

**the Presence of Bromide.** Both *cis*-Me<sub>2</sub>Pt(PMe<sub>2</sub>Ph)<sub>2</sub> (17.1 mg, 3.4 × 10<sup>-2</sup> mmol) and tetra-*n*-butylammonium bromide (1.3 mmol) were weighed into a 25-mL flask, which was sealed with a gas-tight septum and the contents deaerated with a stream of nitrogen. Acetonitrile (2.0 mL) was added and the solution stirred, while a solution of sodium hexachloroiridate(IV) containing 6.6 × 10<sup>-2</sup> mmol in 1.0 mL of acetonitrile was added. Gas liquid chromatography of the reaction after completion [noted by the rapid decoloration of iridium(IV)] showed a trace of methyl chloride, but no methyl bromide. We infer from the absence of methyl cleavage that the oxidation of Me<sub>2</sub>Pt(PMe<sub>2</sub>Ph)<sub>2</sub> followed the usual course to the platinum(IV) species.

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- (18) It is interesting to note that the methane formed in minor but significant amounts from Me<sub>2</sub>Pt(PPh<sub>3</sub>)<sub>2</sub> is relatively more important than ethane from Et<sub>2</sub>Pt(PPh<sub>3</sub>)<sub>2</sub>. The difference could be due to a slower rate of reaction of methyl radicals (compared to ethyl) with hexachloroiridate(IV) in competition with hydrogen transfer from solvent. A more intriguing possibility, however, is an intramolecular hydrogen transfer from the intermediate I directly leading to methane and a carbene complex. [Cf. E. L. Muettterties and P. L. Watson, *J. Am. Chem. Soc.*, **98**, 4667 (1976).] In a preliminary study of the facile reaction of (CD<sub>3</sub>)<sub>2</sub>Pt(PMe<sub>2</sub>Ph)<sub>2</sub> with carbon tetrachloride, only 10% of the methane formed consisted of CD<sub>4</sub>.
- (19) According to Scheme 1, the rate of disappearance of hexachloroiridate(IV) should be reduced by a factor of 2, if all the ethyl radicals formed during the oxidative cleavage of Et<sub>2</sub>PtL<sub>2</sub> were scavenged by oxygen, as recently found in a related example with dialkylmercury.<sup>7b</sup>
- (20) The competition described in eq 18 and 19 is dependent on the concentration of hexachloroiridate(IV). However, depending on the relative rate constants for these processes, the product ratios may be difficult to relate quantitatively to Scheme 1.
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## Electronic Substituent Effects upon the Selectivity of Synthetic Ionophores

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**Abstract:** Substituted dibenzo-18-crown-6 ethers, *cis*- and *trans*-dinitro, *cis*- and *trans*-diamino, tetrabromo, octachloro, and mono- and bis(tricarbonylchromium), have been synthesized and characterized. Investigations on the ability of these crown ethers to extract sodium and potassium salts from water into methylene chloride have been performed. A very pronounced substituent effect has been observed that results in a reversal of the normal selectivity for this process of K<sup>+</sup> > Na<sup>+</sup>.

There has been considerable recent interest in the chemical and physical properties of the synthetic ionophores commonly named crown ethers.<sup>2</sup> Since Pedersen first established these compounds as very efficient coordinating agents for the alkali metal cations,<sup>3</sup> many studies have demonstrated the general concept that the size of the crown cavity plays a large role in determining the thermodynamic stability of the resulting complexes.<sup>4,5</sup> Certain gross substituent effects upon their properties have been observed. For example, there are differences in complexing abilities of the various 18-crown-6

ethers: dibenzo-18-crown-6, dicyclohexyl-18-crown-6, and 18-crown-6.<sup>6</sup> However, such variations with substituent may spring in part, if not mostly, from structural changes that restrict important conformational distortions of the crown upon complexing the metal cation.<sup>7</sup> It has also been established that the solvent environment can cause variations from one ether to another often causing changes in cation selectivity.<sup>8</sup> Apart from these results the overriding factor thought to control the formation of cation-crown complexes is the relative cation-oxygen cavity size. Thus, while 14-crown-4 ethers complex

preferentially with lithium (diameter  $\text{Li}^+$  1.36 Å, cavity, 1.2–1.5 Å), 15-crown-5 ethers prefer sodium ( $\text{Na}^+$  1.99 Å, cavity 1.7–2.2 Å), and in general the 18-crown-6 ethers show a marked selectivity in favor of potassium ( $\text{K}^+$  2.66 Å, cavity  $\approx 2.8$  Å).

The object of this paper is to demonstrate that while keeping the solvent systems constant, and using one basic crown system, dibenzo-18-crown-6 (DBC), important electronic effects are also operating and help determine the relative selectivity exhibited by these ionophores for the alkali metals and indeed are sufficiently large as to reverse the "normal" selectivity as reported in a preliminary communication.<sup>9</sup>

## Experimental Section

Microanalyses were performed by Chemalytics, Inc., Tempe, Ariz., Heterocyclic Chemical Co., Harrisonville, Mo., and Galbraith Laboratories, Knoxville, Tenn. IR spectra were obtained using Perkin-Elmer Model 421 or 237B spectrophotometers with polystyrene as a reference standard.  $^1\text{H}$  NMR spectra were recorded on a Perkin-Elmer R12 or Varian EM-360 instrument with  $\text{Me}_4\text{Si}$  internal standard, and UV spectra were obtained on a Beckman Model DB spectrophotometer. Melting points (or decomposition points) were determined in sealed, evacuated capillaries and are uncorrected. Hexacarbonylchromium was obtained from Alfa Inorganics and Strem Chemicals and was sublimed prior to use. Sodium 4-[*p*-(dimethylamino)phenylazo]benzenesulfonate was J. T. Baker reagent grade and was recrystallized from methanol/water. Dibenzo-18-crown-6 was purchased from Aldrich Chemical Co.

**Preparation of Dibenzo-18-crown-6(tricarbonyl)chromium.** Hexacarbonylchromium (2.2 g, 10 mmol), dibenzo-18-crown-6 (1.8 g, 5 mmol), and decalin (25 ml) were heated at reflux with stirring under nitrogen for 7 days. Sublimed hexacarbonylchromium was returned to the flask mechanically. At the end of the reaction time the hot solution was filtered. Caution: the filtered residue is pyrophoric. Upon cooling, the filtrate produced a yellow, crystalline precipitate (1.2 g). The precipitate was crystallized three times from benzene to yield the desired compound as bright-yellow needles (0.06 g, 48% crude, 2% purified): mp 141–143 °C; NMR ( $\text{CDCl}_3$ )  $\delta$  3.98 (m, 4 H, methylenes), 5.14 (m, 1 H, complexed aromatic), and 6.89 (s, 1 H, uncomplexed aromatic), IR ( $\text{CH}_2\text{Cl}_2$ ) [ $\nu$  ( $\text{C}=\text{O}$ )] 1961, 1875  $\text{cm}^{-1}$ ; UV max ( $\text{CH}_2\text{Cl}_2$ ) 320 nm.

Anal. Calcd for  $\text{C}_{23}\text{H}_{24}\text{O}_9\text{Cr}$ : C, 55.7; H, 4.87. Found: C, 55.8; H, 4.87.

**Preparation of Dibenzo-18-crown-6(hexacarbonyl)dichromium.** Hexacarbonylchromium (2.0 g, 9.1 mmol) and dibenzo-18-crown-6 (1 g, 2.78 mmol) in a 100 ml solution of a 50/50 mixture of THF and 2,2,4-trimethylpentane were refluxed in a quartz flask. After a period of 5 min, all of the reagents had dissolved and the system was irradiated using a Hanovia 450-W mercury lamp source. Irradiation and reflux were continued for 2 h. At this time the solution was pink orange. Reflux was continued for 1 h after which the solution was yellow. Infrared analysis of the resulting solution showed that considerable tricarbonyl complex had formed. The procedure of intermittent irradiation with continuous reflux was continued until a maximum amount of tricarbonyl was obtained by IR analysis. Permanent irradiation was initially used for the synthesis; however, with certain qualities of  $\text{Cr}(\text{CO})_6$  (we did not always resublime this material prior to use) considerable decomposition could take place. This problem was largely alleviated using the procedure described above. Subsequent to the above procedure, the solution was cooled and filtered to remove solid decomposition matter and any unreacted crown ether. Further standing slowly precipitated the title product, often contaminated with unreacted hexacarbonyl. This solid was collected and placed in a sublimation apparatus, and the hexacarbonyl was removed by high-vacuum, low-temperature sublimation. The resultant yellow powder was recrystallized from benzene to form small needle-like crystals: mp 155–158 °C dec; NMR ( $\text{CDCl}_3$ )  $\delta$  3.90 (m, methylenes), 5.10 (m, aromatic), IR [ $\nu$  ( $\text{C}=\text{O}$ )] 1961, 1875  $\text{cm}^{-1}$ .

Anal. Calcd for  $\text{C}_{26}\text{H}_{24}\text{O}_{12}\text{Cr}_2$ : C, 49.4; H, 3.82. Found: C, 49.7; H, 3.83.

The mono chromium complex may also be prepared using the above irradiation/reflux technique. It is important to have an excess of the crown ether to prevent formation of significant amounts of the bis chromium complex. Purification of the mono complex is as above.

Contamination by the bis complex may be checked using liquid gel permeation chromatography. Preferential recrystallization from benzene is used for purification of mixtures, the mono complex being the less soluble. We have, however, often encountered unexpected difficulty preparing large amounts of the mono complex using this technique due to formation of the bis complex as a significant impurity. Such problems are totally absent when using the thermal method described earlier. We have not attempted to use liquid chromatography as a bulk purification technique. Since it is used very efficiently to analyze for mixtures of the mono and bis complex, this should be entirely feasible.

**Preparation of *cis*- and *trans*-Dinitrodibenzo-18-crown-6.** Both isomers were obtained by the method of Feigenbaum and Michel;<sup>10</sup> *trans*-dinitrodibenzo-18-crown-6, mp 245–248 °C (lit. 245–251 °C); *cis*-dinitrodibenzo-18-crown-6, mp 210–212 °C (lit. 208–213 °C). The NMR spectra of the products agreed with the literature.

**Preparation of *cis*- and *trans*-Diaminodibenzo-18-crown-6.** *Cis*. The *cis* isomer was prepared by the procedure of Shchori.<sup>7</sup> Instead of evaporating the 2-methoxyethanol solvent, we allowed the solution to sit for 2 days while fine, white fibers crystallized out of solution. The fibers were collected and dried under reduced pressure. The *cis* isomer had mp 178–184 °C (lit. 177–178, 180–184 °C), yield 42%.

*Trans*. The *trans*-diamino compound was prepared by the same procedure as the *cis* compound. Surprisingly, the *trans* isomer is more soluble in 2-methoxyethanol than is the *cis*. The solution was concentrated to 60% of its volume before a white precipitate formed. This precipitate was collected and dried under reduced pressure. It had mp 196–200 °C (lit.<sup>7</sup> 199–203 °C) and was used in the extraction experiments without further recrystallization, yield 30%.

We could not obtain NMR spectra on either of the diamino compounds because of low solubility in common spectral solvents.

**Preparation of Octachlorodibenzo-18-crown-6.** Octachlorodibenzo-18-crown-6 was prepared by the direct chlorination of dibenzo-18-crown-6. DBC (0.5 g, 1.387 mmol) was dissolved in 15 ml of chloroform with stirring. Dry chlorine gas (Matheson Air Products) was bubbled into the solution at a moderate rate (2 bubbles/s) and after 4 h, a white precipitate formed. The precipitate was collected and dried under reduced pressure in an Abderhalden apparatus with cyclohexane (bp 80.6 °C) refluxing in the outer jacket. It had a sharp melting point of 283 °C. We could not obtain an NMR spectrum of the product because it was too insoluble, yield 0.22 g, 25%.

Anal. Calcd for  $\text{C}_{20}\text{H}_{16}\text{O}_6\text{Cl}_8$ : C, 37.7; H, 2.53; Cl, 44.6. Found: C, 37.1; H, 2.63; Cl, 44.0.

**Preparation of Tetrabromodibenzo-18-crown-6.** Tetrabromodibenzo-18-crown-6 was prepared by the direct bromination of dibenzo-18-crown-6. DBC (1.00 g, 2.8 mmol) was stirred until dissolved into 50 ml of chloroform. A bromine/chloroform solution (0.5 ml of  $\text{Br}_2$  in 30 ml of chloroform) was dropped over a one-half hour period into the stirred solution. An outlet was provided for the  $\text{HBr}$  gas evolved. After approximately one-fourth of the bromine stock solution had been added, a yellow-orange adduct formed. This adduct is a crown ether-bromine complex<sup>11</sup> much like the bromine-dioxane complex.<sup>12</sup>

The adduct and the excess bromine in solution were stirred for 48 h to allow the bromine to complete aromatic substitution of the crown ether. The orange precipitate was collected, washed with 20 ml of chloroform, and air dried. This orange precipitate is tetrabromodibenzo-18-crown-6 complexed with bromine<sup>11</sup> and has mp 200–210 °C. (It loses its orange color at 50 °C.) Yield 1.41 g, 50%. It was stored in the refrigerator.

To remove the complexed bromine from the product, 0.22 g of the orange complex was placed in an Abderhalden apparatus. With a vacuum and cyclohexane (bp 80 °C) refluxing in the outer jacket, the orange color quickly faded. After 18 h, the white powder had reached constant weight and had mp 212–215 °C.

Anal. Calcd for  $\text{C}_{20}\text{H}_{20}\text{O}_6\text{Br}_4$ : C, 35.5; H, 2.96; Br, 47.3. Found: C, 36.2; H, 3.16; Br, 45.6. Integration by NMR shows a 1.0:4 ratio for the aromatic:alkyl hydrogens.

**Preparation of Potassium 4-[*p*-(Dimethylamino)phenylazo]benzenesulfonate.** Potassium carbonate (3.90 g, 28 mmol), anhydrous sulfanilic acid (10.5 g, 61 mmol), and water (150 ml) were warmed until all of the sulfanilic acid dissolved. To this solution was added potassium nitrite (4.3 g, 51 mmol) in 20 ml of water. The resulting solution was cooled to 5 °C. Concentrated hydrochloric acid (7 ml) diluted with 10 ml of water was then added drop by drop with stirring to form the diazonium solution. A solution containing dimethylaniline

Table I<sup>a</sup>

Crown ether	log $K_{ext}$		
	Na <sup>+</sup>	K <sup>+</sup>	$\Sigma\sigma$
<i>t</i> -(NH <sub>2</sub> ) <sub>2</sub> DBC	4.16	4.67	-1.64
DBC	3.99	4.59	0
[Cr(CO) <sub>3</sub> ]DBC	3.97	4.14	1.40
[Cr(CO) <sub>3</sub> ] <sub>2</sub> DBC	3.81	3.51	2.80
<i>t</i> -(NO <sub>2</sub> ) <sub>2</sub> DBC	3.43	3.19	3.14
<i>c</i> -(NO <sub>2</sub> ) <sub>2</sub> DBC	3.46	3.13	3.14
(Br) <sub>4</sub> DBC	3.42	3.38	2.49
(Cl) <sub>8</sub> DBC	3.34	2.81	4.7

<sup>a</sup> Log  $K_{ext}$  determined from average of two extractions with measurements made at two different  $\lambda$  for each extraction. All values  $\pm 3\%$ .

(6 g, 50 mmol) and glacial acetic acid (3 ml) was added to the diazonium solution with stirring. The resulting solution was made alkaline by addition of potassium hydroxide (9.8 g, 175 mmol) in 20 ml of water. The desired product precipitated at once. The product was isolated by suction filtration and was recrystallized from methanol to yield orange needles (10.2 g, 59%): UV max (H<sub>2</sub>O) 464 nm ( $\epsilon$  26 400).

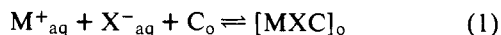
Anal. Calcd for C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>O<sub>3</sub>SK: C, 49.0; H, 4.11; N, 12.2. Found: C, 48.4; H, 4.11; N, 11.9.

**Extraction of Sodium and Potassium Salts by Crown Ethers.** Molar absorptivities of the sodium and potassium 4-*p*-(dimethylamino)phenylazo]benzenesulfonates were measured in CH<sub>2</sub>Cl<sub>2</sub> by addition of crown ether until the salt was dissolved. The molar absorptivities were independent of the crown ether used. For the sodium salt,  $\epsilon_{422}$  26 000 and  $\epsilon_{453}$  22 500. For the potassium salt,  $\epsilon_{422}$  23 700 and  $\epsilon_{453}$  21 800.<sup>13</sup>

The method of Pedersen<sup>4</sup> was used to determine the tendency of the sodium and potassium 4-*p*-(dimethylamino)phenylazo]benzenesulfonates to complex to crown ethers. Ten milliliters of the sodium or potassium salt in distilled water ( $3.00 \times 10^{-3}$  M) was shaken in a separatory funnel for 3 min with 10 ml of crown ether in CH<sub>2</sub>Cl<sub>2</sub> ( $1.83 \times 10^{-4}$  M). Variations of extraction time had no effect upon the resulting salt concentrations in the CH<sub>2</sub>Cl<sub>2</sub> phase. After separation of the layers, the amount of sodium or potassium salt transferred to the CH<sub>2</sub>Cl<sub>2</sub> layer was determined by measurement of absorption of the CH<sub>2</sub>Cl<sub>2</sub> layer at 422 and 453 nm. The crown ethers do not absorb at these wavelengths. At the concentrations used, no sodium or potassium salt was transferred to the CH<sub>2</sub>Cl<sub>2</sub> layer in the absence of crown ether.

## Results and Discussion

We have used the original extraction techniques of Pedersen to evaluate the extraction efficiency of the various substituted crown ethers.<sup>4</sup> This involves measuring the amount of alkali metal salt extracted from an aqueous environment into an organic medium, in the present case methylene chloride. The overall equilibrium studied may be described by the following equation:



where  $C_o$  = crown concentration in the organic medium,  $M^+_{aq} = X^-_{aq}$  = salt concentration in aqueous medium,  $[MXC]_o$  = concentration of crown complexed salt in the organic phase. The results of the extraction experiments are recorded in Table I where the various log  $K_{ext}$  values, determined using the method of Iwachido et al.,<sup>14</sup> are listed for the crown ethers studied. It may be observed that there is a considerable range of values, indicating that the various electronic effects of the aromatic substituent are transmitted to the oxygen crown and have a substantial effect upon the ability of the crown to extract the salts of the two cations studied.

One measure of the electronic effect of a given aromatic substituent is the value of the various  $\sigma_m$ ,  $\sigma_p$ , and  $\sigma_o$  constants.

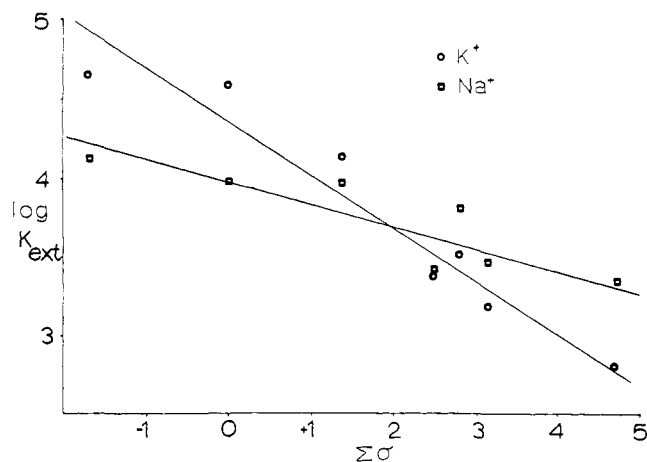


Figure 1. Plot of log  $K_{ext}$  vs  $\Sigma\sigma$ . Correlation coefficients, Na<sup>+</sup>, 0.89; K<sup>+</sup>, 0.96. Slope, Na<sup>+</sup>, -1.44; K<sup>+</sup>, -3.35.

We have attempted to correlate the various log  $K_{ext}$  values with the cumulative  $\sigma$  constants of the multiple substituents. This is complicated by the fact that certain substituents are both ortho and meta, or meta and para with respect to the oxygen crown system. We have used a method for computing the  $\Sigma\sigma$  values illustrated below for tetrabromodibenzo-18-crown-6 ether. Each bromine substituent is both meta and para to the oxygen crown, thus the  $\sigma_m$  (0.39) and  $\sigma_p$  (0.23) values are added to best approximate the overall electronic effect, i.e.,  $\sigma$  value per bromine atom is 0.62. Since all four bromine atoms are equivalent, the total electronic effect of the substituents upon the crown ether can be taken as  $4 \times 0.62 = 2.49$ . The various  $\sigma_m$ ,  $\sigma_p$ , and  $\sigma_o$  values used were taken from ref 15 and 16.

A plot of log  $K_{ext}$  vs.  $\Sigma\sigma$  for the substituted dibenzo-18-crown-6 ethers studied, using the sodium and potassium salts of 4-*p*-(dimethylamino)phenylazo]benzenesulfonate, are presented in Figure 1. From these data four significant features are observed:

a. There is an inverse relationship between the cumulative electron-withdrawing power of the substituents and the ability of the crown ether to extract both the sodium and potassium salts.

b. The response of the sodium and potassium salts, while similar qualitatively, differ quantitatively. The sodium salt extraction is considerably less susceptible to the substituent effect, and the ratio of the slope log  $K_{ext}/\Sigma\sigma$  for K<sup>+</sup>:Na<sup>+</sup> is  $\approx 2.3$ .

c. Crown ethers with cumulatively large electron-withdrawing substituents exhibit a reversal of the "normal" ion extraction selectivity of 18-crown-6 ethers, K<sup>+</sup> > Na<sup>+</sup>.

d. The correlation between log  $K_{ext}$  and  $\Sigma\sigma$  is not perfect, i.e., electronic effects are not totally responsible for the observed variations of extraction efficiency.

The general inverse relationship between log  $K_{ext}$  and the cumulative electron-withdrawing property of the substituents is a direct result of the decrease in basicity of the oxygen crown system. It is well established that the formation constants for complexes formed from a series of ligands and a given metal depends upon the basicity of the ligand, and indeed there is often a linear free-energy relationship between the logarithm of the formation constant and the  $pK_a$  of the ligand.<sup>17,18</sup> Prior to any extraction of the alkali metal salts from water it is necessary for the ionophore to complex the metal cation replacing most, or all, of the waters of solvation. The less basic crowns, i.e., those with electron-withdrawing substituents, are less efficient at this process, and this is illustrated by the data displayed in Figure 1.<sup>19</sup>

The reason for the different response of the sodium and

**Table II.** M–O Distances in Planar 18-C-6 M<sup>+</sup> Complexes<sup>20,21,23</sup>

Complex	M–O, Å		
	Short	Medium	Long
DBC–Na(H <sub>2</sub> O) <sub>2</sub>	2.63	2.68	2.79
DBC–Na(H <sub>2</sub> O)Br	2.60	2.70	2.87
DBC–Na NCS	2.75	2.78	2.87
18-C-6 K	2.77	2.81	2.83

potassium salts to the substitution effect is less obvious than the overall effect itself. Of special significance was the result obtained by studying the extraction properties of DBC-(CO)<sub>3</sub>Cr. Such substitution has almost no effect upon the ability of the crown to extract the sodium salt, while having a significant effect upon the extraction of the potassium salt. This result suggests that the sodium cation, upon complexation by the crown, does not interact greatly with the two oxygen atoms most subject to the electronic effect of the electron-withdrawing tricarbonylchromium group, i.e., catechol oxygens. Thus, in comparison to the potassium ion, the smaller sodium ion is asymmetrically complexed by the crown, suggesting therefore a certain mobility with respect to the crown that is not observed for the snugly fitting potassium ion. Substitution on one ring of an electron-withdrawing group may be offset for the sodium by reinforcing its interaction with the remainder of the crown, while such a process is not available to the potassium ion. The fact that the slope  $\Sigma\sigma$  for sodium is approximately half that for potassium can be explained in light of the previous observation. If, as suggested, the smaller sodium ion is capable of asymmetric complexation by the crown and substituents on one of the rings are having a very small effect upon the complexation, then our method of compilation of  $\Sigma\sigma$ , which takes into account equally all the substituents on the aromatic rings, would be expected to produce a slope for sodium considerably less than that for potassium assuming that all the oxygen atoms interact equally with the potassium. Indeed, a ratio of slopes in the region of 2.0 is entirely expected. Such a view of the complexation of the alkali metals by the crown system is somewhat simplistic; however, it is not entirely without logic and experimental evidence to back it up. Apart from the data cited in this paper, there is published structural data concerning the ability of the sodium to locate asymmetrically within an 18-crown-6 environment. Truter and co-workers have published the structures of three dibenzo-18-crown-6 complexed sodium salts, which differ in the nature of the anion, i.e., Br<sup>-</sup> and NCS<sup>-</sup>.<sup>20,21</sup> While conclusions concerning solution structures drawn from solid structural data are not conclusive, the results of such x-ray analyses do provide precedents for the type of structural variations we are suggesting. In the case of the bromide salt, two crystal structures were obtained in which the sodium was complexed by the crown with either two water molecules, or a single water molecule and a bromide coordinated in the trans apical positions. Close examination of these structural data reveals that, when also coordinated by two equivalent water molecules, the sodium cation is in the plane of the oxygen crown, whereas in the mixed bromide/water salt and also in the isothiocyanate salt where there is only one apical interaction with the sodium, the cation is significantly displaced from the plane of the crown. For each complex the structure of the crown ether is essentially the same. The sodium–oxygen distances are particularly significant and are collected in Table II. In general, the average Na–O distances are significantly greater than those normally observed for Na–O interactions.<sup>22</sup> Secondly, it is apparent that all six Na–O interactions are not equivalent. For each of the three structures it may be seen that there are always two oxygen–sodium distances that are appreciably shorter than the

average and closer to the “normal” value and two distances that are significantly longer than the average. This difference in Na–O distance is enhanced in the sodium bromide salt complex where both a bromide and a water molecule are apically coordinated. As noted by Truter the bromide–sodium distance is very short, 2.82 Å, cf. crystalline NaBr distance of 2.98 Å. This strong interaction is not perpendicular to the plane of the oxygen crown and thus tends to add to the asymmetric placement of the cation in the crown. In the extraction process it is probable that the salt enters the organic phase as either a crown complexed tight ion pair or a crown separated ion pair. In the former case there will be a considerable interaction between the cation and the bulky anion, and this may also tend to add to any asymmetry of cation complexation.

There may also be waters of coordination extracted into the organic phase along with the salt, although we have no evidence for this from our studies. Overall, however, it becomes apparent that there is no reason to expect that the sodium atom will be symmetrically complexed by the crown ethers used in this study, both from intrinsic size considerations and from solvation and ion pairing considerations. The result of this is to effectively reduce the influence of substituents upon one of the aromatic rings.

The intrinsic asymmetry of complexation of the snugly fitting K<sup>+</sup> by the crown is very much less than for Na<sup>+</sup> as observed from the K<sup>+</sup> data in Table II.<sup>23</sup> The snug fit of the K<sup>+</sup> ion also helps reduce further pressures toward asymmetry due to solvation and ion pairing, resulting in a considerable equivalence of K<sup>+</sup>–O interactions. Hence, substituents on both aromatic rings will have a closely equivalent effect, resulting in the observed greater response for K<sup>+</sup> extraction, cf. Na<sup>+</sup> extraction.

The result of these differing substituent effects is to completely reverse the normal selectivity of the DBC ethers when very electron-withdrawing substituents are present on the aromatic rings. This may well be an observation that has significance in the transport of Na<sup>+</sup> and K<sup>+</sup> across cell membranes. It is postulated that the transport selectivity exhibited is related to a phosphorylated (PP) and dephosphorylated protein (P), i.e., PP selectively transports Na<sup>+</sup>, P selectively transports K<sup>+</sup>.<sup>24</sup> While conformational changes upon addition and removal of the phosphate group may well be the major factor involved, it is not possible in the light of the present work to rule out some electronic effects also, especially since the addition of the phosphate group to the protein should by virtue of the electron-withdrawing effect of the group, if it has any electronic effect at all, favor coordination selectivity toward Na<sup>+</sup>.

As mentioned earlier, there are many more variables affecting the complexation of the crown ethers with cations than the electronic effects we are attempting to ascertain. Solvation of the ion pair in both the organic and aqueous phase and the degree to which water remains complexed to the cation in the organic phase will be significant. Solvation of the crown ether itself will also be a factor. For example, it would be expected that the diamino DBC will be significantly more solvated by water molecules due to the polar amino group, and such solvation could effect its relative solubility in the aqueous phase and hence its extraction efficiency. Thus, substituents upon the crown will act in several ways not capable of direct measurement using the simple extraction techniques employed in the present study. Such extra interactions will not vary simply and regularly as the electronic substituent constants, and the deviations from perfection of the plot illustrated in Figure 1 may be understood in terms of these other variables.

**Note Added in Proof:** Subsequent to submission of this paper, Smid and co-workers have reported related substituent effects on the cation complexing ability of benzo-15-crown-5.<sup>25</sup> They find a similar relationship to that reported here for Na<sup>+</sup>

complexation, but a lack of correlation between electronic substituent effect on  $K^+$  complexation. No selectivity reversals were observed. The small size of the 15-crown-5 ring and possible 2:1 complexation to  $K^+$  can account for these differing results.

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## Electrochemistry and Radical Ions of 1,3,5-Tri-*tert*-butylpentalene

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**Abstract:** 1,3,5-Tri-*tert*-butylpentalene has been found to undergo a reversible one-electron oxidation at +0.75 V and a reversible one-electron reduction at -1.45 V vs. SCE. The radical ions were stable at -77 °C and their ESR spectra were obtained. The ESR spectra and redox potentials were found to correlate with simple HMO predictions, and a valence bond treatment indicated the utility of aromatic cyclopentadienyl anions and antiaromatic cyclopentadienyl cations in interpreting the results. A second oxidation or reduction was not observed.

Since pentalene is an  $8\pi$ -electron system which, unlike cyclooctatetraene (COT), should be planar, its electronic properties and reactivity are of interest. For this reason pentalene has been the focus of much synthetic and theoretical work. The parent ring system defied synthesis for many years until de Mayo<sup>2</sup> and Hafner<sup>3</sup> synthesized some unstable mono- and dialkyl derivatives. Finally, Hafner<sup>4</sup> synthesized 1,3,5-tri-*tert*-butylpentalene (**1**), which is stable. Most calculations have examined the chemical, physical, and electronic properties of pentalene and have compared pentalene with COT.<sup>5</sup> One would like to compare the theoretical predictions with experimental data, but so far this has only been done for the electronic spectra.<sup>3,4</sup>

One method for examining electronic structure is electrochemistry. Not only can redox potentials be obtained and correlated with MO calculations,<sup>6</sup> but the electron spin resonance spectra of the resulting radical ions allows for examination of the HOMO and LUMO. Since these orbitals are involved in chemical reactions, predictions concerning reactivity should be possible. The stability of **1** has enabled us to investigate the electrochemistry and radical ions of a pentalene.

## Results

**Determination of Redox Potentials.** The redox potentials for **1** were determined using several electrochemical techniques. All experiments were performed using acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate as supporting electrolyte, and potentials were referenced to a saturated calomel electrode. Dc polarography at a dropping mercury electrode gave a single wave with  $E_{1/2} = -1.46$  V. A plot of  $\log(i/i_d - i)$  vs.  $E - E_{1/2}$  had a slope of -0.059, indicating a reversible one-electron process.<sup>7</sup>

Cyclic voltammetry at a platinum disk gave a reduction couple and an oxidation couple. The oxidation wave was a reversible one-electron process under all conditions with a peak separation of 58 mV and an  $E_{1/2}$  of +0.75 V.<sup>8</sup> The reduction couple showed irreversible behavior which resulted from slow charge transfer at Pt and not product instability<sup>8</sup> (Figure 1).

Second harmonic ac voltammetry<sup>9</sup> confirmed these results. Oxidation at platinum at 45 Hz gave a reversible wave with  $E_{1/2} = +0.75$  V, a peak separation of 80 mV, and a current ratio of 1.1. The reduction at mercury at 45 Hz gave  $E_{1/2} =$