Proton-Ionizable Crown Compounds. 9. Synthesis and Structural Studies of New 14-Crown-4 Compounds Containing a Pyridine or 4-Pyridone Subcyclic Unit

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Four new 14-crown-4 macrocyclic ligands containing either a pyridine or a 4-pyridone subcyclic unit have been prepared. Two of the 4-pyridono-crowns contained lipophilic hydrocarbon substituents. The starting octyl- and benzyl-substituted 4-oxa-1,7-heptanediols were prepared from the 2-octyl- or 2-benzyl-1,3-propanediol. When the two substituted 4-oxa-1,7-heptanediols were treated with tosyl chloride, both the expected 2-substituted-4-oxaheptane-1,7-ditosylates and the ditosylate of the dimeric diol were isolated. X-ray structure determinations were carried out on two of the new 14-crown-4 compounds.

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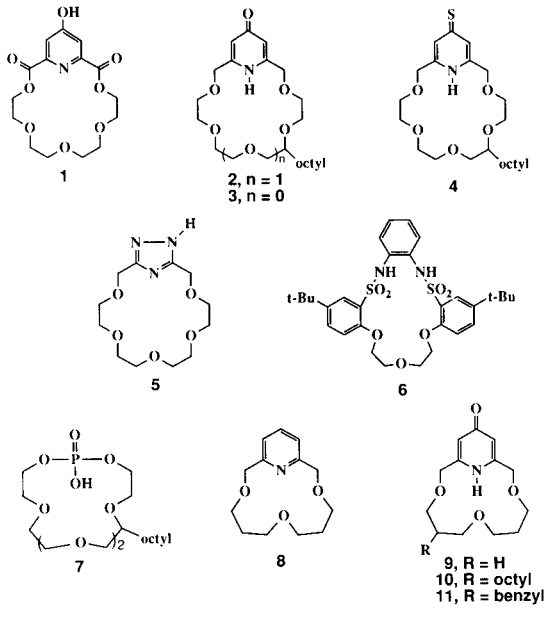
Introduction.

There is considerable interest in the use of proton-ionizable crown compounds for the transport of metal cations from aqueous solutions through an organic membrane. Most researchers have used crown compounds with pendant arms containing carboxyl or phenolic groups [1-4] or crown compounds containing a proton-ionizable group which extends into the macroring cavity [5,6]. We have synthesized a number of macrocyclic ligands where the proton-ionizable group is part of the macrocycle ring. Some of these macrocycles contain the 4-hydroxypyridine **1** in Figure 1 [7], 4-pyridone **2, 3** [8-10], 4-thiopyridone **4** [10], triazole **5** [11,12], and sulfonamide **6** [13] units as sites for proton ionization. We also have reported a crown containing a dialkylhydrogenphosphate **7** [14] unit where the hydroxy group presumably is directed into the cavity.

Figure 1. Structures of Crown Compounds

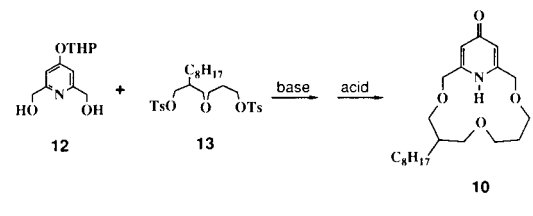


The use of proton-ionizable crown compounds in liquid membrane systems avoids the need for an anion to accompany the cation-macrocycle complex. Thus, the solvation energy of the anion becomes unimportant in the transport process which is driven by opposite metal ion and proton concentration gradients between the source and receiving phases. Compound **2** was found to be a selective transport ligand for potassium ions at source phase *p*H values of 12 and higher [9] while **3** was found to be selective for lithium ions [15]. Bartsch and his coworkers have shown that certain substituted 14-crown-4 compounds have an even greater selectivity for lithium ions than the 15-crown-5 ligands in competitive extractions of alkali metal picrates into an organic layer [2]. These results prompted us to prepare a series of 14-crown-4 compounds containing the pyridine and 4-pyridone subcyclic groups **8-11**, Figure 1. X-Ray crystal structure determinations for **8** and **9** are also reported in this paper. A report of the cation transport by these compounds will be published when the work is completed.

Results and Discussion.

The crown compounds were prepared from the appropriate 2,6-pyridinedimethanols and alkyl ditosylates as shown in Scheme 1 for the preparation of **10**. The starting

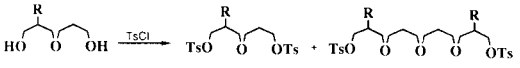
Scheme 1. Preparation of Compound 10.



4-oxa-1,7-heptanediols needed for the preparation of ditosylate compounds **13**, for example, were prepared by reacting the relevant 1,3-propanediol (from the reduction of the appropriately substituted malonic ester) with 3-chloro-1-propanol and base.

The reaction of octyl- and benzyl-substituted diols **14** and **15** with tosyl chloride proved to be interesting (Scheme 2). When the diols were added to tosyl chloride in pyridine, two products were observed. These compounds were readily separated by hplc to give **13** and **16**, the ditosylates of the starting diols, and **17** and **18** the ditosylates of the dimer of the diols (see Scheme 2). When the tosyl chloride was added to the diols in pyridine, only trace amounts of the dimeric products were observed. The structures of **17** and **18** were proved unequivocably by nmr spectroscopy to be those with the substituents on the second carbons from each end of the molecule rather than on the second carbons from the middle oxygen. The hydrogens on the carbon next to the tosylate groups caused a doublet in the nmr spectrum with an area equivalent to 4 hydrogens. The relative area for the doublets was one-half of that observed for the peak corresponding to the same hydrogens on compounds **13** and **16**.

Scheme 2. Preparation of Starting Ditosylate Compounds



The formation of dimeric ditosylates **17** and **18** in the above reactions (Scheme 2) was probably a result of the reaction of a diol with a newly formed mono-tosylate. The regioselectivity of the reaction is most likely due to the steric hindrance of the octyl and benzyl groups. This steric hindrance would cause the hydroxy group on the end away from the substituent to react preferentially with the carbon containing a tosylate group again at the end away from the substituent.

This same reaction was observed with 1-*n*-octyl-3-oxa-1,5-pentanediol, the diethylene glycol analog of **14**. When tosyl chloride was added to this *n*-octyl-substituted glycol, a mixture of the octyl-substituted diethylene glycol and dioctyl-substituted tetraethylene glycol ditosylates were isolated. Analogous to the case above, the octyl groups were substituted on the end carbons of the tetraethylene glycol unit.

The formation of dimeric ditosylates was not observed when unsubstituted glycols were treated with tosyl chloride under the conditions described above. Even though we could not isolate the dimeric ditosylate, Okahara and his coworkers have used a similar reaction to prepare hexa- and octaethylene glycols [16]. They reacted tri- or tetraethylene glycol with a reduced amount of tosyl chloride in the presence of pyridine followed by a strong base to form the dimeric glycols. The first step formed a mono-tosylate which reacted with more glycol in the second step. Our reaction utilizes an excess of tosyl chloride and only pyridine as the base. Substituted systems have not been tried under their reaction conditions.

The structures of all new macrocyclic compounds are consistent with data obtained from nmr and ir spectra, molecular weights, combustion analyses and crystal-structure determinations. Combustion analyses for the new diols and diol ditosylates were not obtained, however, satisfactory combustion analyses were obtained on the macrocyclic derivatives of the open chain glycols.

The crystal structures of compounds **8** and **9** are shown in Figures 2 and 3, respectively. Two crystallographically different molecules of **9** are in the asymmetric unit (Figure 3), labeled A and B. The two molecules of **9** are linked by hydrogen bonds involving the pyridone oxygen of one molecule and the nitrogen hydrogen of the other. This results in the formation of an alternating A-B polymer-like structure. The hydrogen bond data are listed in Table I.

The pyridone ring is not unexpected as it has been found in similar macrocyclic compounds [8]. Both pyridone rings lie in approximately the same plane, and the heterocycle portions of both molecules are on the same side of the chain. The occurrence of **9** in a polymer form accounts for its higher melting point of 180° compared to **8** (120°). The least-squares plane of the hetero oxygens lies at an angle of 74° to the least-squares plane of the pyridone in A, and 71° in B. The sizes of the heterocycle ring cavity are approximately the same for the two molecules of **9**, and also

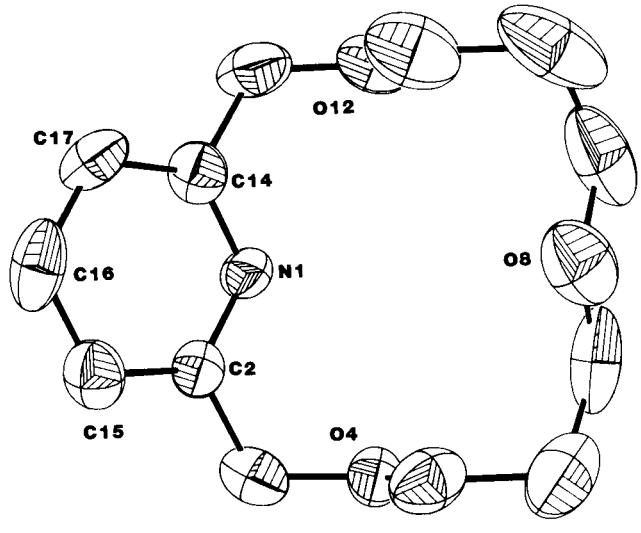


Figure 2. Computer Drawing of **8** With All Hydrogen Atoms Omitted for Clarity.

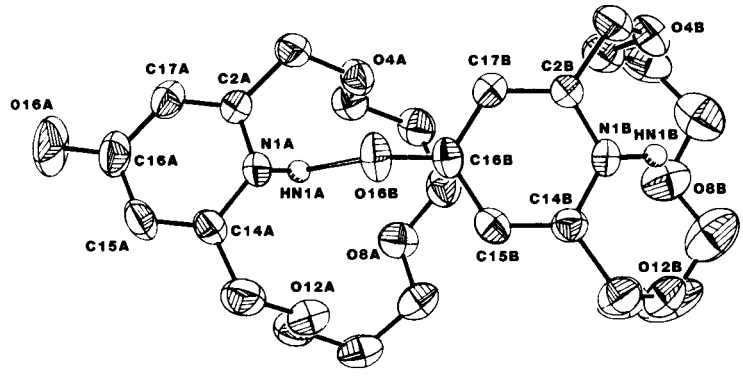


Figure 3. Computer Drawing of **9** With All Hydrogen Atoms Except HNIA and HNIB Omitted for Clarity.

for **8**, with an N1-08 interatomic distance of about 4.0 Å, and an 04-012 interatomic distance of about 4.8 Å. Subtracting two times the Van der Waals radii of oxygen from the X-ray distance gives an excess diameter (the diameter that a cation can occupy if located in the cavity) of 1.1 Å to 2.0 Å, comparing favorably with the Li^+ diameter of 1.48 Å, and comparing marginally with the Na^+ diameter of 2.04 Å [17]. The least-squares plane of the heteroxygens forms an angle of 70° with the plane of the pyridine in **8**.

Table I

Hydrogen Bond Data for **9**

D	H	A	H...A(Å)	D...A(Å)	D-H...A(deg)
N1A	HN1A	O13B	1.89(2)	2.704(2)	158(2)
N1B	HN1B	O13A	1.87(2)	2.705(2)	164(2)

EXPERIMENTAL

Infrared (ir) spectra were obtained on a Beckman Acculab 2 spectrophotometer. The proton nuclear magnetic resonance (nmr) spectra were obtained on a JEOL FX-90Q spectrometer in deuteriochloroform. Crystal structure determinations were done on a Nicolet R3 autodiffractometer. Elemental analyses were performed by MHW Laboratories, Phoenix, Arizona. Molecular weights were obtained by osmometry on a Hitachi-Perkin Model 115 molecular weight apparatus. Melting points were obtained on a Thomas-Hoover melting-point apparatus and are uncorrected. The starting diols and ditosylates were prepared as follows.

4-Oxa-1,7-heptanediol.

1,3-Propanediol (Aldrich, 76.1 g, 1.0 mole) was dissolved in 500 ml of anhydrous tetrahydrofuran (THF). Potassium *t*-butoxide (122.2 g, 1.0 mole) was added and the resulting mixture was warmed to 50-55°. 3-Chloro-1-propanol (Aldrich, 94.5 g, 1.0 mole) was slowly added to the mixture over a 15 minute period. The mixture was stirred at 55° for 6 hours and then refluxed for 24 hours. The solvent was removed under reduced pressure and the organic portion of the residue was dissolved in ether. The filtered ether solution was washed with 5% brine and dried over anhydrous magnesium sulfate. The drying agent was filtered and the product was distilled to give a clear oil, bp 95-110°/0.05 mm; nmr: δ 1.72 (m, 4H), 3.47 (m, 10H). This diol was not further purified but was used as is to prepare the ditosylate.

Table II

Crystal and Experimental Data

Compound	**8**	**9**
Formula	$C_{13}H_{19}NO_3$	$C_{13}H_{19}NO_4$
Mr	237.3	253.3
F(000)	512	540
$\mu(cm^{-1})$	0.90	0.85
Crystal Size	0.20 x 0.20 x 0.30	0.25 x 0.30 x 0.40
Space Group	$P2_12_12_1$	$P\bar{1}$
a(Å)	8.199(1)	8.346(3)
b(Å)	11.020(3)	12.200(3)
c(Å)	14.557(3)	14.301(4)
α(deg)	90	93.47(2)
β(deg)	90	102.30(3)
γ(deg)	90	103.68(2)
V(Å^3)	1315.2(5)	1373.0(7)
Z	4	4
d_x (gcc^{-1})	1.20	1.23
Sin θ/λ max	0.54	0.54
2θ range (deg)	4-45	4-45
hkl range	000 to 8,12,16	0,-13,-15 to 9,12,14
λ(Å)	Mo, 0.71073	Mo, 0.71073
R_m	– – – –	.012
Total Reflections	1433	4029
Unique Reflections	1416	3594
Observed Unique Reflections	799	2641
Unobserved Reflections	617	953
R	0.0737	0.0378
R_w	0.0471	0.0407
Min & Max Peaks in Δ Map	-0.25, 0.26	-0.12, 0.14
Ave Δ/esd	0.012	0.025

2-(*n*-Octyl)-4-oxa-1,7-heptanediol (**14**).

This diol was prepared as above from 100 g (0.5 mole) of 2-(*n*-octyl)-1,3-propanediol (prepared by reducing the octyl-substituted malonic ester), 56.4 g (0.5 mole) of potassium *t*-butoxide and 47.3 g (0.50 mole) of 3-chloro-1-propanol. The product was a clear oil, bp 130-145°/0.05 mm; nmr: δ 0.88 (t, 3H), 1.28 (s, 14H), 1.80 (m, 3H), 3.58 (m, 10H). The diol was not further purified but was used as is to prepare ditosylate **13**.

2-Benzyl-4-oxa-1,7-heptanediol (**15**).

This diol was prepared as above from 33.2 g (0.20 mole) of 2-benzyl-1,3-propanediol (prepared by reducing the benzyl-subtituted malonic

ester), 23.6 g (0.21 mole) of potassium *t*-butoxide and 18.9 g (0.20 mole) of 3-chloro-1-propanol. The product was a clear oil, bp 125-140°/0.05 mm; nmr: δ 1.80 (p, 2H), 2.08 (m, 1H), 2.62 (d, 2H), 2.98 (m, 2H, peak disappeared in dideuterium oxide), 3.58 (m, 8H), 7.24 (m, 5H). This material was not further purified but was used as is to make ditosylate **16**.

4-Oxaheptane-1,7-ditosylate.

4-Oxa-1,7-heptanediol (10.0 g, 0.075 mole) was dissolved in 30 ml of pyridine and the solution was cooled to about 0°. To this solution was slowly added, a solution of 42.5 g (0.22 mole) of *p*-toluenesulfonyl chloride in 50 ml of pyridine. The resulting mixture was allowed to warm to room temperature over a 2 hour period. The reaction mixture was added to a rapidly stirring mixture of ice and water and the solid was filtered. The solid was recrystallized from ethanol to give 15.2 g (46%) of the ditosylate, mp 89-90°; nmr: δ 1.80 (p, 4H), 2.48 (s, 6H), 3.34 (t, 4H), 4.07 (t, 4H), 7.34 (d, 4H), 7.79 (d, 4H). This material was used to prepare **8** and **9**, each of which gave a satisfactory combustion analysis.

2-(*n*-Octyl)-4-oxaheptane-1,7-ditosylate (**13**) and 2,14-Di-(*n*-octyl)-4,8,12-trioxapentadecane-1,15-ditosylate (**17**) (see (Scheme II).

These materials were prepared as above from 16.0 g (0.065 mole) of *p*-toluenesulfonyl chloride. The products were extracted from the aqueous phase with 100 ml of ether. The ether extract was washed successively with 25 ml of cold aqueous hydrochloric acid and 25 ml of saturated aqueous sodium bicarbonate and dried over anhydrous magnesium sulfate. The drying agent was filtered and the solvent was removed under reduced pressure to yield a light yellow oil. A tlc analysis showed two products. The material was separated on hplc using a hexane-ethyl acetate mixture to yield some **13** as an oil and mostly **17** as an oil; nmr of **13**: δ 0.88 (t, 3H), 1.21 (m, 14H), 1.80 (m, 3H), 2.44 (s, 6H), 3.30 (dd, 4H), 4.04 (dd, 4H), 7.34 (d, 4H), 7.79 (d, 4H); nmr of **17**: δ 0.88 (t, 6H), 1.22 (m, 28H), 1.88 (m, 6H), 2.44 (s, 6H), 3.40 (complex m, 12H), 4.02 (d, 4H), 7.32 (d, 4H), 7.76 (d, 4H). Compound **13** was used without further purification to prepare **10**.

Compound **13** was the major product when **14** was added to tosyl chloride in pyridine.

Table III

Atom Coordinates (x 10^4) and Temperature Factors (Å^2 x 10^3) of **8**

atom	x	y	z	Ueq [a]
N1	1147(5)	1173(4)	2376(3)	45(2)
C2	2731(6)	1371(4)	2520(3)	40(2)
C3	3800(6)	251(5)	2473(4)	59(2)
O4	3498(3)	−504(3)	1709(2)	49(1)
C5	3853(7)	81(5)	869(4)	65(3)
C6	3424(10)	−770(6)	102(4)	87(4)
C7	1609(11)	−1032(5)	52(4)	94(3)
O8	807(5)	54(4)	−183(3)	83(2)
C9	−925(3)	−81(7)	−186(5)	100(4)
C10	−1705(9)	1151(7)	−210(4)	106(4)
C11	−1350(9)	1922(6)	638(4)	90(4)
O12	−1915(5)	1281(4)	1409(3)	58(2)
C13	−1609(7)	1930(5)	2226(4)	69(3)
C14	178(7)	2151(5)	2420(4)	50(2)
C15	3382(7)	2490(4)	2730(3)	53(2)
C16	2339(7)	3455(5)	2799(4)	60(2)
C17	723(7)	3305(5)	2629(4)	54(2)

[a] Ueq is defined as one-third of the trace of the orthogonalised Uij tensor.

2-Benzyl-4-oxaheptane-1,7-ditosylate (**16**) and 2,14-Dibenzyl-4,8,12-trioxapentadecane-1,15-ditosylate (**18**).

These compounds were prepared as above for **13** and **17** from 17.45 g (0.078 mole) of **15**, 100 ml of pyridine and 38.6 g (0.20 mole) of *p*-toluenesulfonyl chloride. The crude product was purified by hplc to give 15.2 g (37%) of **16** as an oil and 6.3 g (22%) of **18** as an oil; nmr of **16**: δ 1.76 (p, 2H), 2.08 (m, 1H), 2.40 (s, 3H), 2.44 (s, 2H), 2.56 (d, 2H), 3.29 (m, 4H), 4.04 (m, 4H), 6.95-7.20 (m, 9H), 7.76 (2d, 4H); nmr of **18**: δ 1.76 (p, 4H), 2.08 (m, 2H), 2.40 (s, 6H), 2.60 (d, 4H), 3.20-3.60 (m, 12H), 4.00 (d, 4H), 7.00-7.20 (m, 14H), 7.76 (d, 4H). Compound **16** was not purified but used to prepare **11**.

3,7,11-Trioxa-17-azabicyclo[11.3.1]heptadeca-13,15,1(17)-triene (**8**).

Sodium metal (1.15 g, 0.05 mole) was dissolved in 300 ml of *t*-butyl alcohol. 2,5-Pyridinedimethanol (Aldrich, 2.7 g, 0.02 mole) was added to the base solution at 50°. The mixture was stirred until all the solid dissolved. 4-Oxaheptane-1,7-ditosylate (8.85 g, 0.02 mole) in 60 ml of dioxane was added over a 30 minute period. The resulting mixture was stirred under reflux for 24 hours, cooled, and filtered to remove the solid sodium tosylate. The filtrate was evaporated under reduced pressure and the solid was recrystallized in ethanol to yield the potassium tosylate salt of **8**. The salt was chromatographed on alumina using chloroform and ethanol as eluants to give **8** which was recrystallized from ethyl acetate, 2.0 g (42%), mp 119.5-121°; nmr: δ 1.76 (q, 4H), 3.44 (m, 8H), 4.75 (s, 2H), 7.16 (d, 2H), 7.64 (t, 1H).

Anal. Calcd. for $C_{13}H_{19}NO_3$: C, 65.80; H, 8.07; mol. wt., 237.3. Found: C, 65.74; H, 7.98; mol. wt., 263.

3,7,11-Trioxa-17-azabicyclo[11.3.1]heptadeca-13,16-diene-15(17*H*)-one (**9**).

Sodium (1.3 g, 0.057 mole) was dissolved in 300 ml of refluxing *t*-butyl alcohol. The solution was cooled to 50° and 5.4 g (0.023 mole) of **12** [8] was rapidly added. The mixture was stirred at 50° until **12** dissolved. 4-Oxaheptane-1,7-ditosylate (10.0 g, 0.023 mole) in 70 ml of dioxane was slowly added to the mixture over a period of 30 minutes. The resulting mixture was stirred at reflux temperature for 24 hours, cooled and filtered to remove solid sodium tosylate. The solvents were removed to give a crude yellow oil. The crude product was refluxed in 200 ml of methanol and 3.0 g of *p*-toluenesulfonic acid. The mixture was cooled and neutralized with solid potassium hydroxide. The solvent was removed and the residue was chromatographed on alumina using chloroform and ethanol as eluants. The product was recrystallized from ethyl acetate/ethanol to give white crystals, 1.59 g (28%); mp 179-180°; nmr: δ 1.70 (m, 4H), 3.35 (m, 8H), 4.32 (s, 4H), 6.04 (s, 2H), 9.2 (broad, s, 1H).

Anal. Calcd. for $C_{13}H_{19}NO_4$: C, 61.89; H, 7.19; mol. wt. 252.29. Found: C, 61.62; H, 7.32; mol. wt. 260.

5-(*n*-Octyl)-3,7,11-trioxa-17-azabicyclo[11.3.1]heptadeca-13,16-diene-15(17*H*)-one (**10**) (Scheme I).

This compound was prepared as above for **9** from 1.0 g (0.045 mole) of sodium, 300 ml of *t*-butyl alcohol, 4.78 g (0.02 mole) of **12** and 11.1 g (0.02 mole) of **13** in 50 ml of dioxane. The product was recrystallized from ethyl acetate to give 2.52 g (35%) of **10**, mp 123.5-124.5°; nmr: δ 0.86 (t, 3H), 1.26 (m, 12H), 1.45 (d, 2H), 3.55 (m, 8H), 4.44 (s, 4H), 6.09 (s, 2H), 8.95 (s, 1H).

Anal. Calcd. for $C_{21}H_{35}NO_4$: C, 69.01; H, 9.65; mol. wt., 365.51. Found: C, 68.85; H, 9.52; mol. wt., 350.

5-Benzyl-3,7,11-trioxa-17-azabicyclo[11.3.1]heptadeca-13,16-diene-15(17*H*)-one (**11**).

This compound was prepared as above for **9** from 1.15 g (0.05 mole) of sodium, 300 ml of *t*-butyl alcohol, 4.78 g (0.02 mole) of **12** and 10.7 g (0.02 mole) of **16** in 50 ml of dioxane. The product was recrystallized from ethyl acetate to yield 1.49 g (21%) of fine white crystals, mp 168-169°; nmr: δ 1.48 (m, 2H), 2.16 (d, 2H), 3.52 (m, 8H), 4.48 (s, 4H), 6.16 (s, 2H), 7.24 (m, 5H), 8.94 (s, 1H).

Anal. Calcd. for $C_{20}H_{25}NO_4$: C, 69.95; H, 7.34; mol. wt., 343.12. Found: C, 69.90; H, 7.22; mol. wt., 372.

X-Ray Determinations.

Suitable single crystals of **8** and **9** were prepared. Lattice parameters for each crystal were obtained using least-squares technique on 25 centered 2θ values measured from 6° to 25°. Graphite monochromated molybdenum radiation was used for both studies. Intensities were measured on a Nicolet R3 automated diffractometer using a θ-2θ variable speed scan technique. Crystal data and experimental conditions are summarized in Table II. Trial models for both crystals were obtained using direct methods. After several cycles of refinement, most hydrogen atoms were located in the difference map. However, in the refinement process, positions of all hydrogen atoms except the nitrogen hydrogen of **9** were calculated based on stereochemical considerations. The location of the hydrogen atom on the pyridone nitrogen atom of **9** was obtained from the difference map. Both structures were refined using a cascading least-squares technique. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms for which positions were fixed were allowed to ride on the neighboring carbon atoms and their isotropic temperature factors were fixed at 1.2 times Ueq of that atom. The atomic and thermal parameters of the non-fixed atoms of **8** and **9** are contained in Tables III and IV, respectively. The R and Rw values for **8** were 7.4% and 4.7%, and for **9**, 3.8% and 4.1%. All programs used in the data collection and reduction and in the structure solution are part of the Nicolet R3 system and the SHELXTL program package [18,19].

Table IV

Atom Coordinates (x 10^4) and Temperature Factors ($Å^2$ x 10^3) of **9**

atom	x	y	z	Ueq [a]
N1A	9673(2)	2421(1)	8685(1)	42(1)
HN1A	10421(27)	3050(18)	8787(15)	63(7) [b]
C2A	8010(3)	2424(2)	8542(1)	41(1)
C3A	7618(3)	3556(2)	8406(2)	51(1)
O4A	8412(2)	4147(1)	7734(1)	49(1)
C5A	7800(3)	3615(2)	6767(2)	53(1)
C6A	8750(3)	4325(2)	6134(2)	59(1)
C7A	10623(3)	4409(2)	6378(2)	58(1)
O8A	10872(2)	3312(1)	6231(1)	59(1)
C9A	12601(3)	3298(2)	6481(2)	62(1)
C10A	12711(3)	2086(2)	6478(2)	64(1)
C11A	11899(3)	1481(2)	7214(2)	60(1)
O12A	12676(2)	2107(1)	8137(1)	54(1)
C13A	12063(3)	1573(2)	8893(2)	62(1)
C14A	10197(3)	1452(2)	8797(1)	45(1)
C15A	9036(3)	470(2)	8798(2)	60(1)
C16A	7281(3)	412(2)	8715(2)	62(1)
O16A	6226(3)	-483(1)	8790(2)	108(1)
C17A	6827(3)	1449(2)	8545(2)	52(1)
N1B	4367(2)	7351(1)	8679(1)	43(1)
HN1B	4923(24)	8011(15)	8598(13)	64(6) [b]
C2B	2808(3)	7258(2)	8852(1)	40(1)
C3B	2108(3)	8282(2)	8736(2)	54(1)
O4B	2039(2)	8648(1)	7810(1)	55(1)
C5B	1010(3)	7805(2)	7048(2)	65(1)
C6B	1029(4)	8288(2)	6109(2)	79(1)
C7B	2786(4)	8693(3)	5948(2)	90(2)
O8B	3503(2)	7746(2)	5916(1)	81(1)
C9B	5239(4)	8046(3)	5905(2)	102(2)
C10B	5881(3)	6990(3)	5901(2)	102(2)
C11B	5776(3)	6405(2)	6786(2)	72(1)
O12B	6833(2)	7148(1)	7604(1)	59(1)
C13B	6801(3)	6670(2)	8483(2)	57(1)
C14B	5092(2)	6458(2)	8715(1)	41(1)
C15B	4261(3)	5463(2)	8955(1)	42(1)
C16B	2662(3)	5315(2)	9198(1)	40(1)
O16B	1922(2)	4410(1)	9484(1)	56(1)
C17B	1952(3)	6268(2)	9097(1)	42(1)

[a] Ueq is defined as one-third of the trace of the orthogonalised Uij tensor. [b] Valve is isotropic U.

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