

Unequivocal Evidence for Side-Arm Participation in Crystalline Lariat Ether Complexes

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Considerable study has been made during recent years of syntheses¹ and structures² of lariat ethers so-called because of resemblance of their molecular models to a lasso and their ability to "rope and tie" cations.³ Systematic study of these compounds has provided a conclusive demonstration for intramolecular side arm involvement when NH₄⁺ is complexed in MeOH solution⁴ and strong support for such involvement in Na⁺ binding.⁵ Measurements of ¹³C NMR relaxation times and ²³Na line widths suggest that the side arm contributes significantly to the binding of Na⁺ in the nitrogen-pivot compounds and that these are more dynamic complexing agents than are the corresponding C-pivot compounds.⁶ To date, however, there has been no unequivocal evidence on how the neutral donor groups participate. Results reported here of single-crystal X-ray analyses⁷ of two alkali-metal-nitrogen-pivot lariat ether complexes show that the side arms are intramolecularly involved with the ring-bound cation and what the structural requirements are for such complexation in the solid state.

The structure (*R* = 0.020 for the correct enantiomorph) of the K⁺I⁻ complex of *N*-(2-methoxyethyl)monoaza-18-crown-6 (K⁺⊂5-1-I) is shown in Figure 1 along with a skeletal drawing of donor atoms and metal ion. The skeletal drawing reveals the arrangement of donor atoms about the metal ion. The macroring donor atoms are disposed in a chair conformation with K⁺ distinctly above the plane of four (1,4,10,13) ring oxygen atoms. This chair conformation is typical of 18-crown-6-type complexes with K⁺ and results from the macroring's assuming the D_{3d} conformation.^{8,9} The side-arm oxygen is located underneath the plane in an apical position in the coordination sphere. Iodide occupies the opposite apical position. Binding by the side arm can be pictured as occupying one face of the cavity formed by the macroring donor atoms. The side arm is not cradling the metal ion between it and the macroring but rather is pushing the cation out so that the cation is not immersed so deeply in the ring.

The structure (*R* = 0.028 for the correct enantiomorph) of the *N,N'*-bis(2-hydroxyethyl)diaza-18-crown-6-Na⁺ complex [(Na⁺⊂H1-22-1H)] is depicted in Figure 2 along with a skeletal

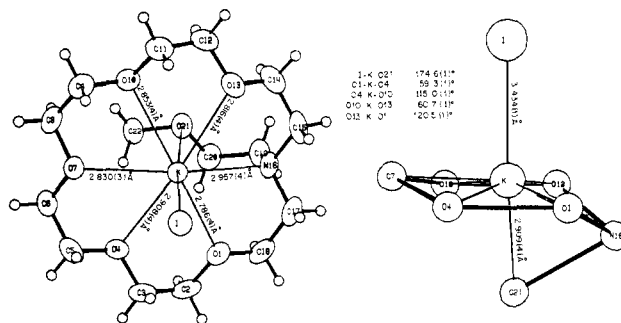


Figure 1. ORTEP drawing of *N*-(2-methoxyethyl)monoaza-18-crown-6-K⁺ complex (left), skeletal drawing of coordination sphere about K⁺ (right).

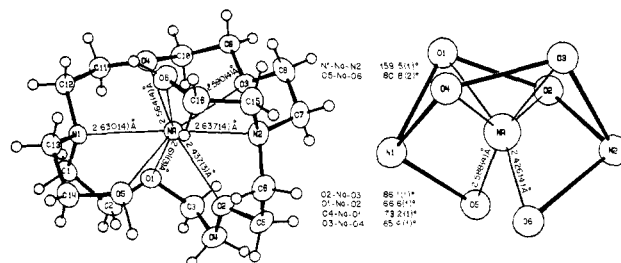


Figure 2. ORTEP drawing of *N,N'*-bis(2-hydroxyethyl)diaza-18-crown-6-Na⁺ complex (left), skeletal drawing of coordination sphere about Na⁺ (right).

Table 1. Comparison of Sodium Complexes of Cryptates and Lariat

	(Na ⁺ ⊂222)	(Na ⁺ ⊂H1-22-1H)	(Na ⁺ ⊂221)
N-Na-N	180° ^a	159.5°	138.1° ^b
<i>R</i> ^b	1.21 Å ^{a,b}	1.14 Å	1.10 Å ^b
N...N	5.504 Å ^a	5.183 Å	4.944 Å ^b
log <i>K</i> _s (MeOH)	>8.00 ^c	4.87 ^d	>8.00 ^c
(MeOH/water, 95/5)	7.21 ^c	4.59 ^d	8.84 ^c

^a Reference 10. ^b Reference 11. ^c Reference 13. ^d Reference 14.

drawing of donor atoms and the metal ion. The arrangement of the macroring donor atoms in a twist-boat structure is seen in the skeletal drawing. The oxygen atom in each sidearm occupies a "flagpole" position. The structure of (Na⁺⊂H1-22-1H) is intermediate between those found for cryptate complexes (Na⁺⊂222)¹⁰ and (Na⁺⊂221).¹¹ A comparison of these three complexes is made in Table I. In (Na⁺⊂H1-22-1H) and (Na⁺⊂222), Na⁺ is octacoordinated while in (Na⁺⊂221), it is heptacoordinated. In the lariat complex, Na⁺ is displaced 0.48 Å toward the macroring from the N...N internuclear line. This phenomenon is observed in (Na⁺⊂221) where Na⁺ is displaced 0.95 Å toward the largest ring. The cavity size of the lariat is intermediate between the two cryptands as seen by two measures: *R*, mean cavity radius, and N...N distance. Given the effective ionic radii¹² for Na⁺(VII) and Na⁺(VIII) of 1.13 and 1.16 Å, respectively the larger binding constant¹³ (log *K*_s) for (Na⁺⊂221) compared to (Na⁺⊂222) has been rationalized¹¹ by the better fit of Na⁺ in (221)'s cavity. The lariat's cavity is more flexible than a cryptand's and can, at least to some extent, adjust to an optimum size for each cation. The poorer binding¹⁴ by the lariat arises, at least in part, from entropic factors since the two donor groups are not physically linked as they are in the cryptands.

In conclusion, the structures demonstrate side arm involvement in the solid state. Although a side arm is cooperating fully in cation

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(7) (K⁺⊂5-1), K₂C₁₅H₂₇N₂O₆, orthorhombic P2₁2₁2₁, *a* = 10.733 (1) Å, *b* = 12.806 (2) Å, *c* = 15.762 (3) Å, *Z* = 4, *R* = 0.020 for 1530 data. (Na⁺⊂H1-22-1H), Na₂C₁₆H₃₄N₂O₆, monoclinic P2₁, *a* = 8.027 (5) Å, *b* = 15.618 (4) Å, *c* = 9.228 (4) Å, β = 107.61 (4)°, *Z* = 2, *R* = 0.028 for 1820 data.

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binding, the remarkable result is that it does not pull the metal ion toward it. Rather, it fills an apical void in the cation's coordination sphere when this space is not filled by macrocyclic donors. The ease of synthesis and the flexibility of the lariats in cation binding promise many applications for these compounds as dynamic complexing agents.

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Registry No. *N*-(2-Methoxyethyl)monoaza-18-crown-6·K⁺, 87226-37-7; *N,N'*-bis(2-hydroxyethyl)-4,13-diaza-18-crown-6·Na⁺·I⁻, 87249-10-3.

Supplementary Material Available: Listings of atomic coordinates and details of X-ray analyses are available (3 pages). Ordering information is given on current masthead page.

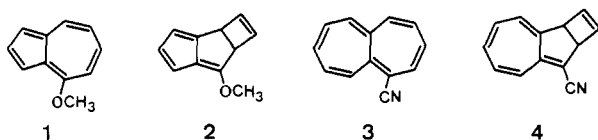
6-Cyanotricyclo[5.5.0.0^{2,5}]dodeca-3,6,8,10,12-pentaene (Cyano-Dewar Heptalene). Synthesis and Isomerizations in Ground and Excited States

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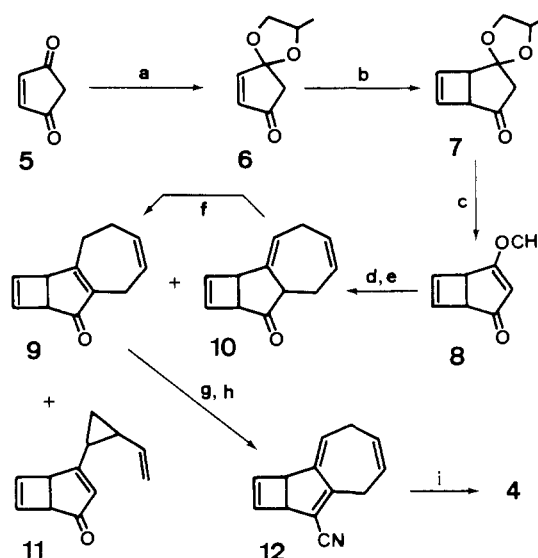
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Stimulated by their intriguing physical and chemical properties,¹ there has been intense recent interest in the valence isomers of alternant aromatic hydrocarbons.² However, very little is known about valence isomers of nonalternant hydrocarbons.³ We have been interested for some time in molecules that are isomers of the nonalternant aromatic hydrocarbon azulene.⁴ In a recent communication, we disclosed the synthesis and properties of 6-methoxytricyclo[5.3.0.0^{2,5}]deca-3,6,8,10-tetraene (**2**), which corresponds to a Dewar type isomer of 4-methoxyazulene (**1**).⁵



We now report, for the first time, the synthesis and isomerizations of a Dewar type isomer of 1-cyanoheptalene (**3**), 6-cyanotricyclo[5.5.0.0^{2,5}]dodeca-3,6,8,10,12-pentaene (**4**). This study will provide not only a new route to the difficultly accessible substituted heptalenes⁶ but also a clear contrast between the roles

Scheme I



^a Propylene oxide, 0.5 equiv of BF₃ etherate, CCl₄, 0 °C, 1 h.
^b HC≡CH, CH₃COCH₃, 100-W high-pressure Hg lamp, -70 °C.
^c HCl/CH₃OH, room temperature, 2.5 h. ^d *cis*- and *trans*-1-lithio-2-vinylcyclopropane, ether/THF, -78 °C, 2.5 h. ^e 1 N HCl, room temperature, 0.5 h. ^f Al₂O₃/benzene. ^g TMSCN, ZnI₂, room temperature. ^h POCl₃/pyridine, 60-70 °C, 2-3 h. ⁱ DDQ/benzene, 60-70 °C, 2 h.

of pentafulvene and heptafulvene chromophores⁷ in the isomerization reactions of **2** and **4**, respectively.

Our approach to the Dewar heptalene skeleton **4** is outlined in Scheme I. Monoacetalization of cyclopent-2-ene-1,4-dione (**5**)⁸ with propylene oxide⁹ furnished enone **6**, which was converted to the key precursor 2-methoxybicyclo[3.2.0]hept-2,6-dien-4-one (**8**)¹⁰ in 30% yield through **7**¹⁰ by photocycloaddition with acetylene, followed by treatment with methanol saturated with hydrogen chloride. Reaction of **8** with a mixture of *cis*- and *trans*-1-lithio-2-vinylcyclopropane¹¹ and subsequent treatment with hydrochloric acid gave, after column chromatography on silica gel eluted with benzene and hexane (1:1), seven-membered annelated ketones **9** (41%)¹⁰ and **10** (22%)¹⁰ and an uncyclized *trans*-cyclopropyl derivative **11** (32%).¹⁰ The β,γ-unsaturated ketone **10** smoothly gave the desired α,β-unsaturated ketone **9** in 90% yield upon rapid filtration through a short plug of alumina (deactivated with 3% of water, benzene). Treatment of **9** with trimethylsilyl cyanide and zinc iodide¹² followed by phosphoryl chloride in pyridine¹³ furnished the unsaturated nitrile **12**¹⁰ in 15.2% yield. Final conversion of **12** into **4**, purified by column

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