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Molecular Structures Department

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MOLECULAR STRUCTURES DEPARTMENT

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Introduction

During the year we moved to Rothamsted in two stages. D. G. Parsons and J. N. Wingfield came early in January and were soon working again in the Bawden Building. The rest of us remained without light or heating in the Aldwych until the end of February when we arrived with our heavy equipment. Our computer was running normally within one week as a result of the efficiency of C. W. Fearne (Computer Department) and IBM. We are very grateful to all the people who have made us so welcome often at inconvenience to themselves. We and our equipment are spread throughout seven other departments, an arrangement which has reduced our efficiency.

Our integrated programme of work on the co-ordination chemistry of alkali and alkaline earth metals has continued and is reported under three headings: synthetic work, solution studies and crystal structure analysis. A new venture aimed at the rational design of molecules is the calculation of conformational energies, the first step in molecular mechanics; the results are promising.

Difficulties in re-installation and instrumental faults put our major piece of X-ray equipment, an automatic diffractometer, out of action for most of the year. We have been fortunate in being able to use those in other laboratories, Imperial Chemical Industries, Sheffield Polytechnic, University of Durham and the University of Leeds. This has incidentally enabled us to compare various instruments and also the new service provided at the Atlas Laboratory, Chilton, for reading the intensities on X-ray films and providing the results in computer-readable form.

We were able to determine the absolute configuration of the potent pyrethroid insecticide 'NRDC 161' which fortunately is itself crystalline; this is one of the structures we have investigated in collaboration with other workers in the agricultural research service (the Insecticides and Fungicides Department of Rothamsted Experimental Station). The other collaborative project was the determination of the molecular structure of dihydrophytuberin a derivative of phytuberin which was extracted from blighted potatoes by the Food Research Institute.

Co-ordination chemistry of alkali metal cations

Synthesis

Macrocyclic compounds. Two series of compounds based on the macrocyclic ring, 15-crown-5, (Fig. 1), have been designed, one to select for potassium and the other to prefer smaller cations. Both make use of the fact that potassium has been found to form complexes, $K(\text{benzo-15-crown-5})_2^+$, in which it is sandwiched between two molecules

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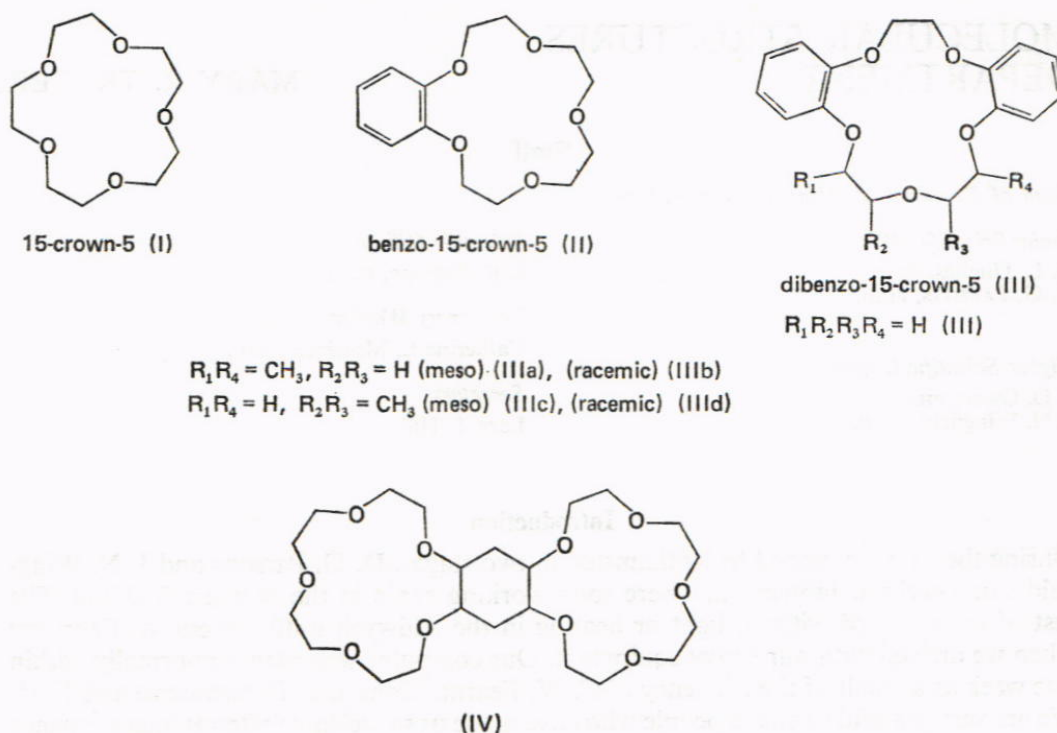


FIGURE 1

of ligand. The compounds intended to be selective for potassium have 15-crown-5 rings joined together in the correct relative orientation. Those described previously (*Rothamsted Report for 1973*, 216) had various groups joining two benzene rings of benzo-15-crown-5 molecules; these proved to give insoluble and probably polymeric complexes. A more rigid tricyclic molecule based on cyclohexane, Fig. 1 IV, is now being synthesised.

The other compounds are derivatives of dibenzo-15-crown-5, with bulky methyl groups in some positions on the macrocyclic ring to prevent formation of sandwich compounds. As the carbon atom to which the methyl is attached is asymmetric, addition of methyl groups to two carbon atoms gives pairs of isomers, meso and racemic. Space-filling models suggest that the racemic molecule IIIb should have the oxygen atoms constrained to form a cavity while the meso isomer IIIa can have all five oxygen atoms coplanar. As expected the latter compound forms a 1 : 2 complex with potassium perchlorate while from the former a lithium complex can be crystallized. (Parsons)

Open chain compounds. Compounds of the type shown in Fig. 2, have been made to act as small, potentially-helical ligands. Crystalline complexes have been obtained of alkali metal salts with the lipophilic anions picrate and tetraphenylborate and microcrystalline complexes with other anions. The compounds with $n = 2$ or 3 and $R = CH_2COOH$ will also form anionic complexes, one acidic hydrogen being replaced by the cation to give salts. (Wingfield)

Solution studies

E.m.f. measurements. Modification of the reference silver/silver chloride electrode has enabled us to increase the scope of measurements we can make in non-aqueous solvents. The change in e.m.f. on addition of complexing agent to a solution of the metal

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salt is observed. If a 1 : 1 complex only is formed the stability constant can be calculated simply from the concentration of uncomplexed ion as measured by the e.m.f. When the metal concentration exceeds that of the ligand, more metal is removed than would be expected for a 1 : 1 complex indicating 2 : 1 complex formation; 1 : 1 and even 1 : 2 complexes appear at higher ligand concentrations. For comparative work on a series of compounds we have measured the change in e.m.f. at the metal : ligand ratio 1 : 1.

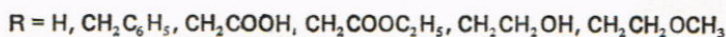
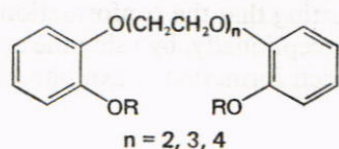


FIGURE 2

Open chain compounds, as expected, had much lower values than cyclic compounds with the same number of oxygen atoms. Some compounds e.g. Fig. 2, $n = 2$, $R = CH_2C_6H_5$ showed extreme selectivity in having a measurable interaction with potassium in methanol solution and none with sodium. For the cyclic compounds of Fig. 1 the e.m.f. changes with potassium decreased as predicted with reduction in the flexibility of the macrocyclic ring i.e. in the order $I > II > III > III_d > III_a > III_b$. The same order was obtained with sodium.

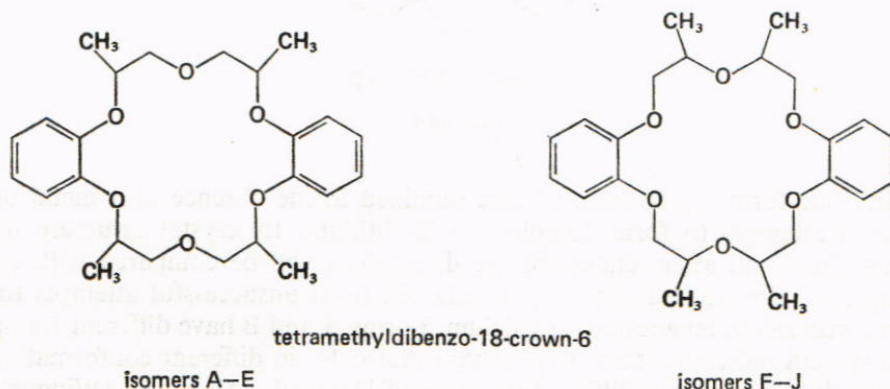


FIGURE 3 Each methyl group may be 'above' or 'below' the plane of the paper giving five possible isomers for each molecule.

The four isomers A-D of tetramethyl-dibenzo-18-crown-6 (Fig. 3) gave similar values for potassium, less than for dibenzo-18-crown-6 itself. (Isomer E, a product obtained in very low yield, is being resynthesised to provide enough for measurement). Steric effects appear to reduce the complexing ability. Sodium gives markedly different results, isomers A and C having smaller effects than isomers B and D; as the method of synthesis (see paper 10) groups isomers into pairs A and B or C and D we use the e.m.f. measurements, and space-filling models to deduce the configuration of the isomers, on the assumption that a lower affinity for sodium is correlated with a less flexible form. (Parsons and Sapsford)

Vibrational spectra. A Cary 83 Raman spectrometer has been set up; this allows us to investigate solid samples and solutions ≥ 0.1 M. Our previous work (see Truter, *Structure and Bonding* (1973), **16**, 71-111) has shown benzo-15-crown-5, Fig. 1, to have

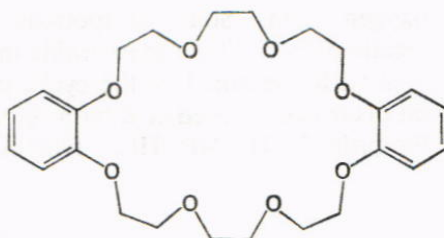
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different conformations in the crystalline solids of the 1 : 1 complex with sodium iodide and the 1 : 2 complex with potassium iodide.

This conformational change is reflected in the Raman spectra in the regions 1350–1200 cm^{-1} and 900–800 cm^{-1} both in the crystal and in methanol solution. The effect in solution persists when the ratio of metal to benzo-15-crown-5 is varied indicating that the conformational change is induced by the cation. Cations smaller than sodium, such as lithium and magnesium, give spectra indicating that the conformation of the molecule is similar to that in the presence of sodium. Exceptionally, by using the anion tetraphenylborate, the conformation required for sandwich formation is exhibited by sodium when the 1 : 2 complex is isolated. (Wingfield)

Crystalline compounds

Crown ethers. Further evidence suggesting a cation-induced change of conformation in the molecule has been obtained for dibenzo-24-crown-8 (Fig. 4). This appears to be



dibenzo-24-crown-8

FIGURE 4

dimorphic; one form, A, is 'normal' and obtained in the absence of a metal or from unsuccessful attempts to form complexes with lithium. Its crystal structure has just been determined and after refinement the dimensions will be compared with those of two complexes. The second form, B, is obtained from unsuccessful attempts to make complexes with silver, magnesium or calcium. Forms A and B have different Raman and infra red spectra indicating that they contain molecules in different conformations and are not merely the results of different packings of identical molecules. (Wingfield)

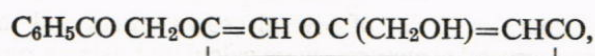
The solution of the crystal structure of the complex (sodium-*o*-nitrophenolate)₂ dibenzo-24-crown-8 was reported last year. The parameters of this structure have been refined for comparison with those of (potassium thiocyanate)₂ dibenzo-24-crown-8 (Mercer & Truter, *Journal of the Chemical Society (Dalton Transactions)* (1973), 2469–2473.

In the sodium complex, a two-fold symmetry axis relates the two halves of the crown ring (c.f. a centre of symmetry in the potassium complex). This allows the crown ring to fold around the two sodium cations inside the ring for improved co-ordination of the cations with the ring oxygen atoms. However, two oxygen atoms are still unable to approach close enough to co-ordinate with the cations, the first example found of ring oxygen atoms not involved in the complexing. The co-ordination spheres of the cations are completed by the bridging contacts of a pair of *o*-nitrophenolate anions. (Hughes)

Phenacyl kojate. Work on this series of compounds (see *Rothamsted Report for 1973*, Part 1, 213) was completed with the determination of the structure of the complex formed

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by pak (5-phenacyl-2-hydroxy-methyl-4*H*-pyran-4-one),



with sodium iodide. Unlike the other alkali metal halide complexes, this compound is hydrated (Fenton, *Journal of the Chemical Society, Dalton Transactions* (1973), 1380–1383) and we have established the formula as $\text{NaI}(\text{pak})_2(\text{H}_2\text{O})_2$. The two (pak) molecules have different environments; one is hydrogen-bonded to a water molecule and makes no contact with sodium while the other molecule co-ordinates one sodium cation by triple chelation and another by the CH_2OH group so that it is strictly comparable with those in the complex potassium iodide $(\text{pak})_2$ (see paper 4). For each sodium four co-ordination positions are accounted for by (pak) and two additional ones are occupied by water molecules. This is an example of a contrast between potassium and sodium involving retention by the latter of part of its sphere of hydration. (Phillips and Truter)

Natural products

From blighted potatoes. Phytuberin is a stress metabolite accumulated in blighted potatoes. Various structural formulae for this sesquiterpenoid compound have been proposed from spectral and chemical data. The correct structure has been determined from the crystal X-ray analysis of a derivative, dihydrophytuberin, $\text{C}_{17}\text{H}_{28}\text{O}_4$. All the atoms, including the hydrogen atoms, were located (see paper 3) and revealed a compact molecule (Fig. 5), in which the acetate group folds round and lies against the rigid

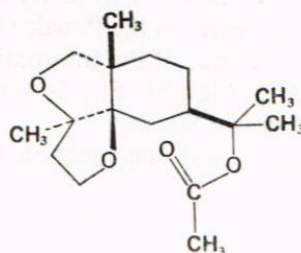
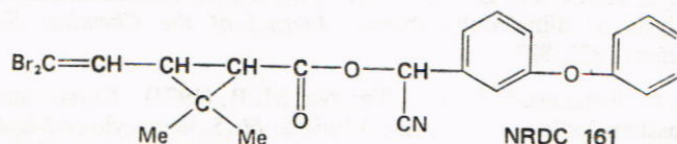


FIGURE 5

skeleton of the 3-ring molecule. The cyclohexane ring has a chair conformation, and the two five-member rings may best be described as having envelope shapes. The bond lengths all appear normal, but the bond angles show the distortions of considerable conformational strain. (Hughes, with Dr. D. T. Coxon, Food Research Institute, Norwich)

Pyrethroid insecticides

The crystal structure of a new pyrethroid of great potency ('NRDC 161') has been solved. The absolute configuration of the most active isomer has been determined and independently confirms the chemical work.



The conformation of the molecule is of interest for structure-activity relationships and other pyrethroids are under investigation. (Owen, with Elliott and Janes, Insecticides and Fungicides Department)

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Molecular mechanics

The conformational energies (C.E.) of several crown ethers and their complexes, with dimensions taken from crystal structures, were calculated using a purely repulsive energy expression for the non-bonded interactions. In all cases the free ligand has a higher conformational energy than the complexed ether. For the two isomers of tetramethyl dibenzo-18-crown-6 (Fig. 3), which give different stoichiometries in their complexes with caesium thiocyanate (Layton, Mallinson, Parsons & Truter, *Journal of the Chemical Society (Chemical Communications)* (1973), 694–695) the C.E. is significantly different being lower for isomer G in CsNCS (isomer G)₂ than for isomer F in CsNCS (isomer F). These preliminary results encourage us to use more sophisticated energy functions to verify them and to estimate possible conformations adopted in solution. (Owen)

Computing

We have transferred our three large programs, NUCLS, ORFFE, and MULTAN from the University College IBM 360 to the RES ICL 4-70. NUCLS required extensive modification and the other two were relatively easy. Many programs have been altered to save paper. (Owen)

Staff and visiting workers

S. E. V. Phillips was awarded the Ph.D. degree of the University of London and left to take up a Post Doctoral Fellowship in the University of British Columbia. We were joined by Catherine L. Mortimer, to work on the Powder Data File, and by I. R. Hanson.

Mary R. Truter attended the conference of the International Union of Crystallography on 'Anomalous Scattering' held in Madrid. She is now Chairman of the Chemical Crystallography Group of the Chemical Society.

One sandwich student, J. Sapsford, and one vacation student, N. Bowden, worked in the Department.

Publications

GENERAL PAPERS

- 1 TRUTER, M. R. (1974) 'Dull' metals prove far from dull. *Spectrum* **122**, 6–9.
- 2 TRUTER, M. R. (1974) Molecular structures of ionophores and their complexes with metal cations. In: *Drugs and transport processes*. Ed. B. A. Callingham. London: Macmillan, pp. 211–225.

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- 3 HUGHES, D. L. & (COXON, D. T.) (1974) Phytuberin; revised structure from the X-ray crystal analysis of dihydrophytuberin. *Journal of the Chemical Society (Chemical Communications)*, 822–823.
- 4 HUGHES, D. L., PHILLIPS, S. E. V. & TRUTER, M. R. (1974) Crystal structure of a complex of potassium iodide with phenacyl kojate: bis(5-phenacyloxy-2-hydroxymethyl-4H-pyran-4-one)potassium iodide. *Journal of the Chemical Society (Dalton Transactions)* 907–911.
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- 6 MERCER, M. (1974) Crystal structure of a dinuclear dinitrogen complex: tetrachloro-*{chlorotetrakis[dimethyl(phenyl) phosphine]rhenium(I)- μ -dinitrogen-methoxymolybdenum(V)-methanol-hydrochloric acid}*. *Journal of the Chemical Society (Dalton Transactions)*, 1637–1640.
- 7 MILBURN, H., TRUTER, M. R. & VICKERY, B. L. (1974) Crystal structure of a sodium complex, *bis-[NN'-ethylenebis(salicylideneiminato) copper(II)]perchloratosodium-p-xylene*. *Journal of the Chemical Society (Dalton Transactions)*, 841–846.
- 8 NAVE, C. & TRUTER, M. R. (1974) The crystal structure of the dihydroperchlorate of 1,4,8,11-tetra-azacyclotetradecane (cyclam). *Journal of the Chemical Society (Dalton Transactions)*, 2351–2354.
- 9 OWEN, J. D. (1974) Absolute configuration of the potent insecticide α -cyano-3-phenoxybenzyl *cis*-2,2-dimethyl-3-(2,2-dibromovinyl)cyclopropanecarboxylate by X-ray crystal structure analysis. *Journal of the Chemical Society (Chemical Communications)*, 859–860.
- 10 PARSONS, D. G. (1975) Synthesis of ten isomers of a macrocyclic polyether, tetramethyl-dibenzo-18-crown-6, and their complexes with salts of alkali metals. *Journal of the Chemical Society (Perkin Transactions I)*, 245–250.
- 11 PHILLIPS, S. E. V. & TRUTER, M. R. (1974) Crystal structure of a complex of caesium thiocyanate with phenacyl kojate, (5-phenacyl-2-hydroxymethyl-4*H*-pyran-4-one) caesium thiocyanate. *Journal of the Chemical Society (Dalton Transactions)*, 2517–2520.