Abstract: Scales of carbenium ion stabilities have been obtained from \( ^1H \) NMR equilibrium studies of mixtures of partly ionized para-substituted diarylmethyl chlorides in CD\( _2 \)Cl\( _2/ \)BCl\( _3 \) at \(-70 \) °C and via calorimetric determination of the heats of ionization (\( \Delta H_f \)) of the alkyl chlorides (Ar\( _2 \)CH\( + \) + BCl\( _3 \) \( \rightarrow \) ArCH\( + \) + BCl\( _4 \) \( \rightarrow \)) in CH\( _2 \)Cl\( _2/ \)BCl\( _3 \) at \(-70 \) °C. The heats of the reactions of diaryl methyl tetrachloroborates with 2-methyl-1-pentene (ArCH\( + \) + BCl\( _4 \) \( \rightarrow \) ArCH\( + \) + BCl\( _4 \) \( + \) CH\( _2 \)CH\( = \)CH\( _2 \) + Cl\( \rightarrow \) ArCH\( + \) + BCl\( _4 \) + CH\( _3 \)CH\( = \)CH\( _2 \)) were determined by low-temperature calorimetry, increase from \(-53.1 \) kJ/mol for (H\( _2 \)C\( = \)CH\( _2 \)H\( _2 \))CH\( + \) + BCl\( _4 \) to \(-33.0 \) kJ/mol for the better stabilized (H\( _3 \)CO\( _2 \)CH\( _2 \))H\( _2 \)CH\( + \) + BCl\( _4 \). In contrast, the heats (\( \Delta H_f \)) of the Lewis acid catalyzed additions of the corresponding para-substituted diarylmethyl chlorides to 2-methyl-1-pentene are independent of the para substituents (\( \Delta H_f = \) \(-86.5 \) ± \( 2.7 \) kJ/mol). Similar values of (\( \Delta H_f \)) were obtained for the addition of p-anisylphenylmethyl chloride to trimethylsilylene, styrene, \( \beta \)-methylstyrene, and isoprene. \( \Delta H_f \) is predominantly determined by the conversion of a \( \sigma \) (C\( = \)C) into a \( \sigma \) (C\( = \)C) bond, and the heats of addition of diarylmethyl tetrachloroborates to alkenes in CH\( _2 \)Cl\( _2 \) are given by the equation (\( \Delta H_f = (9.5 \) ± 6.3) \( \times \) K\( _{a} \) kJ/mol).

Most synthetic reactions that yield carbon-carbon bonds proceed via polar mechanisms. Charged and neutral species may be used as synthetic equivalents of \( \alpha \)- and \( \delta \)-synthons. \(^2\) One conceivable extreme, the reaction of carbenium ions with carbanions, has recently been investigated in detail. \(^1\) In that system, the heats of reaction only depend on the stabilization energies of both ions (\( \Delta K_a \) and \( \Delta K_{a} \)), since the neutral products are characterized by approximately constant \( \sigma \) (C\( = \)C) bond increments. The addition

Table VII. Surface Tension, \( \gamma \) (dyn/cm), of Leucine Solutions at 20 °C as a Function of Concentration and Co-solute

<table>
<thead>
<tr>
<th>concn, mol/L</th>
<th>aqueous solution</th>
<th>saturated glycine solution (22.8 g/100 mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>72.8</td>
<td>75.7</td>
</tr>
<tr>
<td>0.05</td>
<td>72.1</td>
<td>72.1</td>
</tr>
<tr>
<td>0.075</td>
<td>71.3</td>
<td>70.0</td>
</tr>
<tr>
<td>0.1</td>
<td>70.0</td>
<td>69.2</td>
</tr>
</tbody>
</table>

least 100/batch in the presence of hydrophobic additives, while with hydrophilic ones all the crystals appeared at the bottom of the crystallizer.

Analytical Methods for Quantitative Evaluation of Crystal Orientations. Complete orientation of the glycine crystals was established by the following four independent methods:

a. Crystal Coloring. Crystal coloring experiments were carried out in the presence of very small amounts (0.01% w/w, which does not have any kinetic effect) of the resolved yellow dye N\( ^{+} \)4,2-dinitrophenyl-(S)-lysine, which is enantioselectively occluded into the (010) oriented glycine crystals, thus imparting to them a yellow color. These crystals are easily differentiatated visually from the non-colored (010) oriented counterpart.

b. Enantiomeric HPLC Measurements. Samples (20 mL) were injected onto a reverse-phase column (25 cm \times \) 4.6 mm) self-packed with 5 \( \mu \)m Nucleosil C18 (Machery Nagel), with a mobile phase composition of an aqueous solution of cupric acetate (4 \times \) 10\(^{-3} \) M) and \( N,N \)-di-n-propyl-(S)-alanine (8 \times \) 10\(^{-3} \) M) at pH 5.3-5.5. \(^1\) The samples were prepared by dissolving the whole batch of floating crystals, after thorough washing in water, into the appropriate amounts of mobile phase.

c. Morphology of the Crystals. The (010) and (010) oriented glycine crystals assume an enantiomorphous morphology in two-dimensional projection at the interface and are therefore visually differentiable. This differentiation was confirmed by all four methods described above.

d. Crystallographic Measurements. The direction of the crystallographic axes and the Miller indexes of the basal (010) faces were assigned by X-ray diffraction measurements on a Siemens diffractometer after the presence of high concentrations of leucine (>1.5%) of low enantiomeric excess of the additive used, the appropriate concentration was determined which yields complete orientation of the glycine crystals. In the presence of high concentrations of leucine (>1.5%) of low enantiomeric excess, the floating crystals of glycine are very thin plates. Their orientation was therefore confirmed by all four methods described above.

Surface Tension Measurements. These were performed on a semiautomatic Fisher surface tensiometer by the du Nouy method with use of a platinum iridium ring, for saturated solutions of glycine containing up to 0.1 mol/L of additive.

Acknowledgement. We thank Prof. Z. Berkovich-Yellin for discussions, E. Gati Shavit for her skilful help, the Israel Academy of Science and Humanities, the U.S.-Israel Binational Foundation, Jerusalem, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support. L.A. is a recipient of the Charles S. Revson Career Development Chair.
of carbenium ions to alkenes is a related reaction type. The Lübeck group has recently developed methods to generate 1:1 addition products via Lewis acid catalyzed reactions of alkyl halides with alkenes, and the kinetics of the model reaction 1 have been determined. In previous work, it has been shown that the heats of ionization of tertiary cumyl alcohols in SbF₅, FSO₃H/SO₂ClF at −55 °C are linearly correlated with δ values. Figure 1 shows that the free energies of ionization of diarylmethyl chlorides also give a fair correlation with ∑δ°. The ¹H NMR shifts of the methine protons in the diarylcarbenium ions are correlated by δ values. The correlation equation (r = 0.980) is ∆G°f = 5 + 26δ° (kJ/mol).

Table II. Comparison of Various Stability Scales of Para-Substituted Diarylcarbenium Ions 1°-XY (kJ/mol)

<table>
<thead>
<tr>
<th>X,Y</th>
<th>∆G°f</th>
<th>∆H°</th>
<th>∆S°</th>
<th>δ</th>
<th>pK+°</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCH₃,CH₃</td>
<td>0.0</td>
<td>-5.71</td>
<td>-7.9</td>
<td>-0.2</td>
<td>57.8</td>
</tr>
<tr>
<td>OCH₃,OPh</td>
<td>1.3</td>
<td>-3.4</td>
<td>-5.1</td>
<td>0.0</td>
<td>61.1</td>
</tr>
<tr>
<td>OCH₃,Cl</td>
<td>2.1</td>
<td>-1.3</td>
<td>-2.5</td>
<td>0.1</td>
<td>63.0</td>
</tr>
</tbody>
</table>

In this paper we present a thermochemical study of the ionization of diarylmethyl chlorides (1-X,Y) and their addition reaction with alkenes.

1. Ionization of Diarylmethyl Chlorides. Equilibrium Studies—Free Energies of Ionization. Since the data on diarylcarbenium ion stabilities that are available refer to different media, we obtained a more comprehensive set of data by NMR spectroscopic studies of equilibria involving diarylmethyl tetrachloroborates in CH₂Cl₂ at −70 °C.

Table III. Heats of Ionization (ΔH°) of Para-Substituted Diarylmethyl Chlorides 1-X,Y in CH₂Cl₂/BCl₃ at −70 °C (kJ/mol).

<table>
<thead>
<tr>
<th>X,Y</th>
<th>∆H°</th>
<th>∆H°/kcal/mol</th>
<th>∆S°/cal/mol°C</th>
<th>∆S°/kcal/mol°C</th>
<th>R°<em>{+} + R°</em>{-}Cl</th>
<th>R°<em>{+} + R°</em>{-}Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCH₃,CH₃</td>
<td>-18.3 ± 3.1</td>
<td>14.4 ± 1.0</td>
<td>-32.6 ± 2.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
| OCH₃,OPh | -27.9 ± 2.1 | 17.4 ± 2.0 | -45.4 ± 2.9 | -12.8 | -9.6 | 0.6 J/mol for 1-O-Me, 1°-Me, and ∆S° = 0.6 J/mol for 1-O-Me, 1°-Me. These numbers

In previous work, it has been shown that the heats of ionization of tertiary cumyl alcohols in SbF₅, FSO₃H/SO₂ClF at −55 °C are linearly correlated with δ° values. Figure 1 shows that the free energies of ionization of diarylmethyl chlorides also give a fair correlation with ∑δ°. The ¹H NMR shifts of the methine protons in the diarylcarbenium ions are correlated by δ = 8.79 + 0.027ΔG°f to the relative carbenium ion stabilities of Table II.

In this paper we present a thermochemical study of the ionization of diarylmethyl chlorides (1-X,Y) and their addition reaction with alkenes.

1. Ionization of Diarylmethyl Chlorides. Equilibrium Studies—Free Energies of Ionization. Since the data on diarylcarbenium ion stabilities that are available refer to different media, we obtained a more comprehensive set of data by

show that the TΔS term is smaller than the error limits of ΔΔG° at -70 °C. The data of Table I, therefore, represent differences in enthalpy, which can independently be determined by calorimetry.

Calorimetric Studies—Enthalpies of Ionization. The diarylmethyl chlorides listed in Table I are completely ionized in the presence of 1:1 (OMe,OMe)-200 (1:Me,Me) equiv of BCl3 in CH2Cl2 at -70 °C, and we determined the heats of reaction (ΔHr) by breaking amphoteric diarylmethyl chlorides 1-X,Y in the Lewis acid solution. According to Scheme I, heats of ionization (ΔHi) can be obtained by correcting ΔHr for the integral heats of solution (ΔHs) of the pure diarylmethyl chlorides in CH2Cl2 (Table III). ΔHs was not dependent on the total ion concentration within the range of our study (10⁻⁵ - 10⁻³ M), where ion pairing predominates. ¹⁻³

The comparison of ΔΔG° (equilibrium) and ΔHi (calorimetry) in Table III shows that both scales are parallel within the limits of experimental error (ΔΔG° ±0.4 kJ/mol; ΔHi ±2.5 kJ/mol; average values). We conclude again that the differential entropies of ionization for two different diarylmethyl chlorides [ΔΔS = ΔS(RCl) - ΔS(RCl)] are close to zero. This relation has earlier been derived from pκA/ΔHi correlations ²⁵ and from correlations of solvolysis rates versus ionization enthalpies.¹²

While ΔΔS = 0, the absolute magnitude of ΔS1 must be quite substantial, since 1-Me,Me ionizes only partially in BCl3/CH2Cl2 at -70 °C though the ionization can be estimated to be exothermic by approximately -25 kJ/mol from pκA (Table II). For the ionization of 1-Me,Me under these conditions, ΔH1 was derived to be -70 kJ/mol;²⁶ with ΔHs = -32.6 kJ/mol we obtain ΔS1 = -126 J/K/mol. Reported values for ΔS1 range from -50 to -150 J/K/mol.¹²

Comparison of Different Carbene Ion Stability Scales. Scales of carbene ion stabilities have proven to be mutually convertible.²⁸,²⁹ Heats of ionization of carbene ion precursors in different Lewis acid media differ by a heat of transfer term (ΔHi). ΔHi is mainly determined by carbon–leaving group bonding, Lewis acid–solvent bonding, and general dielectric solvation. ΔHi is constant for different cations, if they are solvated likewise within each medium. This is usually true for large, delocalized cations in nonpolarizable media.²⁸,²⁹,¹⁴ Comparison of ΔHi for 1-Me,Me in CH2Cl2/BCl3 at -70 °C with the heat of ionization of the corresponding alcohol in SF5, HSOF3, SO2ClIF at -55 °C yields ΔHi = -143 kJ/mol for these media. With this number, we can convert the large variety of ΔHi data obtained in superacidic media into the CH2Cl2/BCl3 system to predict the feasibility of carbene ion–alkene reactions in this medium.

The pκA values ³⁰ of four diaryl carbene ions are linearly related to ΔHi (Figure 2). The slope of the correlation line, ΔHi = mpκA + b, corresponds to that obtained in superacidic media.²⁸ (m(CH3Cl)/BCl3 = -6.3 kJ/mol; m(superacid) = -6.9 kJ/mol), while the intercepts [b(CH3Cl)/BCl3 = -96 kJ/mol; b(superacid) = -250 kJ/mol] differ by a value close to ΔHi.

2. Calorimetric Study of the Addition of Diarylmethyl Chlorides to Alkenes. Addition of Diarylmethyl Chlorides to 2-Methyl-1-pentene. The addition of diarylmethyl chlorides to 2-methyl-1-pentene in CH2Cl2 at -70 °C is selectively terminated after the formation of the 1:1 products. ³⁵ We have evaluated the heats of addition (ΔHs) in two different ways.

In approach A (Scheme I), a definite amount of neat alkene was added to an excess of completely ionized 1-X,Y. In order to obtain ΔHs for the CH2Cl2-solvated components, we have to correct the observed heats of reaction (ΔHi(alkene)) for the heats of ionization of 1-X,Y (ΔHi see above), the heats of solution of the alkene in CH2Cl2 (ΔHs), and the complexation enthalpy (ΔHc) of the addition products with the Lewis acid (eq 3). The latter was determined by introducing CH2Cl2 solutions of the adducts 3-X,Y into mixtures of CH2Cl2/BCl3.

\[
\Delta H_a = \Delta H_i(\text{alkene}) - \Delta H_s - \Delta H_c
\]

(3)

In approach B, ΔHs was obtained by introducing samples of pure RCl into a solution of excess alkene in CH2Cl2/Lewis acid (Scheme III). For the evaluation of ΔHi, the heat of reaction ΔHi(RCl) has to be corrected for the heats of solution of 1-X,Y in CH2Cl2 (ΔHs) and ΔHc (eq 4). ΔHi ought to be further corrected

\[
\Delta H_a = \Delta H_i(\text{alkene}) - \Delta H_s - \Delta H_c
\]

(4)
Preliminary force field studies showed that steric effects, the extent of alkyl halide substitution, and loss of alkene \( \pi \)-resonance usually make only a minor contribution to \( \Delta H_f \). Since steric effects and \( \pi \)-resonance contributions are small for the compounds investigated, the corresponding values of \( \Delta H_f \) fall within the same range.

3. Conclusion. A Correlation Equation of Carbon–Carbon Bond Formation. The heats of coordination (\( \Delta H_{coord} \)) of different carbocations with various carbocations in benzene, acetonitrile, and toluene have previously been derived to follow eq 5. The heat of the reaction of carbene tetrachloroborate

\[
\Delta H_{coord} = \text{const} + apK_R + b pK_a
\]

chloroborates with alkynes in CH\(_2\)Cl\(_2\) yielding unionized adducts 3 (\( \Delta H_f \)) is given by eq 6. Since the \( \Delta H_f \) values are almost constant when strong steric effects are absent and \( \Delta H_f \) is linearly correlated with \( pK_R \), eq 6 is equivalent to eq 7.

\[
\Delta H_f = \text{const} + apK_R + bpK_a \approx 9.5 + 6.3pK_a \text{ (kJ/mol)}
\]

While the carbene is replaced by a neutral nucleophile, the anion stability term (\( pK_a \)) of eq 7 is omitted in eq 7. The constants in eq 5 and 7 include a C–C bond increment and an ion solvation term. In addition, the constant in eq 7 incorporates a C–C bond increment, the enthalpy for the separation of C1– from the complex anion and the interaction of BC1\(_3\) with the solvent. Whereas \( a' \) which is of similar magnitude as \( a \) (eq 7), is expected to be almost invariant toward a change of solvent and counterion, \( const' \) will increase with increasing solvent polarity and increasing acceptor strength of the Lewis acid.

The free enthalpy of the carbenium tetrachloroborate additions is given by eq 8.

\[
\Delta G^0_f = \Delta G^0 + \Delta G'_{(RX)} = \Delta H_f - T \Delta S_f
\]

With the incremental system reported by Benson,\(^{20}\) the entropy of addition (\( \Delta S_f \)) for the reaction of diarylmethyl chlorides with 2-methyl-1-pentene is estimated to be \( \Delta S_f = -164 \text{ J/K/mol} \), and \( \Delta S_f \) was calculated to be approximately \(-130 \text{ kJ/mol} \) (see above). Substitution of these numbers in eq 8 yields eq 9.

\[
\Delta G^0_f = 16 + 6.3pK_a \text{ (kJ/mol at } -70^\circC)\]

Since \( \Delta H_f \) and \( \Delta S_f \) probably \( \Delta S_f \) fall within the same range for a variety of alkyl halides and alkenes, the addition of carbenium tetrachloroborates to alkynes is thermodynamically unfavorable in CH\(_2\)Cl\(_2\) at \(-70^\circC\), if \( pK_R > -2.6 \). Different values are obtained when steric interactions cannot be neglected and when the products are stabilized by complexation with the Lewis acid. We are currently investigating the influence of alkene and alkyl halide variation on \( \Delta H_f \) and \( \Delta G^0_f \) by force field methods.

Experimental Part

General Procedures. Diarylmethyl chlorides 1-X,Y and their alkene addition products were prepared according to literature procedures.\(^{11,19}\) Alkenes were dissolved in LiAlH\(_4\) prior to use or employed as purchased (isoprene, styrene; Aldrich Gold Label). For the equilibrium studies, gaseous BC1\(_3\) (99.9\%; Messer Griesheim) was transferred via gas-tight syringes. For calorimetric studies, a 1 M solution of BC1\(_3\) in CH\(_2\)Cl\(_2\) (Aldrich) was used. The ZnCl\(_2\).NEt\(_2\) catalyst was prepared according to ref 16. CH\(_2\)Cl\(_2\) was subsequently stirred over CaCl\(_2\), concentrated gaseous BC1\(_3\) and finally Na-Pb alloy (Fluka). CD\(_2\)Cl\(_2\) was stored over Na-Pb alloy (Fluka). 1-M solution of BC1\(_3\) in CH\(_2\)Cl\(_2\) (Aldrich) was used. The ZnCl\(_2\).NEt\(_2\) catalyst was prepared according to ref 16. CH\(_2\)Cl\(_2\) was subsequently stirred over CaCl\(_2\), concentrated gaseous BC1\(_3\) and then BC1\(_3\) was stirred over Pd(OH)\(_2\) and finally Na-Pb alloy (Fluka). CD\(_2\)Cl\(_2\) was stored over Na-Pb alloy (Fluka). CD\(_2\)Cl\(_2\) was stored over Na-Pb alloy (Fluka). Edsible crystals are reported relative to Si(CH\(_3\)\(_2\)).

Errors given are mean standard deviations of measured quantities. Errors of derived data have been evaluated according to laws of propagation of errors.

Equilibrium Studies. Partial ionization of the mixtures of the alkyl halides is usually obtained by adding 0.5–1 equiv of BC1\(_3\) in CD\(_2\)Cl\(_2\) at \(-70^\circC\). 1H NMR spectral data are given in the supplementary material.


Typical example: p-Anisyl(p-phenoyxphenyl)methyl chloride (1-O Me,OPh; 40.2 mg, 0.124 mmol) and p-anisyly-tolylmethyl chloride (1-O Me,Me, 72.4 mg, 0.293 mmol) were dissolved in 0.6 mL of CDCl3 in an NMR tube. 1, 1,2,2-Tetrachloroethane (20.0 mL, 31.5 mg, 0.188 mmol) was added as standard. Partial ionization of the mixture is accomplished by addition of 2.3 mL (0.094 mmol) of BCl3 gas at -70 °C.

OMe,OPh; 6
40.2 mg, 0.124 mmol) and p-anisyl-p-tolylmethyl chloride (1-O Me,Me, 72.4 mg, 0.293 mmol) were dissolved in 0.6 mL of CDCl3 in an NMR tube. 1, 1,2,2-Tetrachloroethane (20.0 mL, 31.5 mg, 0.188 mmol) was added as standard. Partial ionization of the mixture is accomplished by addition of 2.3 mL (0.094 mmol) of BCl3 gas at -70 °C.

The signals of para methyl (δ = 2.33, 1-O Me,Me, δ = 2.58, 1-O Me,Me), para methoxy (δ = 3.75, 1-O Me,Me, 1-O Me,OPh; δ = 3.42, 1-O Me,OPh, and methine protons (δ = 6.14, 1-O Me,OPh; δ = 6.17, 1-O Me,Me; δ = 8.94, 1-O Me,OPh; δ = 9.13, 1-O Me,Me) in both carbenium ion and precursors were recorded with those of tetrachloroethane (δ = 6.01). The signal integrals gave nine equations for the determination of the concentrations of 1-O Me,Me, 1-O Me,OPh, 3.75, 1-OMe,Me; 6.14, 1-OMe,Me; 6.17, 1-OMe,Me; 8.94, 1-OMe,OPh; 9.13, 1-OMe,Me) in both carbenium ion and precursors were recorded with those of tetrachloroethane (δ = 6.01). The signal integrals gave nine equations for the determination of the concentrations of 1-O Me,Me, 1-O Me,OPh, 1-O Me,Me, and 1-O Me,Me. Regression analysis led to KMe3 = 0.0480 and ΔGMe3 = 5.13 kJ/mol. Further determinations of ΔGMe3 for six different samples (ΔGMe3 = 4.84, 5.15, 5.36, 4.71, 5.02, 5.60 kJ/mol) gave an average value of ΔGMe3 = 5.1 ± 0.3 kJ/mol.

Calorimetric Studies. General Procedures. A calorimeter of the type previously described was used with minor modifications. Experimental details and procedures closely followed the description given there. Determination of the heat capacity of the calorimeter was undertaken and checked independently by the determination of the heat of interaction of tetrahydrofuran with SbCIS in CH2Cl2 at -55 °C.

Heats of Addition of Diarylmethyl Chlorides to 2-Methyl-1-pentene. A 1 M solution of BCl3 in CH2Cl2 (10 mL) or of ZnCl2(OEt2)2 in CH2Cl2 (5 mL) was added to a solution of the alkene (1 mL) in CH2Cl2 (10 M). The heat of reaction upon introduction of 0.50-0.75 mmol of the neat diarylmethyl chloride was recorded. Heats of solution of the diarylmethyl chlorides in CH2Cl2 were determined separately.

Heats of Addition of Diarylcarbenium Ions to Alkenes. Heats of addition to alkenes were recorded at 25 °C as 5-20% solutions in CH2Cl2. All alkenes have been introduced as 5-20% solutions in CH2Cl2 and heats of dilution were neglected.

Heats of Interaction with BCl3. Solutions of the addition products in CH2Cl2 were sealed in an ampule. The heat of reaction upon its introduction into excess BCl3/CH2Cl2 was recorded.

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Supplementary Material Available: 1. NMR spectral data for diarylmethyl chlorides 1-XY and diarylcarbenium tetrachloroborates in CDCl3 at -70 °C and compilations of NMR spectroscopic determinations of K and ΔG (5 pages). Ordering information is given on any current masthead page.

Host-Guest Complexation. 45. A Highly Preorganized Chromogenic Spherand Indicator System Specific for Sodium and Lithium Ions

Donald J. Cram,* Richard A. Carmack, and Roger C. Helgeson

Contribution from the Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024. Received July 9, 1987

Abstract: The synthesis and chromogenic properties of 1 as a sodium and lithium ion selective indicator system are described. The pK values of 1 in the absence and presence of various metal ions were measured in 80% dioxane-20% water (v/v) (observed). Observed values were as follows: Li+, 5.9; Na+, 6.9; K+, 12.7; Ca2+, 12.8; Mg2+, 13.2; 1.5-diazabicyclo[4.3.0]non-5-ene (DBN), 13.0. The noncomplexing model system 21 gave a pK value of 10.8 in the same medium. Spherand 1 is yellow (λmax 396 nm; εmax 17 500 L/(mol·cm)), whereas spheralexes 1'-Li+ (λmax 586 nm, εmax 35 500 L/(mol·cm)), and 1'-Na+ (λmax 596 nm, εmax 35 500 L/(mol·cm)) as well as uncomplexed 1' (λmax 610 nm, εmax 53 000 L/(mol·cm)) are deep blue or violet in 80% dioxane-20% water (v/v) and other solvents. Thus, 1 is a chromogenic ion-selective indicating system capable of detecting Li+ and Na+ at concentrations as low as 10-8 M in the presence of other common ions. The binding free energies of spherands 4-6 binding lithium picate and sodium picate at 25 °C in CDCl3 saturated with D2O were measured and found to range between 8.4 and 12.5 kcal mol-1, somewhat higher than those for 7, but much lower than those for 2.

This paper describes the synthesis and properties of 1 as an ion-selective chromogenic indicator system for Na+ and Li+. The binding properties and ion selectivities of analogues 2-8 are compared.

Spherand 2 binds lithium, sodium, and potassium picrates at 25 °C in CDCl3 saturated with D2O with ΔG values of >23, 19.3, and <5 kcal mol-1. The very strong binding of Li+ and Na+ and nondetectable binding to K+ have been attributed to the high complementarity and preorganization of the cavity in 2.

The crystal structure of 2 shows it contains a hole lined with 24 electrons having a diameter between that of Li+ and Na+. The six octahedrally arranged oxygens defining the cavity are shielded from solvation by six aryl and six methyl groups to provide a microdielectric environment for complexation between that of a hydrocarbon. The potassium ion is too large to enter this structurally defined cavity. Divalent ions of small to medium size can enter the cavity, but much lower than those for 2.

(1) We gratefully acknowledge support of this research from the Division of Basic Sciences of the Department of Energy.

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