a longer retention time than the cis. Anal. Calcd for $C_{28}H_{20}O_4$: C, 79.98; H, 4.79. Found (cis isomer): C, 79.50; H, 4.81. Found (trans isomer): C, 79.65; H, 4.83.

Reduction of 1-Naphthoyl Chloride. Solutions of 1.9 (10 mmol) or 3.81 g (20 mmol) of 1-naphthoyl chloride were electrolyzed under a cathodic potential of -1.30 V vs. SCE. The electron consumption was 1 F mol^{-1}. *trans*-1,2-Bis(1-naphthyl)-1,2-ethenediol di-1-naphthoate was obtained in 93% yield. After crystallization from CH_3OH–$CHCl_3$ it had the following mp 241 °C; IR (KBr) 1730 cm^{-1}. UV ($CHCl_3$) λ_{max} 242 nm; ^1H NMR ($CDCl_3$), absence of signals for nonaromatic protons, broad band centered at δ 7.6; mass spectrum (70 eV), *m/e* (relative intensity) 620 (5), 449 (3), 326 (1), 265 (30), 155 (95), 127 (100), 101 (20), 77 (27). Anal. Calcd for $C_{44}H_{28}O_4$: C, 85.14; H, 4.55. Found: C, 85.34; H, 4.49.

A sample prepared by the procedure of Trisler and Kawasaki[8,9] showed the same properties as the product obtained by electrolysis.

Reduction of 2-Naphthoyl Chloride. Samples of 2-naphthoyl chloride (10 or 20 mmol) were electrolyzed under a potential of -1.40 V vs. SCE, and *trans*-1,2-bis(2-naphthyl)-1,2-ethenediol di-2-naphthoate was obtained in 92% yield. The electron consumption was 1 F mol^{-1}. The product was crystallized from $CHCl_3$: mp 292 °C; IR (KBr) 1733 cm^{-1}; UV ($CHCl_3$) λ_{max} 247 nm; ^1H NMR ($CHCl_3$) did not give satisfactory results because of the low solubility of the compound, but in deuterioacetone a weak band centered at δ 8.05 was observed; mass spectrum (70 eV), *m/e* (relative intensity) 620 (3), 449 (2), 265 (4), 155 (43), 127 (100), 101 (21), 77 (34). Anal. Calcd for $C_{44}H_{28}O_4$: C, 85.14; H, 4.55. Found: C, 85.31; H, 4.59.

Reduction of Bibenzoyl in the Presence of Benzoyl Chloride. Solutions containing 2.10 g (10 mmol) of bibenzoyl and 2.81 g (20 mmol) of benzoyl chloride were electrolyzed under a -0.9-V cathodic potential vs. SCE, a potential at which only the bibenzoyl is reduced. The electron consumption was 2 F mol^{-1} of bibenzoyl. The product had the same physical, spectroscopic, and GC properties as *cis*-stilbenediol dibenzoate and showed no depression in melting point when mixed with an authentic sample. The yield was quantitative based on bibenzoyl.

Acknowledgment. We thank Dr. J. Cambronero and Dr. J. Aquirre of ACEDESA for their kindness in allowing us the use of their NMR spectrometer.

Registry No. Benzoyl chloride, 98-88-4; *cis*-stilbenediol dibenzoate, 1924-28-3; *trans*-stibenediol dibenzoate, 1924-29-4; 1-naphthoyl chloride, 879-18-5; *trans*-1,2-bis(1-naphthyl)-1,2-ethenediol di-1-naphthoate, 79722-54-6; 2-naphthoyl chloride, 2243-83-6; *trans*-1,2-bis(2-naphthyl)-1,2-ethenediol di-2-naphthoate, 79722-55-7; bibenzoyl, 134-81-6.

Carbon-13 Nuclear Magnetic Resonance as a Probe for the Structural Assignment of 1,4,5-Trisubstituted Imidazoles

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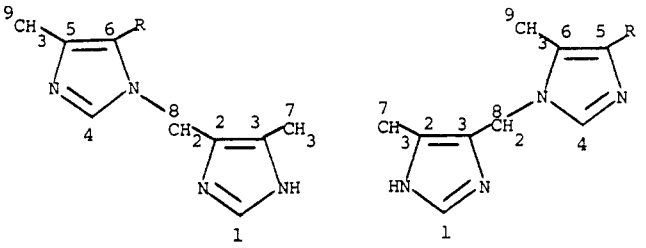
We have synthesized a pair of 1,4,5-trisubstituted imidazole esters, **1a** and **1b**, by the alkylation of 4-methyl-5-carbethoxyimidazole with 4-methyl-5-(chloromethyl)-imidazole. A marked solvent effect on the ratio of **1a** to **1b** was observed. When the reaction was carried out in dimethylformamide, **1a** was favored by a 3:1 ratio, whereas **1b** was favored (4:1) in methoxyethanol. We were unable to study this solvent effect in other solvents because of the low solubilities of the imidazoles.



1a R = CO_2Et **1b** R = CO_2Et

4a R = $^{10}CH_2OH$ **4b** R = $^{10}CH_2OH$

In an attempt to establish the structure of these pairs of constitutional isomers, we examined their proton magnetic resonance spectra; but the evidence was inconclusive. Methods for distinguishing between 1,4- and 1,5-disubstituted imidazoles by cross-ring coupling constants,[1] use of lanthanide shift reagents,[2] and carbon-13 chemical shifts have been reported,[3] and only the last of these methods was useful to us. We have extended the use of the carbon-13 chemical shift method by making use of model compounds to carry out statistical chemical shift correlations to establish the structure. This approach involved synthesizing the model compounds and using measurements from them to estimate the carbon-13 chemical shifts expected for **1a** and **1b**. Statistical analysis was then applied to correlate these estimated chemical shifts with experimental values obtained from measurements with the two isomers of compound **1** (experimentally labeled **1x** and **1y**) which were to be identified. This method eliminates the necessity of making unambiguous assignments.

Scheme I illustrates how the model compounds were selected. Moiety C is a common structural feature to both **1a** and **1b**. The readily available 4-methyl-5-(hydroxymethyl)imidazole (**3**) was used as a model for this moiety.

Compounds **2a** and **2b** were synthesized unambiguously (see below) and used as models for moieties A and B, respectively. Carbon-13 chemical shifts observed for **2a** and **3** were used to estimate shifts for **1a**, neglecting the bridging methylene carbon. Similarly, shifts observed with **2b** and **3** were used to estimate shifts for **1b**.

The rationale for the described analysis required the unambiguous syntheses of 1,4-dimethyl-5-carbethoxyimidazole (**2a**) and 1,5-dimethyl-4-carbethoxyimidazole (**2b**). The synthesis of **2a** was reported by Staab and Schwalbach,[4] who methylated 4-methyl-5- carbethoxyimidazole with methyl sulfate.

The structure of the product (**2a**), which was an oil [bp 96 °C (1 torr)], was confirmed by the reaction of 4-methyl-5-carbethoxyoxazole with methylamine. We treated 4-methyl-5-carbethoxyimidazole with NaH/CH_3I in THF at 0 °C and obtained a mixture of an oil [bp 95 °C (0.1 torr)] and a solid (mp 81 °C). While the proton NMR spectrum of the oil was identical with that of compound **2a** prepared by Staab and Schwalbach, the proton NMR spectrum of the solid showed this to be the isomeric compound **2b**. Finally, **4a**, **4b**, and model compound **3** were obtained by reducing **1a**, **1b**, and 4-methyl-5-

(1) H. R. Mathews and H. Rappoport, *J. Am. Chem. Soc.*, **95**, 2297 (1973).
(2) E. E. Glover and D. J. Pointer, *Chem. Ind. (London)* 412 (1976).
(3) H. J. Sattler, V. Stoeck, and W. Schunack, *Arch. Pharm.*, **308**, 795 (1975).
(4) H. A. Staab and G. A. Schwalbach, *Justus Liebigs Ann. Chem.* **715**, 128 (1968).

0022-3263/82/1947-0144$01.25/0

Scheme I

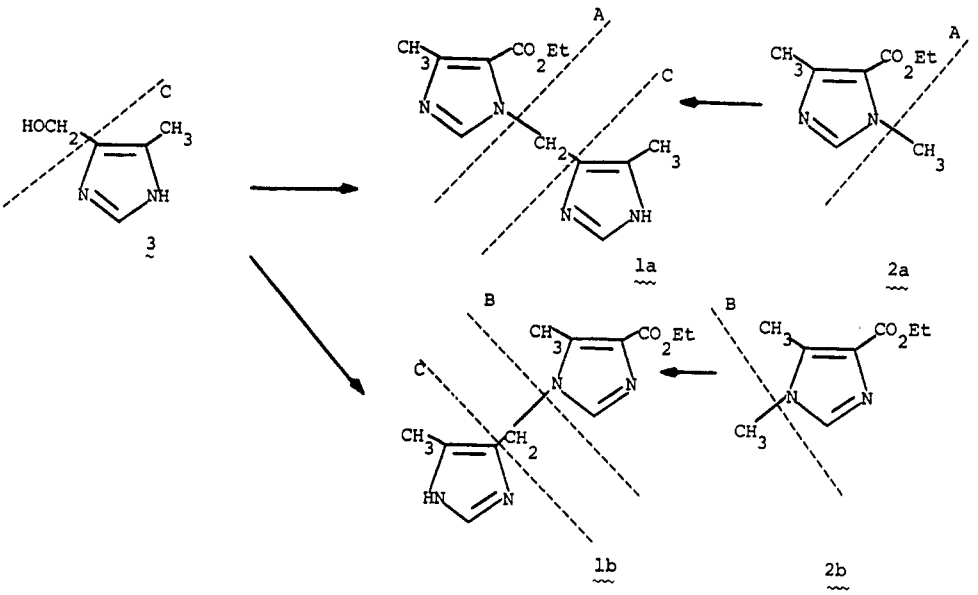


Table I. Correlation of Observed and Estimated Chemical Shifts for the Assignment 1x to 1a and 1y to 1b[a]

1x				1y			
δ_{obsd}[b]	δ_{est} for models 2a + 3	compd	Δ,[c] $\lvert\delta_{obsd} - \delta_{est}\rvert$	δ_{obsd}[b]	δ_{est} for models 2b + 3	compd	Δ,[d] $\lvert\delta_{obsd} - \delta_{est}\rvert$
160.55	160.55	2a	0.00	163.33	163.61	2b	0.28
146.71	147.13	2a	0.42	137.00	137.83	2b	0.83
140.85	141.53	2a	0.68	135.48	136.14	2b	0.66
133.87	132.34	3	1.53	134.07	132.34	3	1.73
129.35	129.68	3	0.33	129.46	129.68	3	0.22
124.92	125.68	3	0.76	128.38	128.56	2b	0.18
117.78	118.71	2a	0.93	124.74	125.68	3	0.94
59.78	59.84	2a	0.06	59.22	59.33	2b	0.11
15.54	15.55	2a	0.01	14.34	14.47	2b	0.13
14.10	14.22	2a	0.12	9.72	9.45	2b	0.27
9.20	9.09	3	0.11	9.27	9.09	3	0.18

[a] Observed bridging methylene carbon shift for 1x is 42.21 ppm. Observed bridging methylene carbon shift for 1y is 41.08 ppm. Observed hydroxymethylene carbon shift for 3 is 52.84 ppm. [b] $n = 11$. [c] $\sigma = 0.68$. [d] $\sigma = 0.73$.

Table II. Correlation of Observed and Estimated Chemical Shifts for the Assignment 1x to 1b and 1y to 1a

1x				1y			
δ_{obsd}	δ_{est} for models 2b + 3	compd	Δ,[a] $\lvert\delta_{obsd} - \delta_{est}\rvert$	δ_{obsd}	δ_{est} for models 2a + 3	compd	Δ,[b] $\lvert\delta_{obsd} - \delta_{est}\rvert$
160.55	163.61	2b	3.06	163.33	160.55	2a	2.78
146.71	137.83	2b	8.88	137.00	147.13	2a	10.13
140.85	136.14	2b	4.71	135.48	141.53	2a	6.05
133.87	132.34	3	1.53	134.07	132.34	3	1.73
129.35	129.68	3	0.33	129.46	129.68	3	0.22
124.92	128.56	2b	3.64	128.38	125.68	3	2.70
117.78	125.68	3	7.90	124.74	118.71	2a	6.03
59.78	59.33	2b	0.45	59.22	59.84	2a	0.62
15.54	14.47	2b	1.07	14.34	15.55	2a	1.21
14.10	9.45	2b	4.65	9.72	14.22	2a	4.50
9.20	9.09	3	0.11	9.27	9.09	3	0.18

[a] $\sigma = 4.60$. [b] $\sigma = 4.65$.

carboxyethylimidazole, respectively, with lithium aluminum hydride.

Discussion of Results

On the left in Table I is shown a comparison of carbon-13 chemical shifts for sample **1x** (mp, 116–120 °C) of unknown structure (i.e., **x** is either **a** and **b**) with estimated shifts for **1a** (derived from **2a** and **3**). On the right in Table I is shown a comparison of chemical shifts for unknown sample **1y** (mp, 197–200 °C; i.e., **y** is either **b** or **a**) with estimated shifts for **1b** (derived from **2b** and **3**). Similarly, Table II shows a comparison of chemical shifts for sample **1x** with estimated shifts for structure **1b** and a comparison of shifts for sample **1y** with estimated shifts for structure **1a**.

The standard deviations (σ) of 0.68 and 0.73 ppm given in Table I are a measure of the spread of the differences from zero[5], when estimated shifts are subtracted from

(5) Davis, O. L.; Goldsmith, P. L.; Eds. "Statistical Methods in Research and Production", Longman Group LTD, London, 1976, Chapter 3, p 40.

Table III. Carbon-13 Spectral Data for Alcohols 4a (Sample 4x) and 4b (Sample 4y)[a]

4a				4b			
δ_{obsd}	multiplicity ($^1J_{CH}$)	probable assignt	$^1J_{CH}$, Hz	δ_{obsd}	multiplicity	probable assignt	$^1J_{CH}$, Hz
137.31	d	4	207.0	137.64	s	5	
136.58	s	5		136.86	d	4	207.0
135.46	d	1	207.0	135.50	d	1	207.0
130.41	s	3		130.19	s	3	
127.69	s	6		126.85	s	6	
127.11	s	2		127.16	s	2	
52.85	t	10	142.6	57.66	t	10	141.6
41.78	t	8	139.6	41.96	t	8	138.7
12.27	q	9	127.0	9.54	q	7	128.3
9.40	q	7	127.9	8.57	q	9	127.6

[a] s = singlet, d = doublet, t = triplet, and q = quartet. Chemical shift reference CD_3OD taken as 49.0 ppm relative to Me_4Si. Concentration 50 mg/mL of CD_3OD.

observed shifts, for the assignments **1x** to **1a** and **1y** to **1b**. The largest difference was 1.73 ppm.

The standard deviations of 4.60 and 4.65 in Table II apply to the alternative assignments of **1x** to **1b** and **1y** to **1a**. The largest difference in this case was 10.13 ppm with 12 differences exceeding 2 ppm, which is subjectively a value above which a match might be considered as unsatisfactory. Thus, the preferred assignments are **1x** to structure **1a** and **1y** to structure **1b**. Thus, the perferred assignments are **1x** to structure **1a** and **1y** to structure **1b**. A weakness of this statistical evaluation is that it contains no measure of the significance of the differences between the standard deviation given in Table I and those given in Table II. A more rigorous statistical method is the Wilcoxon matched pairs signed-ranks test, details of which can be found in ref. 6. A discussion of the method is not included here. When the method is applied to **1x** and **1y** for the assignment **1x** to **1a** and **1y** to **1b**, p is less than 0.01; i.e., there is less than 1 chance in 100 of the assignment being incorrect.

For completeness, we include in Table III the carbon-13 data obtained in [$^2H_4$]methanol for the two alcohols **4a** and **4b**, which were obtained by reduction of esters **1a** and **1b**, respectively. The distinctive chemical shifts and multiplicities of the hydroxymethylene carbon peaks allow them to be assigned unequivocally.

On comparing isomeric structures **4a** and **4b**, one sees that the hydroxymethylene carbon in **4a** experiences an upfield shift not present in **4b** but comparable in magnitude to that reported by Sattler.[3] Thus the spectrum of the sample **4x** showing the chemical shift of 52.85 ppm is assigned to **4a**, and the spectrum of the sample **4y** showing the chemical shift of 57.66 ppm is assigned to structure **4b**.

Experimental Section

Proton spectra were run on a Perkin-Elmer R32 spectrometer operating at 90 MHz. Carbon spectra were run on either a Varian CFT 20 or a JEOL PFT100P spectrometer operating at 20 or 25 MHz, respectively.

1-[(4-Methyl-5-imidazolyl)methyl]-4-methyl-5-carbethoxyethylimidazole (1x, x = a). 4-Methyl-5-carbethoxyimidazole (75 g, 0.49 mol) and 4-methyl-5-chloromethylimidazole HCl salt (80 g, 0.48 mol) were dissolved in DMF (1.2 L). Triethylamine (100 g, 1 mol) was added, and the exothermic reaction was maintained at 50–60 °C for 6 h. DMF was removed under vacuum, leaving a mixture of isomers **1a** and **1b** (3:1 ratio)[9] as an oil (80 g), which was chromatographed on silica with EtOAc–MeOH–NH_3 (75:25:1) as an eluant to yield a white solid: 11 g (9%); mp 116–120 °C; NMR (Me_2SO-d_6) δ 1.26 (t, 3 H, J = 7.3 Hz), 2.15 (s, 3 H), 2.35 (s, 3 H), 4.22 (q, 2 H, J = 7.3 Hz), 5.35 (s, 2 H), 7.59 (s, 1 H), 7.73 (s, 1 H); exact mass calcd for $C_{12}H_{16}N_4O_2$ m/e 248.1273, found m/e 248.1260.

1-[(4-Methyl-5-imidazolyl)methyl]-4-methyl-5-(hydroxymethyl)imidazole (4x, x = a). Ester **1x** (8 g, 32 mmol) was added to a solution of $LiAlH_4$ (5 g, 0.13 mol) in THF (150 mL). The reaction was refluxed for 3 h, and water (10 mL) was added. The filtered solids were extracted with methanol, and removal of the solvent gave a solid which was recrystallized from ethanol: mp 183–185 °C); NMR (Me_2SO-d_6) δ 2.01 (s, 3 H), 2.18 (s, 3 H), 4.40 (s, 2 H), 4.80 (s, 2 H), 7.73 (s, 1 H), 7.42 (s, 1 H). An alcoholic solution treated with HCl gas gave the 2HCl salt: 6.0 g (67%); exact mass calcd for $C_{10}H_{14}N_4O$ m/e 206.1168, found m/e 206.1161.

1-[(4-Methyl-5-imidazolylmethyl]-5-methyl-4-carboxyimidazole (1y, y = b). 4-Methyl-5-(carboxyethyl)imidazole (123.2 g, 0.8 mol) dissolved in dry methoxyethanol (1.8 L) at 90 °C was added to a mixture of 4-methyl-5-(chloromethyl)imidazole HCl salt (1.36.6 g, 0.8 mol) and Et_3N (101 g, 1 mol) at -45 °C. The temperature rose to -10 °C. After 12 h of heating, the reaction was cooled and filtered. the filtrate was concentrated to a crude product mixture of **1a** and **1b** in a 1:4 ratio.[9] Liquid chromatography on silica with EtOAc–MeOH–NH_3 (80:20:1) as the eluant yielded **1y**: 39.9 g (18%); mp 197–200 °C; NMR (Me_2SO-d_6) δ 1.30 (t, 3 H), J = 6 Hz), 2.17 (s, 3 H), 2.55 (s, 3 H), 4.30 (q, 2 H, J = 6 Hz), 4.90 (s, 2 H), 7.33 (s, 1 H), 7.43 (s, 1 H); exact mass calcd for $C_{12}H_{16}N_4O_2$ m/e 248.1273, found m/e 248.1260.

1-[(4-Methyl-5-imidazolyl)methyl]-5-methyl-4-(hydroxymethyl)imidazole (4y, y = b). Ester **1y** (4.7 g, 19 mmol) was added under nitrogen to a suspension of $LiAlH_4$ (5 g, 0.13 mol) in dry THF (500 mL). After the mixture was stirred at room temperature for 5 h, water (20 mL) was added, and the filtered residue was extracted with ethanol (3 × 200 mL). The required base was isolated from the filtrate and recrystallized from ethanol: mp 214–215 °C dec); NMR (Me_2SO-d_6) δ 2.13 (s, 3 H), 2.14 (s, 3 H), 4.19 (s, 2 H), 4.80 (s, 2 H), 7.32 (s, 1 H), 7.35 (s, 1 H). An alcoholic solution treated with HCl gas gave the 2HCl salt: 2.3 g (44%); exact mass calcd for $C_{10}H_{14}N_4O$ m/e 206.1168, found m/e 206.1163.

1,4-Dimethyl-5-carbethoxyimidazole (2a) was prepared according to procedure reported by Staab and Schwalbach.[4] The product was an oil: bp 97 °C (0.1 torr); ^1H NMR data agreed with reported values; ^{13}C NMR (Me_2SO-d_6) δ 160.55, 147.13, 141.53, 118.71, 59.84, 34.35, 15.55, 14.22.

1,5-Dimethyl-5-carbethoxyimidazole (2b). Sodium hydride (50% oil dispersion, 16 g, 0.33 mol) was added in two portions to a suspension of 4(5)-methyl-5(4)carbethoxyimidazole[7] (50 g, 0.32 mol) in 300 mL of dry THF. After the hydrogen evolution had ceased, methyl iodide (26 mL, 0.28 mol) was added dropwise,

(6) Siegel, S. "Non-parametric Statistics for Behavioural Science"; McGraw-Hill: New York, 1956.
(7) H. Bohme and H. Schneider, *Chem. Ber.*, **91**, 992 (1958).
(8) British Patent 1 341 376; *Chem. Abstr.* **80**, 95958 (1974).
(9) The ratio of **1a** and **1b** was determined by HPLC under the following conditions: column, μ-Porasil, 30 cm × 3.9 mm i.d.; mobile phase, $CHCl_3$/MeOH/NH_4OH in the ratio of 90:10:1; flow rate, 1 mL/min; detection, UV at 254 nm.

and the reaction was stirred overnight. The reaction mixture was filtered, and the filtrate was stripped to give an oil which was chromatographed on silica gel with chloroform to yield two products. The first product (an oil) corresponded to **2a**. The second product was recrystallized from benzene and petroleum ether to give a pure product (**2b**): 12 g (22%); mp 81–84 °C; NMR (Me_2SO-d_6) δ 1.4 (t, 1 H), 2.30 (s, 3 H), 3.53 (s, 3 H), 4.55 (q, 2 H), 7.5 (s, 1 H); ^{13}C NMR (Me_2SO-d_6) δ 163.61, 137.83, 136.14, 128.56, 59.33, 31.23, 14.47, 9.45. Anal. Calcd for $C_8H_{12}N_2O_2$: C, 57.13; H, 7.19; N, 16.65. Found: C, 56.90; H, 7.22; N, 16.66.

4(5)-Methyl-5(4)-(hydroxymethyl)imidazole (3). The HCl salt of **3** was prepared according to the procedure reported in the literature.[8] The free base was liberated by dissolving a sample of HCl salt in water which was basified to pH 9 and extracted with *n*-BuOH. The *n*-butanol solution was dried and concentrated to half of the original volume. Crystalline solid **3** (mp 129–132 °C, 80% recovery) was isolated: ^{13}C NMR (Me_2SO-d_6) δ 132.34, 129.68, 125.68, 52.84, 9.09. Anal. Calcd for $C_5H_8N_2O$: C, 53.56; H, 7.19; H, 7.19; N, 24.98. Found: C, 52.84; H, 7.13; N, 24.44.

Acknowledgment. We express our appreciation to Dr. L. Jackman, Dr. J. Stedman, and Dr. D. Daniel for their helpful discussions.

Registry No. 1a, 79731-12-7; **1b**, 79731-13-8; **2a**, 35445-32-0; **2b**, 74531-82-1; **3**, 29636-87-1; **3**·HCl, 38585-62-5; **4c**, 79731-14-9; **4a**·2HCl, 79731-15-0; **4b**, 79731-16-1; **4b**·2HCl, 79731-17-2; 4-methyl-5-carbethoxyimidazole, 51605-32-4; 4-methyl-5-chloromethylimidazole hydrochloride, 51605-33-5.

Crown Cation Complex Effects. 16. Solvent Dependence of the 15-Crown-5 and 18-Crown-6 Equilibria with Sodium Cation[1]

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During the 14 years since Pedersen reported the first syntheses of the compounds he dubbed crown ethers,[2] a large number of binding constants have been reported. The data have often tended to apply to specific compounds and single solvents although a number of more detailed studies have recently appeared.[3] Lamb and co-workers have systematized a large number of binding constants in a recent monograph.[4] Despite these efforts, it is surprising to note that the solvent dependence of the binding data for two of the simplest crowns, 15-crown-5 and 18-crown-6, has not been reported.[5] Since such data are valuable for comparison with more elaborate macrocycles of interest to us,[6] we record here our own observations.

Table I. Sodium Cation Binding by 15-Crown-5 and 18-Crown-6

wt % of MeOH	mol fraction of MeOH	15-crown-5 K_s	15-crown-5 log K_s	18-crown-6 K_s	18-crown-6 log K_s
0	0	6.2	0.79	63 (6.3)[a]	1.80 (0.8)[a]
20	0.123	30.9	1.49	151	2.18
40	0.273	51.0	1.71	293	2.47
60	0.458	164	2.21	644	2.81
80	0.692	448	2.65	1759	3.25
90	0.835	926	2.97	5378	3.73
100	1.000	1780	3.25	22580	4.35

[a] Value from ref 10, see line B on Figure 1 and the text.

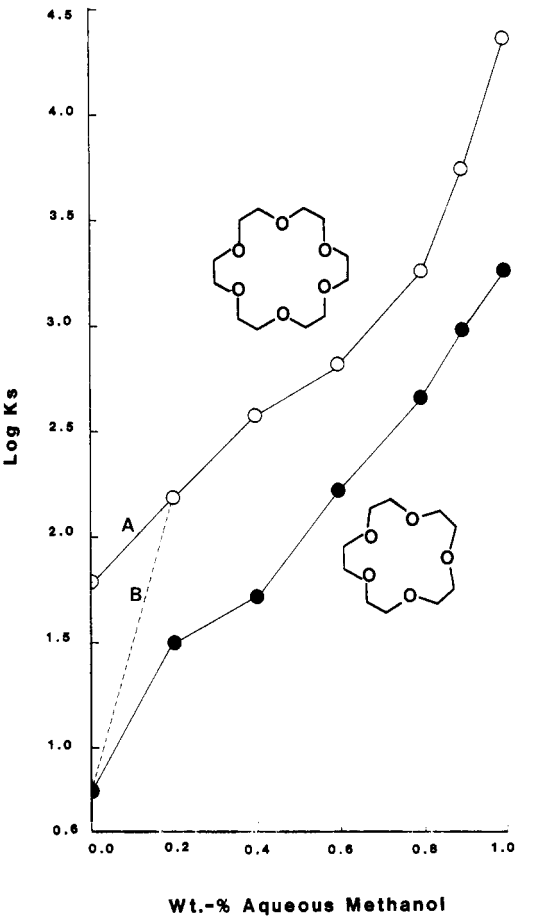

Figure 1. Solvent dependence of Na^+ binding by 15-crown-5 and 18-crown-6.

In Table I are collected the binding constants[7] for the reaction illustrated in eq 1. The two crowns studied are

$$\text{crown} + Na^+ \overset{K_s}{\rightleftharpoons} (\text{crown}\cdot Na)^+ \qquad (1)$$

15-crown-5 and 18-crown-6. The solvents chosen for these studies are methanol–water mixtures. The percentages reported are by weight at 25 °C. The corresponding mole fractions were calculated. Whenever possible, calibration was attempted with literature values. For example, our value of log K_s for 15-crown-5 in pure water was 0.79 and the reported value is 0.70.[9] The binding constant for

(1) Previous paper in this series: Ahern, M. F.; Leopold, A.; Beadle, J. R.; Gokel, G. W. *J. Am. Chem. Soc.*, in press.
(2) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *87*, 7017.
(3) (a) Laszlo, P. *Angew, Chem., Int. Ed. Engl.* **1978**, *17*, 254. (b) Popov, A. I. *Pure Appl. Chem.* **1979**, *51*, 101. (c) Kolthoff, I. M.; Chantooni, M. K. Jr., *Anal. Chem.* **1980**, *52*, 1039. (d) Cox, B. G.; Garcia-Rosas, J.; Schneider, H. *J. Am. Chem. Soc.* **1981**, *103*, 1054. (e) Lin, J. D.; Popov, A. I. *J. Am. Chem. Soc.* **1981**, *103*, 3773.
(4) Lamb, J. D.; Izatt, R. M.; Christensen, J. J.; Eatough, D. J. "Coordination Chemistry of Macrocyclic Compounds"; Melson, G. A., Ed.; Plenum Press: New York, 1978; Chapter 3, p 45.
(5) Binding data are available for a number of cations in a number of solvents, but differences in methods, solvents, and other variables complicate comparisons. Kolthoff[2c] has recently reported on binding constants for 18-crown-6 and Na^+ in six different solvents but no mixtures.
(6) Schultz, R. A.; Dishong, D. M.; Gokel, G. W., *Tetrahedron Lett.*, **1981**, 2623 and references therein.
(7) Binding constants were measured in the designated weight-percent solvent at 25.0 ± 1.0 °C, using a Corning Model 476210 electrode and an Orion Model 501 or 701 "Ionalyzer" millivolt meter according to the procedure of Frensdorff.[8] All apparatus was contained in a N_2-flushed drybox and solution temperature was maintained by using circulating di-*n*-butyl phthalate as a heat-transfer fluid.

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