base, which consists largely of oxygen-containing natural products, will, in general, require the creation of new, class-specific data bases. This has already been accomplished for a series of diterpenoid alkaloids.[38] We are willing to collaborate with other interested investigators in such efforts (See Experimental Section).

Experimental Section

These programs are implemented in the ALGOL-like BCPL program language[47] on a Digital Equipment Corp. KI-10 computer at the SUMEX-AIM computer facility at Stanford. The programs are available to an outside community of investigators via a nationwide computer network to the limit of available resources. Export of the programs to other DEC PDP-10 or PDP-20 systems or other computers supporting BCPL (e.g., IBM-370) is possible. However, additional work remains before the programs become polished enough for mass export. Meanwhile, within the limits of our resources, we are prepared to collaborate in the ^{13}C-based solution of nontrivial structure problems for outside investigators who lack appropriate computer facilities.

Acknowledgment. We thank the National Institutes of Health (Grant No. RR-00612 and AM-04247) for their generous financial support and the United Kingdom Science Research Council for a grant to N.A.B.G. (B/RF/4955). Computer resources were provided by the SUMEX facility at Stanford University under National Institutes of Health Grant No. RR-0785.

Registry No. 4, 73809-96-8; **5**, 75991-61-6; **11**, 63399-37-1; **13**, 75919-20-9; **14**, 75947-44-3; **16**, 75919-21-0; **22**, 75919-22-1; **24**, 75919-23-2.

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[47] M. Richards and C. Whitby-Strevens, "BCPL—The Language and Its Compiler", Cambridge University Press, Cambridge, 1979.

Carbanions. 5.[1] Preparation and ^{1}H and ^{13}C NMR Spectroscopic Structural Study of the 4-Hydridopyridyl Anion and 4,4′-Bis(hydridopyridyl) Dianion. Absence of Homoazacyclopentadienyl Ion Character

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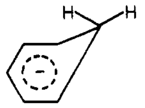
Received November 12, 1980

The 4-hydridopyridyl anion (**3**) was prepared and studied by NMR spectroscopy. By analogy with the cyclohexadienyl anions, ion **3** was shown to be planar with no 1,5-homoaromatic overlap occurring. Temperature-dependence studies showed that there is no change in the structure of **3** down to −40 °C and consequently no puckered form could be frozen out. At room temperature anion **3** was slowly converted into the 4,4′-bis(hydridopyridyl) dianion (**7**). The structure of **7** was also confirmed by its independent preparation.

Our preceding study of the cyclohexadienyl anion **1** by NMR spectroscopy as well as by MINDO/3 calculations concluded that ion **1** was a planar nonhomoaromatic species with no significant contribution, if any, by the homocyclopentadienyl anion **2**.[2] The methylene protons were equivalent even at −60 °C (at 300 MHz) and thus no indication for **2** was obtained. Recently Haddon[3] calculated that structure **1** was the major energy minimum for the C_6H_7 potential-energy surface and was 36 kcal/mol lower in energy than **2**.

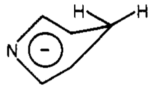
1



2

Bodor and Pearlman[4] in 1978 reported the results of their MINDO/3 study of dihydropyridine anions and related dihydropyridyl species. They concluded that the 4-hydridopyridyl anion (**3**) should be planar (within 0.5°) with the charge delocalized over the five atoms. Although these calculations on bond angles and geometry were similar to those for the 1,4-cyclohexadienyl anion, no experimental data were available. The possibility of 1,5-homoaromatic overlap in the case of the 4-hydridopyridyl anion (**3**) was difficult to completely rule out, at least as possible contribution of the homoazocyclopentadienyl anion (**3a**) to the structure of **3**.

3



3a

Recently Fraenkel et al.[5] reported their work on the generation of spirodihydroaromatic anions and in this study reported the ^{13}C NMR shifts of 4,4-dimethyl-1-lithio-1,4-dihydropyridine (**4**).[4] They concluded, from the equivalence of the methyl protons in the ^{1}H NMR spectrum and the methyl carbons in the ^{13}C NMR spectrum

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[1] For Part 4 see: Olah, G. A.; Hunadi, R. J. *J. Am. Chem. Soc.* **1980**, *102*, 6989.

[2] Olah, G. A.; Asensio, G.; Mayo, H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1978**, *100*, 4347.

[3] Haddon, R. C. *J. Org. Chem.* **1979**, *44*, 3608.

[4] Bodor, N.; Pearlman, R. *J. Am. Chem. Soc.* **1978**, *100*, 4946.

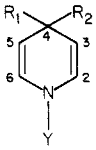
[5] Rizvi, S. Q. A.; Foos, J.; Steel, F.; Fraenkel, G. *J. Am. Chem. Soc.* **1979**, *101*, 4488.

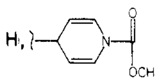
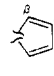
[6] Birch, A. J.; Karakhanov, E. A. *J. Chem. Soc., Chem. Commun.* **1975**, 480.

[7] Foos, J.; Steel, F.; Rizvi, S. Q. A.; Fraenkel, G. *J. Org. Chem.* **1979**, *44*, 2522.

0022-3263/81/1946-0715$01.00/0 © 1981 American Chemical Society

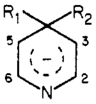
Table I. ^{13}C NMR Chemical Shifts (δ) of Dihydropyridines^{c}

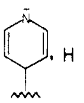


R_1, R_2	Y	$C_{2,6}$	$C_{3,5}$	C_4	R_1, R_2	C=O	other
H, H^{a}	$CO_2CH_2CH_3$	123.9	105.6	22.7	-	151.3	OCH_2CH_3, 62.3 OCH_2CH_3, 14.6
CH_3, CH_3^{b}	$CO_2CH_2CH_3$	120.3	115.9	30.8	32.5	151.5	OCH_2CH_3, 62.3 OCH_2CH_3, 14.5
H, H	CO_2CH_3	123.8	105.1	22.7	-	151.8	OCH_3, 53.2
 ^{b}	CO_2CH_3	125.6, 124.2	107.3, 106.0	39.6		151.8	OCH_3, 53.2
 ^{b}	$CO_2CH_2CH_3$	124.0	106.2	54.1		151.5	OCH_2CH_3, 62.5 OCH_2CH_3, 14.5 β, 147.3 γ, 130.1

^{a} This work. ^{b} See ref 7. ^{c} Run in CDCl/Me_4Si.

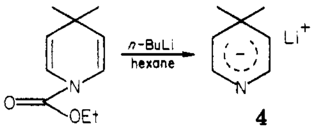
Table II. ^{13}C NMR Chemical Shifts of Dihydropyridine Anions and Model Systems



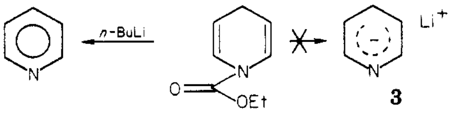
cleavage reagent	solvent	R_1, R_2	^{13}C chemical shifts, δ						
			C_1	$C_{2,6}$	$C_{3,5}$	C_4	α	β	γ
K^+ O-*t*-Bu^-	Me_2SO-d_6	H, H	-	127.9	97.1	27.9			
n-BuLi/ TMEDA^{a}	hexane	CH_3, CH_3	-	127.9	91.7	30.8	33.0		
K^+ O-*t*-Bu^-	Me_2SO-d_6		-	128.6	98.1	52.0			
n-BuLi/ TMEDA^{a}	hexane	$(CH_2)_6$	-	137.1	103.3	29.1	46.6	30.7	21.5
CH_3Li^{a}	Et_2O	$(CH_2)_4$	-	140.2	91.8	57.0	153.6	123.5	
 ^{b}	NH_3	H, H	78.0	131.8	7.58	30.0			
 ^{b}	NH_3	CH_3, CH_3	78.0	127.0	90.9	33.5	32.9		

^{a} See ref 5. ^{b} See ref 2.

even down to −60 °C, that there was no 1,5-homoaromatic overlap and thus ion 4 is planar. They were, however, not able to prepare the parent system, the 4-hydridopyridyl anion 3 from the corresponding 1,4-dihydropyridylurethane derivative 6 even at −78 °C and obtained only pyridine under their reaction conditions with *n*-butyllithium.



5 4



6 3

We present now our findings concerning the preparation of the parent 4-hydridopyridyl anion (3) by the potassium *tert*-butoxide cleavage of 6 and present evidence for the structure of this interesting anion. We also studied and prepared by an independent route the related 4,4′-bis(hydridopyridyl) dianion 7, which is readily formed by the dimerization of 3.

Results

Treatment of urethane 6[8] (prepared by the Birch reduction of pyridine and subsequent addition of diethyl carbonate[5,7]) with an excess of potassium *tert*-butoxide in Me_2SO-d_6 under an argon atmosphere at room temperature gave anion 3 (as a deep red solution). Anion 3 was stable at room temperature for approximately 1 h after which it was increasingly converted to the dimeric 4,4-bis(hydridopyridyl) dianion 7.[9] The structure of 7 was

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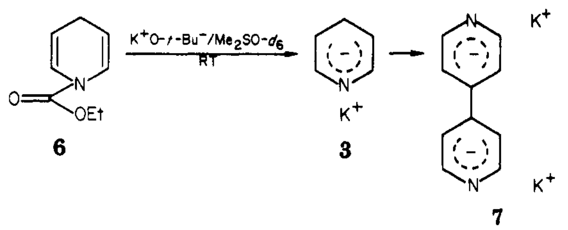
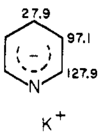
[8] Urethanes 6 and 8 were sensitive to O_2 and unstable above 0 °C and were stored at freezer temperatures under an argon atmosphere.



confirmed by synthesizing bisurethane 8[6,8] and converting it to dianion 7 as outlined in Scheme I. The ^{13}C NMR chemical shifts of dianion 7, obtained by the cleavage of urethane 8 with K$^+$ O-*t*-Bu$^-$, were identical with those of the species obtained when 6 was cleaved with potassium *tert*-butoxide and allowed to stand at room temperature for 3 h. The ^{13}C NMR chemical shifts of 3, 6, 7, and 8 are given in Tables I and II and the ^{1}H NMR chemical shifts are listed in Table III.

Anion 3 was obtained as a deep red solution in Me$_2$SO-d_6 and its NMR spectra were recorded immediately. Although we could not prepare anion 3 in THF (due to the low solubility of potassium *tert*-butoxide in THF), we were able to prepare this anion in a minimum amount of Me$_2$SO-d_6 and add THF to lower the freezing point of the solution. In this manner, we were able to examine the ^{13}C and ^{1}H NMR spectra of 3 at different temperatures and found that the proton spectra did not show any changes and the most characteristic C-4 carbon shifts remained unchanged to −40 °C. Below this temperature the solutions solidified and no high-resolution spectra could be obtained. One explanation of these data is that the anion is planar and a puckered form of 3 is not involved even at lower temperatures (at least to −40 °C).

It has been shown that in alternating π-delocalized ions the charge is localized at the odd-numbered carbons[10] (the even carbons remain almost uncharged) while in homoaromatic ions, according to the ^{13}C NMR chemical shifts, the charge is distributed over all the olefinic carbon atoms.[2] Examination of the ^{13}C NMR shifts of anion 3, compared to anions 4,[5] 10,[2] 11,[2] and 12,[7] shows that in the case of potentially homoaromatic homoazacyclopentadienyl anions such a distinction of delocalization is impossible based on the shifts of the olefinic carbons alone. In all five anions, the ^{13}C NMR shift of C-2 is nearly the same, this being expected for anions 3, 4, 10, and 11 since there is little or no charge delocalization of the negative charge into this position. Anion 12 is, however, aromatic and the charge is therefore expected to be delocalized. The C-3 shifts are more difficult to correlate but some of the difference in the chemical shifts of anions 3 and 4 can be attributed to the different counterions and the presence of methyl groups in 4. The C-4 shift of ion 3, however, is most significant in answering the question of whether there is homoaromatic character in this ion.



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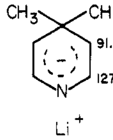
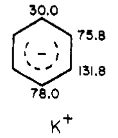
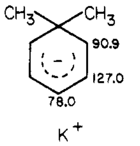


4



10



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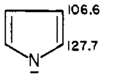
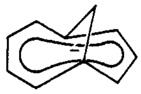


12

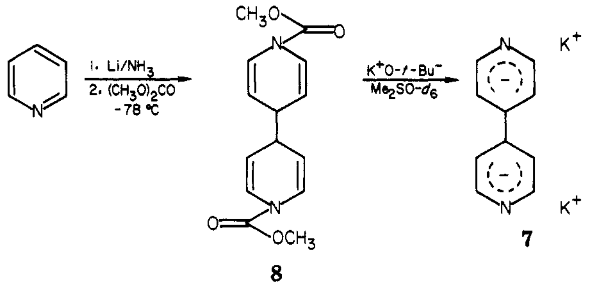
In the ^{13}C NMR spectra of homoaromatic species, the ^{13}C shift of the bridging methylene carbon is significantly deshielded due to its position over a ring current. For example, the bridging carbon of the homocyclooctatetraene dianion is found at δ(^{13}C) 66.6,[12] of the tropylium cation at δ(^{13}C) 43.7,[13] and of the homocyclopropenyl cation at δ(^{13}C) 54.0.[14] Even in the case of anion 13 (higher analogue



13

of the homocyclopentadienyl anion with extended conjugation), the bridging methylene carbon is at δ(^{13}C) 42.1.[15] Examining anion 3, we find that the C-4 shift is at δ(^{13}C) 27.9 which is much too shielded to be a carbon atom located over a homoaromatic ring current. Additional evidence is found in the ^{1}H NMR spectrum of anion 3 where the shift of the protons attached to C-4 is an important probe for the presence or absence of homoaromaticity. If the dihydropyridine anion 3 would have homoaromatic character (with an induced diamagnetic ring current resulting from a homoaromatic overlap of 6π electrons), we would expect the ^{1}H NMR spectrum to show the syn proton at C-4 (the proton located over the ring) to be substantially shielded. In the case of the homotropylium cation, H_{syn} is at δ −0.73[16] and correspondingly H_{syn} in the homocyclooctatetraene dianion is found at δ −1.2.[12] In the ^{1}H NMR spectrum of anion 3, no protons were observed above ~δ 0.8. Therefore it seems unlikely that 3 is a conformation which would allow C-4 to be located over a

Scheme I



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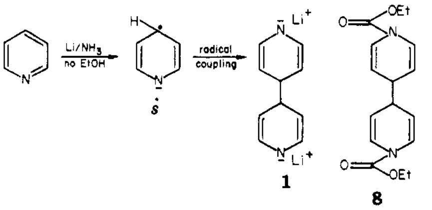
[9] During the Birch reduction of pyridine,[6] anion 7 must be also formed since dimeric *N*-(carbomethoxy)dihydropyridines were obtained in high yield.



[10] O'Brien, D. H.; Russell, C. R.; Hart, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 7427.

[11] Fraenkel, G.; Ho, C. C.; Liang, Y.; Yu, S. *J. Am. Chem. Soc.* **1972**, *94*, 4732.

[12] Barfield, M.; Bates, R. B.; Beavers, W. A.; Blacksberg, I. R.; Brenner, S.; Mayoll, B. I.; McCullock, C. S. *J. Am. Chem. Soc.* **1975**, *97*, 900.

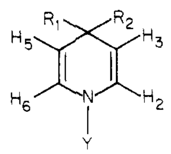
[13] Olah, G. A.; Liang, G.; Paquette, L. A.; Broadhurst, M. S.; Warner, P. *J. Am. Chem. Soc.* **1973**, *95*, 3386.

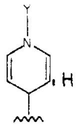
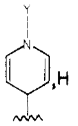
[14] Olah, G. A.; Staral, J. S.; Liang, G. *J. Am. Chem. Soc.* **1974**, *96*, 6233.

[15] (a) Hunadi, R. J.; Helmkamp, G. K. *J. Org. Chem.* **1978**, *43*, 1586. (b) Hunadi, R. J. Ph.D. Thesis, University of California, Riverside, CA, 1977.

[16] Winstein, S.; Kaesz, H. D.; Kreiter, C. G.; Friedrich, E. *J. Am. Chem. Soc.* **1965**, *87*, 3267.

Table III. ^{1}H NMR Chemical Shifts (δ)[a] of Dihydropyridine and Dihydropyridine Anion



			^{1}H chemical shifts			
solvent	R_1, R_2	Y	$H_{2,6}$	$H_{3,5}$	R_1, R_2	Y
$CDCl_3$	H, H	CO_2Me	6.87	4.93	2.85	OCH_3, 3.86
$CDCl_3$	H, H	CO_2Et	6.75	4.88	2.83	OCH_2CH_3, 4.23 OCH_2CH_3, 1.28
THF	CH_3, CH_3	CO_2Et	6.75	4.73		
$CDCl_3$		CO_2Me	6.87	4.93	3.06	OCH_3, 3.86
Me_2SO-d_6	H, H	K	6.65	4.88	*c*	-
Me_2SO-d_6		K	6.78	4.37	2.80[d]	-
hexane	CH_3, CH_3	Li	6.25	4.30		-

[a] Relative to Me_4Si. [b] See ref 5. [c] Resonance obscured by another absorption. [d] Multiplet.

homoaromatic ring. The structure of **3** therefore most likely is planar and no homoaromatic overlap is involved.

Experimental Section

Pyridine, tetrahydrofuran, dimethyl carbonate, diethyl carbonate, and potassium *tert*-butoxide were obtained from Aldrich Chemical Co. Lithium was purchased from Alfa-Ventron and Me_2SO-d_6 from Merck, Sharpe and Dome. All these materials, except for tetrahydrofuran which was distilled from potassium benzophenone ketyl and stored under nitrogen, were used without further purification.

***N*-Carboethoxy-1,4-dihydropyridine (6).**[6,17] To a mixture of 79.0 g (1.0 mol) of pyridine in 1 L of ammonia, at -78 °C under nitrogen, were added 21.0 (3.0 mol) of lithium and 117 mL (2.0 mol) of ethanol portionwise over a period of 1 h. After the mixture was stirred for an additional hour at -78 °C, 118 g (1.0 mol) of diethyl carbonate was added and the reaction mixture was warmed to -33 °C for an additional hour. Addition of 500 mL of dry ether followed by evaporation of the ammonia and careful addition of 500 mL of water gave 107.9 g (70%) of a light orange liquid after workup (wash with saturated NaCl, dry over $MgSO_4$, and remove solvent). Distillation gave 86.1 g (56%, not optimized) of a colorless liquid [bp 50-51.5 °C (0.25-0.40 mm); lit.[7] bp 52 °C (0.12 mm)]. This liquid could be stored at freezer temperatures under argon for weeks. ^{13}C and ^{1}H NMR data are summarized in Tables I and III, respectively.

4-Hydridopyridyl Anion (3). Anion **3** was prepared by the treatment of urethane **6** with 1.4 equiv of potassium *tert*-butoxide in Me_2SO-d_6 (reverse addition) at 0 °C followed by warming to room temperature (the reaction was performed in a 10-mm, dry NMR tube covered with a septum). A deep red solution was obtained after mixing at room temperature. ^{13}C and ^{1}H NMR data are given in Tables II and III, respectively.

Bis(*N*-carbomethoxy)-1,1′,4,4′-tetrahydro-4,4′-bipyridine (8).[6] Urethane **8** was prepared in an analogous manner to **6** except no ethanol was added to the reaction. Dihydropyridine **8** was obtained as an air-sensitive, orange oil after chromatography on neutral alumina and was stored at freezer temperatures under argon to avoid decomposition. ^{13}C and ^{1}H NMR data are given in Table I and III, respectively.

Preparation of the 4,4′-Bis(hydridopyridyl) Dianion (7) from Bis(*N*-carbomethoxy)-1,1′,4,4′-tetrahydro-4,4′-bipyridine (8). Anion **7** was prepared similarly to anion **3** except that 2.5 equiv of potassium *tert*-butoxide per equivalent of urethane **8** was used (a deep red solution was obtained). NMR data are given in Tables II and III.

Low-Temperature Study of the 4-Hydridopyridyl Anion (3). Potassium *tert*-butoxide (3.3 mmol) was dissolved in 0.5 mL of Me_2SO-d_6 (using a vortex stirrer) and 2.42 mmol of urethane **6** was added at 0 °C. THF (1 mL) was added after mixing at 15-20 °C, and the solution, after mixing, was used for variable-temperature NMR studies in the range of -40 to 25 °C.

Nuclear Magnetic Resonance Studies. **^{1}H NMR** spectra were obtained by using either a Varian Associates A56/60 or Em-360 spectrometer equipped with variable-temperature probes. Internal Me_4Si was used as the reference for both the neutral precursors and anions.

^{13}C NMR studies were carried out by using a Varian FT-80 NMR spectrometer equipped with a broad-band decoupler, variable-temperature probe and 32K memory capacity computer. Chemical shifts were measured from internal Me_4Si.

Acknowledgment. Support of our research by the National Science Foundation is gratefully acknowledged.

Registry No. **3**, 75961-68-1; **6**, 40339-63-7; **7**, 75961-69-2; **8**, 30081-42-6; *N*-(carbomethoxy)-1,4-dihydropyridine, 33707-37-8; pyridine, 110-86-1; diethyl carbonate, 105-58-8.

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(17) Pugmire, R. J.; Grant, P. M. *J. Am. Chem. Soc.* **1968**, *90*, 4232.