


Fig. 1. Stereoscopic view of the KNCS hexaether complex. The K⁺ and NCS ions occupy crystallographic inversion centres; the anions are disordered.

=1.33+1.40 Å). The thiocyanate anions also sit on crystallographic inversion centres and are hence unquestionably disordered; each terminal atom, N or S, is 3.19 Å from a K⁺ ion and close to the threefold axis of the hexagon, thus completing hexagonal bipyramidal coordination.

In the isomorphous RbNCS and CsNCS complexes (Fig. 2) the cations are displaced from the mean plane of the hexagon, by 1.19 Å (Rb⁺) and 1.44 Å (Cs⁺). Since the radius of the cavity (1.40 Å) is only a little smaller than the ionic radius of Rb⁺ (1.48 Å) one might have expected to find this ion at the centre of the hexagon, possibly slightly dilated. However, in the (Rb,Na)NCS complex (II) (Bright & Truter, 1970) the Rb⁺ ion lies 0.94 Å out of the mean oxygen plane and is coordinated to the nitrogen of a thiocyanate anion at 2.94 Å in addition to the six oxygens at 2.86–2.94 Å. This tendency to depart from the oxygen plane goes even further in the complex with the unsubstituted hexaether. The Rb⁺···O distances are longer (because of the non-planarity of the oxygen hexagon they fall into two groups, 2.93–3.00 Å and 3.01–3.15 Å), but the weaker ion-dipole interactions have to be set against stronger ion-pairing for there are now additional coordination sites from thiocyanate anions at 3.02 Å. The crystal-structure analysis shows that these anions are disordered, with a 4:1 preference for the nitrogen atom to occupy the coordination site.

As noted earlier, the structure of the CsNCS complex is very similar. The even greater displacement (1.44 Å) of the cation from the mean oxygen plane is not accompanied by any appreciable change in the ring conformation. The Cs⁺···O distances again fall into two groups, 3.04–3.10 Å and 3.16–3.27 Å, and the two additional coordination sites, here exclusively nitrogen atoms (the thiocyanates are ordered) are at 3.30 and 3.32 Å.

The sodium complex: an irregular conformation

Whereas Rb⁺ and Cs⁺ are too large to fit into the cavity, Na⁺, with ionic radius of 0.95 Å, is too small to fill it. Since the hexagon of oxygen atoms cannot be

contracted much without introducing intolerable O···O repulsions, the following other possibilities can be considered: (1) the Na⁺ sits at the centre of the hexagon with non-optimal Na⁺···O distances of 2.8 Å. This is roughly what was found in the (Rb,Na)NCS complex of (II) (Bright & Truter, 1970); (2) the Na⁺ deviates from the centre, making shorter contacts with some oxygens, longer ones with others, as occurs in the NaBr·2H₂O complex of (II) (Bush & Truter, 1971); (3) the Na⁺ 'rattles' in the cavity, a possibility that would be expressed in unusually large vibration parameters; (4) the hexaether adopts a different conformation, more compatible with the coordination preferences of the cation. This is what occurs in the NaBr complex of the *cis-anti-cis* dicyclohexyl hexaether (III), where the hexagon of oxygens is elongated along one diagonal and contracted along the other two; the centrally located Na⁺ ion thus makes two long distances (2.97 Å) and four shorter ones (2.68 Å), besides coordinating to water molecules at 2.34 Å above and below the mean plane of the hexagon (Mercer & Truter, 1973). A much more drastic conformational change occurs in the NaNCS complex of the unsubstituted hexaether (Dobler, Dunitz & Seiler, 1974). One of the oxygen atoms is drawn out of the mean plane of the other five by 1.95 Å to give a somewhat irregular pentagonal pyramidal coordination of the Na⁺ ion (Fig. 3). The kink in the ring leaves the relative positions of 13 of the 18 atoms more or less unaltered; the ones that move are in the -CH₂-CH₂-O-CH₂-CH₂- fragment containing the 'apical' oxygen. The Na⁺···O distances are 2.45 Å (apical oxygen) and 2.47–2.62 Å (pentagon) with an additional oxygen from a water molecule at 2.32 Å at the opposite apex of a bipyramid. The irregular conformation of the ring required to produce this 5+1+1 coordination is doubtless strained but much less so than corresponding conformations of the dibenzo-substituted hexaether (II) or either of the two known dicyclohexyl isomers (III) (*cis-syn-cis* and *cis-anti-cis*) would be. The conformational strain is evidently compensated for by better coordination with the smaller cation, but the energy balance depends on such a com-

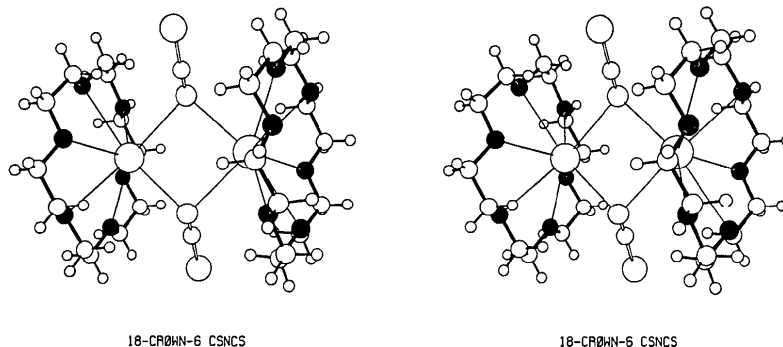


Fig. 2. Stereoscopic view of the dimeric structural unit of the CsNCS hexaether complex. The same kind of unit occurs in the RbNCS complex.

plicated interplay of various factors that it can hardly be appraised intuitively. The fact that the Ca^+ ion, with approximately the same radius as Na^+ , occurs in an undistorted, or only slightly distorted, 6+2 environment in the unsubstituted hexaether, whereas Na^+ occurs in the highly distorted but more compact 5+1+1 environment may suggest that the energy difference between these alternatives is small. We leave the problem, for what it is worth, as a future exercise for protagonists of force-field calculations.

The uncomplexed hexaether

Whereas the conformation of uncomplexed 1,7,10,16-tetraoxa-4,13-diazacyclooctadecane, (IV), (Herceg & Weiss, 1972) is virtually identical with that in its KNCS complex (Moras, Metz, Herceg & Weiss, 1972) and similar to the D_{3d} conformation of the hexaether, the unsubstituted hexaether adopts a quite different conformation (Fig. 4) (Dunitz & Seiler, 1974a). In contrast to the D_{3d} conformation, in which all subunits are equivalent, the conformation of the uncomplexed hexaether contains three kinds of $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$ unit, *ap,sc,ap* (as in the D_{3d} conformation), *ap,ap,ap* and *sc,sc,ap*. Infrared spectral evidence (Dale & Kristiansen, 1972) suggests that essentially the same conformation occurs in the liquid as in the crystal.

The 'equilibrium cavity'

The interaction of cations with multidentate ligands is often discussed in terms of a simple model based on the supposed significant existence of an 'equilibrium cavity', an arrangement of coordinating sites favourable for taking up the cation [see Simon, Morf & Meier (1973) for details]. It is assumed that the free-energy change involved in the formation of such a cavity is independent of cation radius and charge and hence has no effect on the ion specificity; however, the energy required to adjust the size of the cavity to the ionic radius is supposed to influence the specificity. We see that such a model is quite inappropriate for the crown ethers discussed here: (a) for cations larger than K^+ the size and shape of the cavity remains essentially constant; ions too large to fit the cavity penetrate as far as they can and make up for the poorer coordination with the ligand by interacting with anions; (b) for cations smaller than K^+ a completely different arrangement of coordinating sites may be adopted; the energy required to form this new cavity may be very different in the unsubstituted and substituted hexaethers. Stability constants for complexes between hexaethers and alkali cations have been measured in methanol (Frensdorff, 1971); the K^+ complexes are 10–100 times more stable than Na^+ and Cs^+ complexes, which are of roughly

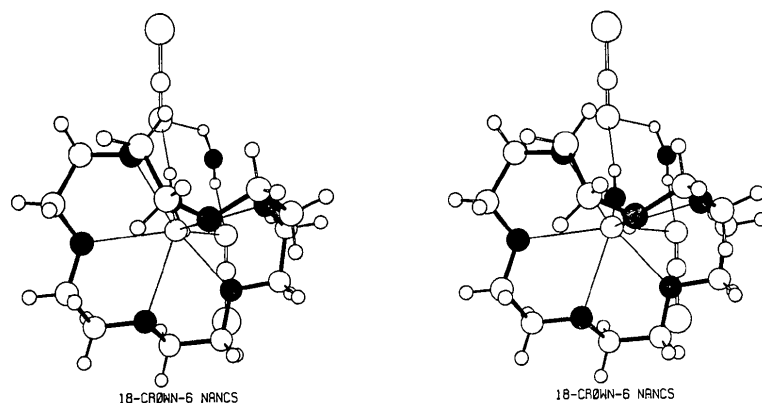


Fig. 3. Stereoscopic view of the hydrated NaNCS hexaether complex, showing the irregular conformation of the hexaether. The Na^+ ion has pentagonal bipyramidal coordination.

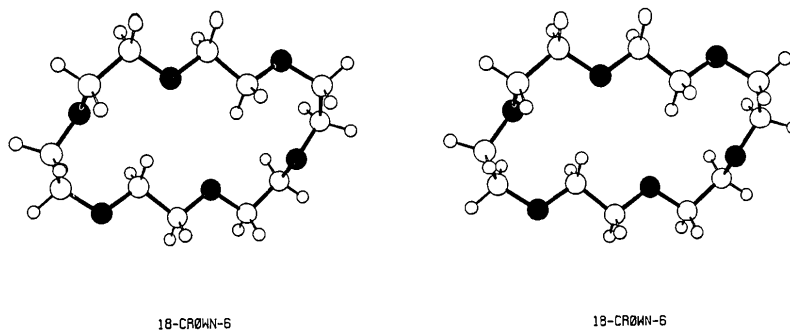


Fig. 4. Stereoscopic view of the conformation adopted by the uncomplexed hexaether.

equal stability. Qualitatively, these results seem quite in line with our structural findings. However, the stabilities depend on so many incompletely understood factors that a quantitative theory seems out of the question for the time being.

The short C–C distances: real or apparent?

Table 1 summarizes bond distances and angles resulting from our refinements of five crystal structures of (I) and its complexes with various cations. If the bond distances are compared with reference values of 1.523 and 1.423 Å for C–C and C–O respectively, as found by electron diffraction for gas-phase 1,4-dioxane (Davis & Hassel, 1963), it is immediately obvious that the mean values obtained in our work are too short.

As discussed in an earlier paper (Dunitz & Seiler, 1973) the bond lengths are sensitive to the weighting scheme used in the least-squares analyses. The distances cited in Table 1 for the uncomplexed ligand and for the K⁺ and Na⁺ complexes result from refinement with a modified weighting scheme; with experimental weights, the C–C bond lengths come out even shorter (by about 0.010–0.015 Å) while the C–O bonds are unchanged or perhaps a shade longer (less than 0.01 Å). The C–C bond lengths reported for the Rb⁺ and Cs⁺ complexes (refined with unit weights) are appreciably shorter than for the other three cases. If we had based all our refinements on unit or experimental weights, we would have reported C–C distances of 1.48–1.49 Å and C–O distances of 1.41–1.42 Å for all five analyses, values very close to those found in previous studies of other macrocyclic polyethers and their complexes.

Is the shortening of the C–C bonds found in these analyses genuine or an artificial effect of thermal motion? It is well known that separations between the mean positions of atoms undergoing large curvilinear motions cannot be interpreted as interatomic distances (Busing & Levy, 1964). Approximate corrections can be made for rigid-body libration of the molecule as a whole (e.g. Cruickshank, 1956) but corresponding corrections for internal motions depend on the model assumed for these motions and are at best merely qualitative. For the five structures discussed here the agreement between U_{ij} tensor components found and those calculated from rigid-body thermal-motion analysis (Cruickshank, 1961; Schomaker & Trueblood, 1968) is not very good; the values of $\langle(\Delta U_{ij})^2\rangle^{1/2}$ thereby obtained are: 0.0044, 0.0063, 0.0040, 0.0049

and 0.0064 Å² for the uncomplexed hexaether and its Na⁺, K⁺, Rb⁺ and Cs⁺ complexes respectively. These values are many times greater than the corresponding values of $\langle\sigma^2(U_{ij})\rangle^{1/2}$ and the poor agreement obtained can plausibly be ascribed to large amplitude internal ring vibrations (mainly torsional vibrations) that invalidate the rigid-body assumption.

Since, in the dibenzo series, the C–O bonds and the C–C bonds in the aromatic rings are normal, Mercer & Truter (1973) are inclined to believe that the shortening of the aliphatic C–C bonds is genuine. This is in contrast to previous suggestions (Bush & Truter, 1971, 1972) that the shortening could result from neglect of thermal-motion corrections. We have also changed our minds about this question, but the other way. We tended first to rely on the atomic positions found by our work and were persuaded that the shortening of C–C bonds in these complexes was real and attributable to effective positive charges induced on the carbon atoms by the cations and electronegative substituents. Non-empirical SCF calculations show that in hydrogen-like molecules with nuclear charges fractionally greater than unity the equilibrium nuclear distance is slightly decreased (Dunitz & Ha, 1972). We later found that least-squares analysis with modified weights (Dunitz & Seiler, 1973) led to slightly longer C–C bonds than those obtained with experimental or unit weights. The modified weighting system tends to move the atomic position from the centroid of a non-centric density peak towards the peak maximum. Non-centric peaks can result from asymmetric charge distributions in polar bonds and from anharmonic vibrations of the atoms along curvilinear paths. The corrections for these effects depend on the extent and quality of the high-order intensity data. With suitable weighting of the existing data the mean C–C distances in the uncomplexed hexaether and in its Na⁺ and K⁺ complexes increased from about 1.490 Å to 1.505 Å, and it seems very likely that an improvement in the quality of the high-order data (attainable, for example, by low-temperature measurements) would lead to a further increase. The C–O bond lengths are far less affected.

As mentioned above, it seems likely that torsional vibrations of the 18-membered ring are important in all five crystal structures. Torsional vibrations have the interesting property that, although they actually preserve equilibrium bond distances and angles, their effect is to shorten the apparent bond distances, widen

Table 1. *Summary of bond distances (Å) and angles (°) observed for 1,4,7,10,13,16-hexaoxacyclooctadecane in five crystal structures*

Structure	The range of each parameter (and its mean value) is given.											
	C–C		C–O			C–O–C			O–C–C			
Free ligand	1.505	(1.507)	1.509	1.403	(1.410)	1.426	113.3	(113.5)	114.0	106.4	(109.8)	114.6
NaNCS	1.491	(1.502)	1.511	1.410	(1.423)	1.437	111.4	(113.3)	116.5	106.0	(109.2)	113.6
KNCS complex	1.497	(1.504)	1.507	1.414	(1.418)	1.424	111.6	(112.2)	112.9	107.5	(108.5)	109.4
RbNCS complex	1.476	(1.489)	1.500	1.401	(1.414)	1.435	110.9	(112.3)	114.1	108.6	(109.4)	110.5
CsNCS complex	1.464	(1.475)	1.491	1.392	(1.418)	1.445	111.3	(113.0)	113.9	108.6	(109.8)	111.0

the apparent bond angles and leave the torsion angles unchanged. This is because the curvilinear motion of the atoms involved produces a displacement of the peak centroid along the internal bisector of the bond angle, *i.e.* in the plane of the atom and its two bonded neighbours.

Since the oxygen atoms in the ring all point inward, the displacements of the centroid produced by libration and by torsional vibration are in opposite senses and tend to cancel each other. For the carbon atoms, the displacements are roughly in the same direction and reinforce each other. This may be the reason why the C-C bonds appear to be shortened more than the C-O bonds.

In conclusion we tend to think that the bond shortenings observed in cyclic polyethers and their complexes, and also in many ethylenediamine complexes [see Bush & Fenton (1971) for examples], are largely, if not completely, spurious effects due to inadequate treatment of certain kinds of thermal motion in the crystals, and we hope to check this by suitable low-temperature studies.

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References

- BRIGHT, D. & TRUTER, M. R. (1970). *J. Chem. Soc. (B)*, pp. 1544-1550.
- BUSH, M. A. & FENTON, D. E. (1971). *J. Chem. Soc. (A)*, pp. 2446-2450.
- BUSH, M. A. & TRUTER, M. R. (1971). *J. Chem. Soc. (B)*, pp. 1440-1446.
- BUSH, M. A. & TRUTER, M. R. (1972). *J. Chem. Soc. Perkin II*, pp. 341-344.
- BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142-146.
- CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 757-758.
- CRUICKSHANK, D. W. J. (1961). *Acta Cryst.* **14**, 896-897.
- DALE, J. (1963). *J. Chem. Soc.* pp. 93-111.
- DALE, J. & KRISTIANSEN, P. O. (1972). *Acta Chem. Scand.* **26**, 1471-1478.
- DAVIS, M. & HASSEL, O. (1963). *Acta Chem. Scand.* **17**, 1181.
- DOBLER, M. (1972). *Helv. Chim. Acta*, **55**, 1371-1384.
- DOBLER, M., DUNITZ, J. D. & KILBOURN, B. T. (1969). *Helv. Chim. Acta*, **52**, 2573-2583.
- DOBLER, M., DUNITZ, J. D. & SEILER, P. (1974). *Acta Cryst.* **B30**, 2741-2743.
- DOBLER, M. & PHIZACKERLEY, R. P. (1974a). *Helv. Chim. Acta*, **57**, 664-674.
- DOBLER, M. & PHIZACKERLEY, R. P. (1974b). *Acta Cryst.* **B30**, 2746-2748; 2748-2750.
- DUNITZ, J. D. & HA, T. K. (1972). *Chem. Commun.* pp. 568-569.
- DUNITZ, J. D. & SEILER, P. (1973). *Acta Cryst.* **B29**, 589-595.
- DUNITZ, J. D. & SEILER, P. (1974a). *Acta Cryst.* **B30**, 2739-2741.
- DUNITZ, J. D. & SEILER, P. (1974b). *Acta Cryst.* **B30**, 2750.
- FRENSDORFF, H. K. (1971). *J. Amer. Chem. Soc.* **93**, 600-606.
- GROTH, P. (1972). *Acta Chem. Scand.* **25**, 3189-3191.
- HERCEG, M. & WEISS, R. (1972). *Bull. Soc. Chim. Fr.* pp. 549-551.
- ITAKA, Y., SABAMAKI, T. & NAWATA, Y. (1972). *Chem. Lett.* pp. 1225-1230.
- KILBOURN, B. T., DUNITZ, J. D., PIODA, L. A. R. & SIMON, W. (1967). *J. Mol. Biol.* **30**, 559-563.
- KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521-523.
- MERCER, M. & TRUTER, M. R. (1973). *J. Chem. Soc. Dalton*, pp. 2215-2220.
- METZ, B., MORAS, D. & WEISS, R. (1973). *Acta Cryst.* **B29**, 1377-1381, 1382-1387, 1388-1393.
- MOORE, C. & PRESSMAN, B. C. (1964). *Biochem. Biophys. Res. Commun.* **15**, 562-567.
- MORAS, D., METZ, B., HERCEG, M. & WEISS, R. (1972). *Bull. Soc. Chim. Fr.* pp. 551-555.
- MORAS, D., METZ, B. & WEISS, R. (1973). *Acta Cryst.* **B29**, 383-388, 388-395.
- MORAS, D. & WEISS, R. (1973). *Acta Cryst.* **B29**, 396-399, 400-403, 1059-1063.
- MUELLER, P. & RUDIN, D. O. (1967). *Biochem. Biophys. Res. Commun.* **26**, 398-404.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 2nd ed., p. 189. Ithaca: Cornell Univ. Press.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63-76.
- SEILER, P., DOBLER, M. & DUNITZ, J. D. (1974). *Acta Cryst.* **B30**, 2744-2745.
- SIMON, W., MORF, W. E. & MEIER, P. C. (1973). *Struct. Bond.* **16**, 113-160.
- STEFANAC, Z. & SIMON, W. (1966). *Chimia*, **20**, 436.
- TRUTER, M. R. (1973). *Struct. Bond.* **16**, 71-111.