

This difference is significant even when one takes into account the uncertainty involved in using the ferrocene/ferrocinium couple to compare the potential scales.

It has been suggested⁶ that correlations between anodic oxidation potentials and gas phase ionization potentials of organic compounds could be used for the prediction of oxidation potentials for electrochemical syntheses of organic compounds. An inspection of Table 2 shows that, indeed, the oxidation potentials follow the ionization potentials (1-propanol, 2-propanol, 1-butanol, and 2-butanol have approximately equal ionization potentials).

However, comparison with the data reported for some aliphatic hydrocarbons⁴ and the information given by Miller⁶ indicate that the oxidation potentials of aliphatic alcohols are about 200–400 mV less anodic than the IP values would suggest. Thus solution phase ionization requires less energy than gas phase ionization in the case of these alcohols. The reasons for such a difference require further investigation.

Experimental. The solvents were purified by standard methods.⁷ The aliphatic alcohols were analytical grade products, which were dried with anhydrous potassium carbonate. Tetrabutylammonium tetrafluoroborate was prepared by neutralizing the commercially available tetrabutylammonium hydroxide with tetrafluoroboric acid and recrystallizing the product from methanol.

The linear sweep experiments were performed with a Chemical Electronics potentiostat and sweep generator using a x/y -recorder for registering the voltammograms. A three-compartment glass cell equipped with an adjustable Luggin capillary was used in the experiments. The working electrode was made from 0.5 mm platinum wire, a platinum disc served as the counter electrode and the reference electrode consisted of a silver wire dipping into a solution containing 0.01 M silver perchlorate.

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On the Crystal Structure of a Complex between Potassium *p*-Toluenesulfonate and 1,4,7,10,13,16-Hexaoxa-cyclooctadecane

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The conformation of cyclic oligo-ethers related to ethylene oxide has recently been studied by Dale and Kristiansen by infrared spectroscopy.¹ It is concluded that the 18-ring hexa-ether adopts a D_{3d} conformation when complexing alkali cations, but an entirely different one when crystallizing alone. To obtain more detailed information about the conformation of the complex, an X-ray analysis has been carried out on the complex between potassium tosylate and 1,4,7,10,13,16-hexaoxacyclooctadecane.

The crystals are orthorhombic ($a=8.17$, \AA , $b=11.73_1$, \AA , $c=24.19_3$, \AA) with space group $P2_12_12_1$ and four formula units in the cell ($\rho_{\text{calc}}=1.34$ g cm^{-3} , $\rho_{\text{obs}}=1.35$ g cm^{-3}). About 3000 reflections were registered on an automatic four-circle diffractometer with a highly orientated graphite crystal monochromator and

Table 1. Fractional atomic coordinates and anisotropic thermal vibration parameters.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
K ⁺	07836	04242	07242	01887	00603	00139	00103	00115	-00006
S	-10048	84825	15550	02090	00867	00158	-00311	00180	00034
O ₇	-08784	84983	09511	04151	00725	00162	-00977	-00216	00015
O ₈	-25121	80225	17604	01299	01672	00359	00471	00165	00665
O ₉	-05887	96082	17696	03022	00883	00204	-00490	00143	-00176
C ₁₃	05647	75392	17697	02487	00709	00052	-01234	00034	-00029
C ₁₄	01948	64047	18283	05092	01077	00133	00371	-00222	00070
C ₁₅	14813	56594	19468	03077	01437	00175	-00677	-00248	-00245
C ₁₆	31185	60133	20466	02121	01074	00131	00979	00174	-00120
C ₁₇	34024	72196	19900	02638	00896	00226	-01341	-00266	00061
C ₁₈	21590	79850	18551	02165	00365	00247	00325	-00178	00136
C ₁₉	44438	52051	21984	04157	01183	00349	02894	-00169	-00105
O ₁	41237	-03065	04673	04055	03678	00806	02934	02307	02637
O ₂	34139	10104	14235	02782	03152	00407	-03991	-01239	01456
O ₃	08035	24306	14261	06600	00907	00471	-02467	02736	-00625
O ₄	-16700	21368	06415	02492	02189	00896	00390	00277	02119
O ₅	-08985	07589	-03378	04408	03847	00323	-04456	-01236	01299
O ₆	13539	-07516	-02544	10987	00885	00587	-02769	03506	-00603
C ₁	50307	-06533	07799	05219	05097	01166	07170	02499	03916
C ₂	52146	04390	11582	01268	02989	00228	00094	00085	00633
C ₃	38818	17012	15780	06518	01809	01029	-04410	-03780	01440
C ₄	22393	21194	18833	07763	02339	00135	02620	-01256	-00499
C ₅	-03129	24985	16727	16661	01499	01099	-03816	07685	-01025
C ₆	-13830	30036	12118	09277	00977	00640	-02271	00216	-00804
C ₇	-22471	26340	03234	03593	03619	01312	00041	-00011	03533
C ₈	-26166	17164	-01260	04192	02186	00286	00712	-01263	00248
C ₉	-18677	03898	-04300	06158	04906	00589	-07833	-02217	01794
C ₁₀	-01077	-06019	-06910	09411	02221	00355	-00211	-02800	-00610
C ₁₁	23142	-11213	-04680	09948	01485	00953	00895	02456	-01104
C ₁₂	38310	-13034	-00501	04128	02000	00895	00112	01456	-01647

MoK α -radiation. 1671 reflections were recorded as observed using an observed-unobserved cutoff at $2.5\sigma(I)$.

The potassium and sulphur positions were obtained from a three-dimensional Patterson map, and the structure was refined by Fourier methods and full-matrix least squares technique.* Anisotropic thermal vibration parameters were introduced for the 30 nonhydrogen atoms. The R_w -value arrived at (hydrogens not included) was 9.8% for 1671 observed reflections. The corresponding parameters are given in Table 1.

Fig. 1 shows the resulting structure viewed along [100].

Bond distances and angles as well as the thermal parameters, indicate that the 18-membered ring has a disordered structure while the potassium tosylate is ordered.

* All programs used are included in this reference.

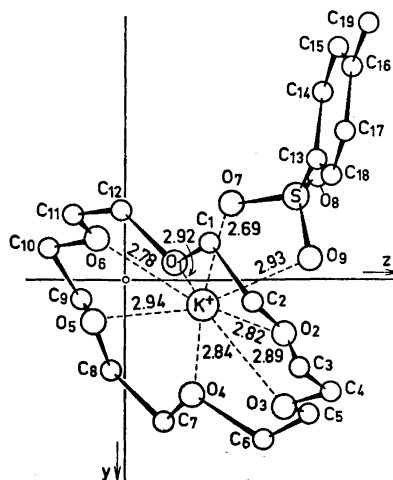


Fig. 1. Schematic drawing of the structure arrived at, viewed along [100].

The bond distances O_1-C_{11} , O_2-C_{33}, \dots , O_6-C_{11} range from 0.93 Å to 1.13 Å while O_1-C_{12} , O_2-C_{23}, \dots , O_6-C_{10} lie between 1.61 Å and 1.86 Å. The C-C distances and several bond angles obtained for the 18-ring are also unreasonable. The maximum root mean square amplitudes of O_1, \dots, O_6 range from 0.6 Å to 0.7 Å (corresponding to B -values from 30 Å² to 40 Å²). The carbon atoms C_{2n+1} have r.m.s. values of 0.7 Å–0.9 Å, while those of C_{2n} lie between 0.4 Å and 0.6 Å. While these findings suggest a disordered structure of the 18-membered ring, bond distances and angles of the tosylate anion (listed in Table 2) are normal. An ordered structure of the potassium tosylate is also confirmed by the reasonable results of the thermal analysis.

Table 2. Bond distances and angles of the tosylate anion. (E.s.d.'s of distances and angles are about 0.01 Å and 1°, respectively).

Distance	(Å)	Angle	(°)
S-O ₇	1.46	O ₇ -S-O ₈	114
S-O ₈	1.43	O ₇ -S-O ₉	109
S-O ₉	1.46	O ₈ -S-O ₉	115
S-C ₁₃	1.77	O ₇ -S-C ₁₃	104
C ₁₃ -C ₁₄	1.37	O ₈ -S-C ₁₃	107
C ₁₄ -C ₁₅	1.40	O ₉ -S-C ₁₃	107
C ₁₅ -C ₁₆	1.42	S-C ₁₃ -C ₁₄	118
C ₁₆ -C ₁₇	1.44	S-C ₁₃ -C ₁₈	119
C ₁₇ -C ₁₈	1.40	C ₁₃ -C ₁₄ -C ₁₅	118
C ₁₈ -C ₁₃	1.42	C ₁₄ -C ₁₅ -C ₁₆	124
C ₁₆ -C ₁₉	1.49	C ₁₅ -C ₁₆ -C ₁₇	115
		C ₁₆ -C ₁₇ -C ₁₈	122
		C ₁₇ -C ₁₈ -C ₁₃	118
		C ₁₈ -C ₁₃ -C ₁₄	123
		C ₁₅ -C ₁₆ -C ₁₉	123
		C ₁₇ -C ₁₆ -C ₁₉	122

The average structure arrived at for the cyclic ether has roughly D_{3d} symmetry with the coordination distances to K^+ as shown in Fig. 1. The potassium is eight-coordinated with an average K-O distance of 2.85 Å, somewhat shorter than the corresponding value (2.88 Å) for the ten-coordinated K^+ in the complex of potassium iodide with 2,3:17,18-dibenzo-1,4,7,-

10,13,16,19,22,25,28 - decaoxycyclotriacont-2,17-diene.³

The disorder may be described in terms of two sites (containing molecules of the same D_{3d} conformation) rotated *ca.* 30° with respect to each other about the approximate threefold axis of rotation (Fig. 2). No attempts to refine the structure under these assumptions have been made.

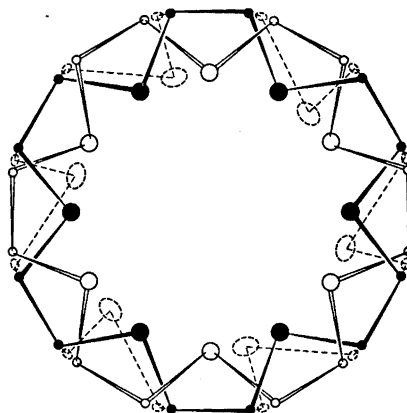


Fig. 2. Schematic drawing indicating the disorder of the 18-membered ring. The full and open circles correspond to the two molecular sites (rotated *ca.* 30° with respect to each other about the approximate threefold axis of rotation). The dotted lines indicate the average structure.

A list of observed structure factors is available by request to the author.

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