Figure 1. ESR spectrum of a 2×10^{-3} M solution in heptane: (a) of **2** at 20 °C; (b) of **1** at 20 °C; (c) of **2** at −60 °C.

of a hyperfine structure corresponding to a strong exchange case. Such evidence is given in the ESR spectrum of compounds **1** and **2**[17] (Chart II).

At 20 °C, a 2×10^{-3} M solution of **1** in heptane (Figure 1b) shows a four-line spectrum at $g_M = 2.126$, $a_{Cu} = 65$ G. At 20 °C, a 2.10^{-3} M solution of **2** in heptane (Figure 1a) shows at $g = 2.047$ four peaks assigned to the interaction of the electron spin with one copper nucleus. The weighted average $(g_{Cu} + 2g_L)/3 = 2.046$ is close to the experimental value. Similarly, the 22-G splitting is close to $a_{Cu}/3 = 21.66$ G. At −60 °C (Figure 1c), one of the four lines resolves to show four extra lines separated by 5 G. They may be ascribed to four of the five lines expected for two equivalent nitrogen atoms separated by $a_N/3 = 5$ G. The spectrum (Figure 1a) shows one additional three-peak signal at higher field ($g = 2.0065$) with a splitting of 15 G, the intensity of which increases with time. Such a signal is typical of an isolated nitroxide and can be attributed to either a reversible decomplexation or an irreversible decomposition possibly by electron transfer. The fact that a red powder deposits in the ESR tube upon standing seems to support the latter possibility, but does not exclude a reversible reaction. Such complex may be useful in the study of both phenomena.

To our knowledge, complex **2** is thus the first example of a three-electron, three-nucleus system for which the strong exchange case has been characterized by both the *g*-factor value and the hyperfine structure.[21]

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(16) I.e. in the isolated ligand.
(17) Microanalysis are in agreement with the structures. $F = 250°$ (1) and $F = 224°$ (2). They are prepared by standard method from the corresponding keto ester and copper acetate. Magnetic susceptibility of **2** has been reported.[18] Although keto esters are not so good chelating agents as β-diketones, this new ligand type permits the easy introduction of various groups. The *tert*-butyl substituent[19,20] provides steric protection and solubility in organic solvents. Complexes **1** and **2** are indeed soluble in all organic solvents that we have examined.
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Experimental Observation of the Effect of an Oriented Positive Monopole on Carbon-13 Chemical Shifts of a Naphthalene Derivative. Crown Ether Conformational Changes and Their Effect on an Attached Naphthalene System

Sir:

The variation of ^{13}C chemical shifts of 2,3-naphtho-20-crown-6 (**1**) were noted as increasing mole ratios of alkali
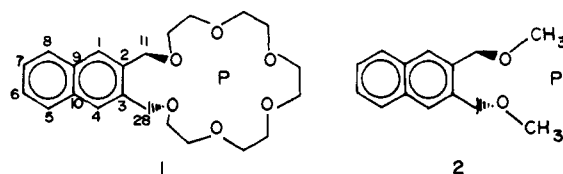
metal, calcium, and barium salts were added. The data indicate that the naphthalene carbon chemical shifts are generally independent of crown ring conformation changes, independent of the polarizability of the perturbing cation, generally independent of the anion present, but dependent on cation charge, and correlated roughly with cation-induced charge density changes as calculated semiempirically. These results relate to theoretical treatments[1] of monopole effects on ^{13}C NMR chemical shifts, to conformational changes required as crown ethers complex cations, and also to the effects of salts on fluorescence, phosphorescence, and radiationless decay of crown **1** as reported recently.[2]

Experimental determinations of the effects of a noncovalently bound monopole on ^{13}C chemical shifts (or any other property for that matter) are rare.[3] Figure 1 shows the ^{13}C chemical shifts of uncomplexed 2,3-naphtho-20-crown-6 (**1**) in methanol-d_4 and the effect of 1:1 complexation[4] of Na⁺, K⁺, Rb⁺, Cs⁺, Ca²⁺, and Ba²⁺ salts on those shifts. Assignments for the naphthalene carbons are based on ytterbium shift stu-
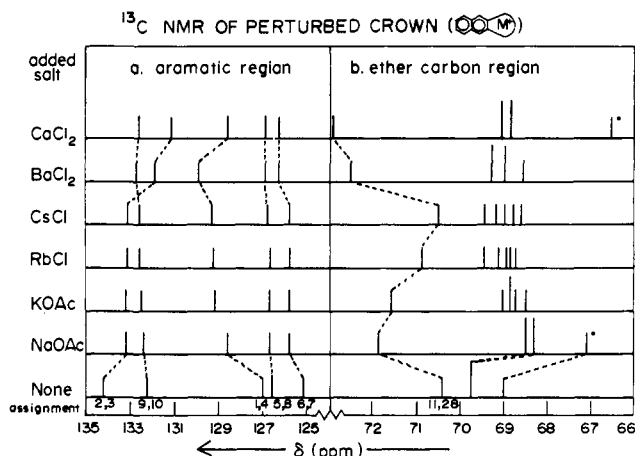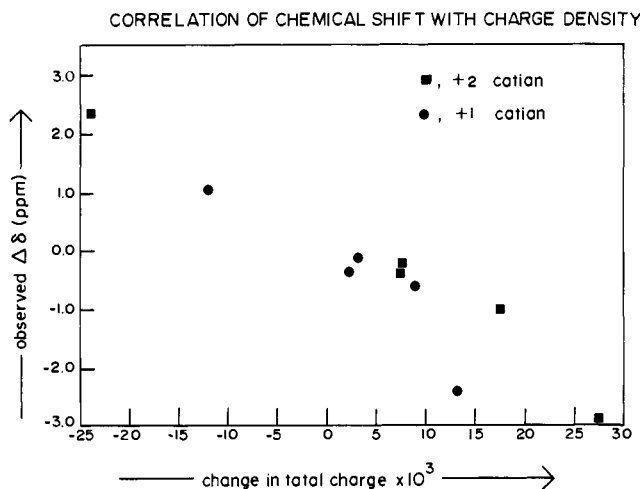
Figure 1. [13]C chemical shifts (relative to internal methanol-d_4 at 47.0 ppm) of 2,3-naphtho-20-crown-6 (1) and its 1:1 complexes with Na^{+}, K^{+}, Rb^{+}, Cs^{+}, Ca^{2+}, and Ba^{2+} salts (>2-fold excesses of salt were used).[4] Crown concentrations in methanol-d_4 are ~0.1 M. Part a includes the aromatic carbon signals and part b the methylene carbon signals. The two signals with asterisks in part b are due to the same carbon.

Figure 2. [13]C chemical shift changes ($\Delta\delta$) of the naphthalene carbons of 1 caused by 1:1 complexation of Cs^{+} (●) and Ba^{2+} (■) vs. the calculated (INDO)[9,10] charge changes of the same carbons in 2 when a +1 (●) and +2 (■) monopole are placed at position P. The slope is 99 ppm/electron, and the linear correlation coefficient (r) = −0.943.

dies,[5a,b] [1]H–[13]C coupling, and Stothers' assignments[6] for 2,3-dimethylnaphthalene. The C-11,28 signal was assigned on the basis of deuterium exchange experiments.[5c] The shifts were unaffected by anion changes involving Cl^{−}, CH$_3$CO$_2$[−], and F^{−}, but higher concentrations (>0.3 M) of NaI, NaBr, NaClO$_4$, KI, CsBr, BaBr$_2$, and CaCl$_2$ cause small upfield shifts in all the naphthalene and crown ether carbons. A bulk solvent effect or an interaction of the naphthalene π system with these anions may be responsible.[7]

An important feature of the results is the general coincidence of the chemical shift approached by a given equivalent set of aromatic carbons (e.g., 2,3 or 6,7) as complexation with any alkali metal cation becomes complete (the effect of Na^{+} on the 1,4 carbons is more complex). This convergence is observed despite the variation of ionic radius from 0.95 Å for Na^{+} to 1.69 Å for Cs^{+}, and the variation in relative polarizability[8] (in cm[3] × 10^{−24}) from 0.25 for Na^{+} to 2.40 for Cs^{+}. These data suggest that the naphthalene carbon chemical shifts are influenced largely by the field effect of the positive monopole held in the crown ether ring. A superimposed effect on the 1,4 carbons by na[+] complexation is also indicated. The observation that Ba^{2+} complexation causes shifts in the same direction but of greater magnitude than that seen for alkali metals also supports the suggestion that a field effect is operative. The shifts with complexed Ca^{2+} are evidently influenced by conformational changes (see below).

Semiempirical calculations (INDO)[9] of 2 with perturber (P as shown in 2) absent were compared with those with P resembling +1 and +2 monopoles.[10] The charged species were placed 6.97 Å from the center of the 9,10 bond on the C_2 axis, and all atomic coordinates for 2 were taken from an x-ray structure determination of the potassium complex of 1.[11] Figure 2 shows the change in total (only the valence shell is considered) charge calculated for each naphthalene carbon plotted vs. the experimental change in chemical shift caused by complete complexation. The correlation (r = 0.94) is not too bad considering that experimental (Cs^{+} and Ba^{2+}) and calculated results for both +1 and +2 ions are shown. Despite the reluctance of the 1,4 carbons to fall in line, this agreement,[12] whatever its underlying cause,[1a] suggests again that the field effect is dominant. The slope of 99 ppm/electron is a little low compared with those calculated for benzene ring systems.[13]

Few studies of conformational changes caused by complexation of crown ethers in solution have been reported.[3,14] The use of proton–proton coupling constants of the ethylene

units to determine dihedral angles before and after complexation by the crown[3a] cannot be readily applied to 1 and many other crown ethers because of the coincidence of the proton chemical shifts. Consideration of ^{13}C chemical shifts of the crown methylene carbons (shown in Figure 1b) suggests some general conclusions[15] about conformational adjustments required of the crown ring as different cations are complexed. It is assumed that conformational changes are major contributors to the observed crown shifts.

The overall pattern of methylene chemical shifts in Figure 1b suggests that Cs^{+} complexation requires less extensive conformational changes than those required for smaller cations. As cation size is decreased from that of Cs^{+} to Rb^{+} to K^{+} the overall pattern remains similar, except for the increasing downfield shift of carbons 11 and 28 (the 70.42-ppm signal of uncomplexed 1).[16] This behavior suggests that conformational changes in the C-11,28 region of 1 allow crown accommodation to cation size. A conrotatory twisting about the C-2,11 and C-3,28 bonds would, for example, reduce the crown girth. The overall pattern changes abruptly with Na^{+} complexation, presumably owing to a major alteration of crown conformation. In this case a folding of the crown ring can be envisioned. The notion that the size of the complexed cation governs crown conformation and thus chemical shifts would suggest that the effects of Ba^{2+} (ionic radius (i.r.) = 1.35 Å) and K^{+} (i.r. = 1.33 Å) be similar and that effects of Ca^{2+} (i.r. = 0.99 Å) and Na^{+} (i.r. = 0.95) also be related. The patterns in Figure 1b show this to be true. A comparison of Figures 1a and 1b indicates that the mechanism for perturbation of the naphthalene moiety is largely independent of crown ring conformation[17] except when small cations (Na^{+}, Ca^{2+}) are complexed.[18]

The electron density changes and conformational adjustments discussed above correlate simply with two changes in excited-state properties of 1 which are observed upon complexation of the same salts in alcohol glass at 77 K.[2] One is a uniform increase of 100 cm^{−1} in the S_1–S_0 energy separation in 1 caused by Na^{+}, K^{+}, Rb^{+}, and Cs^{+} complexation. This change may be due to the presence of a +1 charge. The other is a change in the relative intensities of the 0,0 band and the 512-cm[−1] band[19] (the 510-cm[−1] band is presumably included) in the phosphorescence spectrum ("naphthalene-like" spectra are seen).[2] The relative intensities of these two bands change in a manner which correlates with the shifting of the C-11,28 ^{13}C NMR signals shown in Figure 1b. Complexation of Cs^{+} by 1 gives the most crown-like spectrum with the 0,0 and

512-cm^{-1} bands of about equal intensity (unperturbed **1** has a broad, flat emission presumably involving both the 0,0 and 512-cm^{-1} bands). However, complexation of Na$^+$ causes the 0,0 emission to be about twice the intensity of the 512-cm^{-1} peak, and the K$^+$ and Rb$^+$ effects on **1** fall smoothly between the Cs$^+$ and Na$^+$ extremes. Conformational changes in the C-11,28 region discussed above could affect the 512-cm^{-1} (and/or the superimposed 510-cm^{-1}) normal coordinate motions[20] and thus cause the changes in phosphorescence structure (the same general changes occur in the lower energy emission peaks built on the 1379-cm^{-1} mode).

Surprisingly, the complexation induced changes in rate constants for excited-state processes[2] are not correlated with crown ether conformational changes. This is so despite the dependence of the rate for radiationless decay of the triplet (k_{dl}) and S$_1$-T$_1$ intersystem crossing (k_{isc}) on vibrational overlap[21] and the dependence of the fluorescence rate constants (k_f) of naphthalene derivatives on vibronic coupling.[22] These observations are important in judging the usefulness of crown ether models like **1** for the study of excited-state perturbation by oriented cations. In the case of crown **1** it seems likely that conformationally independent cation–chromophore interactions are responsible for changes in k_f and other rate constants observed upon complexation. Thus those rate constant changes may give direct indications of the intrinsic properties of excited states and perturbers.

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(16) This assignment is also based on the similarity of the chemical shift of the 11 (and 28) carbon in **1** and the corresponding carbons in the bis(methoxymethyl) ether **2** (see note 5c).
(17) The field effect of a monopole centered in the crown ring (stretched or contracted as required) meets this criterion.
(18) Crown folding may be the cause of the difference in the naphthalene 1,4-carbon shift observed when **1** complexes Na$^+$, though it is not clear what set of conformational changes affecting carbons 1 and 4 would leave the shifts for carbons 2 and 3 "normal". With Ca^{2+} complexation the C-1,4 upfield shift is large enough to counteract the charge-related downfield shift shown by Ba^{2+}. The 2,3 shift may also be influenced toward higher field by Ca^{2+}-induced conformational shifts and/or a change in average Ca^{2+} position. See E. L. Eliel et al., *J. Am. Chem. Soc.*, **97**, 322 (1975).
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A Versatile and Expedient Synthesis of α,β-Unsaturated Ketones. Utilization of the β-Epoxy Sulfone Functional Group as the Enone Progenitor

Sir:

In connection with our synthetic program we required expedient methodology for the preparation of a variety of α,β-disubstituted cycloalkenones **1**. We specifically desired a strategy which would afford products formally derived from the doubly charge-inverted ynone synthon **2**[1,2] such that R^1 and R^2 could be introduced sequentially as an organolithium reagent and an alkylating agent, respectively.
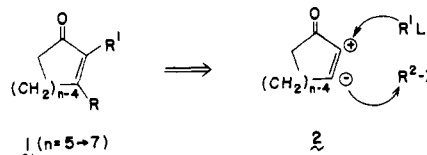
Since β-keto sulfones have recently been shown to be excellent enone precursors (**3** → **1**),[3] and, also, since oxidation of an alcohol to a ketone (**4** → **3**) should pose no severe limitations, we selected dianion **5** as the target molecule for our synthetic efforts. C-Alkylation of **5** would be conceptually expected to produce β-hydroxy sulfone **4** after protonation. Dianion **5** is the formal result of a Michael-type reaction of an organolithium reagent with γ-oxido α,β-unsaturated sulfone **6**, a species which should in turn be produced by base-catalyzed β-elimination of β-epoxy sulfone **7**. The entire five-reaction sequence (**7** → **1**) should furthermore be achievable in a "one-" or "two-pot" chemical operation without any purification of intermediates!

We are exceptionally pleased to report that this is indeed the case. Reaction of β-epoxy sulfone **7a**[4,5] (THF, 0.25 M, −78 °C) with 1 equiv of phenyllithium produces γ-oxido α,β-un-