NMR Studies of Picolyl-type Carbanions. VI.[1,2] Anions Produced by Reactions of Methyl-substituted Quinolines and Isoquinolines with Butyllithium

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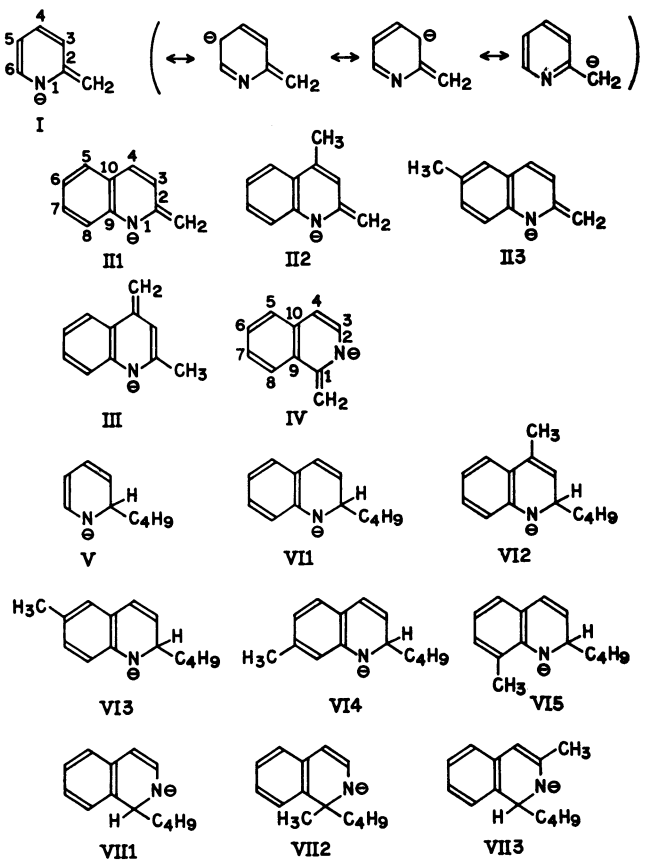
The ^{13}C and ^{1}H NMR spectra have been observed for the title anions with lithium as a counter ion in polar solvents. Two kinds of anions are formed by lithium-proton exchange and addition of butyllithium. The charge distributions in the anions are discussed in terms of the σ-included ω-HMO method. The former anions can be regarded as picolyl-type carbanions, but the latter ones are ionic species having two of three basic characteristics on picolyl-type carbanions.

In our previous papers, the ^{1}H, ^{7}Li, and ^{13}C NMR spectra were observed for charge-delocalized anions, I and III (shown below).[1,3,4] The studies have now been extended to the anions produced by reactions of methyl-substituted quinolines and isoquinolines with butyllithium. The present paper deals with charge distributions in the anions in terms of their ^{13}C chemical shifts and total ($\sigma+\pi$) electron densities. The anions prepared are numbered as follows:



Experimental

The method of preparation of the anions is similar to that described previously.[3]

The ^{13}C spectra were measured at 22.6 and 25.0 MHz on a Hitachi R-42FT and a JEOL JNM-FX100 spectrometers respectively. The chemical shifts were evaluated with the solvent peaks used as an internal reference and then converted to δ_c values from TMS by taking 26.4 and 37.0 ppm for tetrahydrofuran (THF) and hexamethylphosphoric triamide (HMPA) respectively.

Theoretical Calculation

The total electron densities on the atoms were calculated for the anions by the σ-included ω-HMO method.[5] In this study, the fourth and the fifth terms in Eq. 1 (shown below), called through space effects, were introduced into the calculation of the π-electron density. The Coulomb integral associated with the π-AO of the λ-th atom, α_λ^π, is, therefore, given by

$$\alpha_\lambda^\pi = \alpha + \delta_\lambda^\pi\beta + \omega^\pi\Delta Q_\lambda^\tau\beta + \sum_\mu \omega'^\pi\Delta q_\mu^\pi\beta + \sum_\nu \omega''^\pi\Delta q_\nu^\pi\beta, \quad (1)$$

where

$$\Delta Q_\lambda^\tau = \Delta Q_\lambda^\sigma + \Delta q_\lambda^\pi, \quad (2)$$

ΔQ_λ^τ, ΔQ_λ^σ, and Δq_λ^π are the net total, σ-, and π-electron densities on the atom λ respectively. The atom μ is adjacent to the atom λ and, further, the ν is adjacent to the μ. The values of ω'^π and ω''^π are assumed to be $\omega^\pi/1.5$ and $\omega^\pi/6.0$ respectively.[6] The resonance integral for the $\lambda-\mu$ bond, $\beta_{\lambda\mu}^\pi$, is given by

$$\beta_{\lambda\mu}^\pi = k_{\lambda\mu}^\pi\beta. \quad (3)$$

The parameters associated with π- and σ-AO's, used in the calculation, δ_λ^π, $k_{\lambda\mu}^\pi$, ω^π, δ_λ^σ, $k_{\lambda\mu}^\sigma$, and ω^σ, were taken from the paper of Miyajima *et al.*[5] This MO calculation was carried out using the Okitac-4300C computer system.

Results and Discussion

Typical spectra of the anions are shown in Figs. 1 and 2. The ^{1}H and ^{13}C chemical-shift data are given in Tables 1 and 2 respectively.

Reactions of Methyl-substituted Quinolines and Isoquinolines with Butyllithium. In methyl-substituted quinolines, 2-methyl-, 2,4-, and 2,6-dimethylquinolines, having a 2-methyl group, underwent metal-proton exchange to give charge-delocalized anions, II(III—II3),[4] but 4-, 6-, 7-, and 8-methylquinolines, having no 2-methyl group, did addition of butyllithium to give anionic σ-complexes, VI2—VI5. In the case of 2,4-dimethylquinoline, as well as 2,4-dimethyl- and 2,4,6-trimethyl-

Table 1. The proton chemical shifts of the anions, in THF at 60 MHz, in ppm[a)]

Anion	Assignment 2-H	3-H	4-H	5-H	6-H	7-H	8-H	CH_2		CH_3	
III[b)]		5.92	6.19	6.46	6.06	6.60	6.25	2.88	3.09		
II2[b)]		5.88		6.75	6.03	6.62	6.31	2.88	3.07	c)	
II3[b)]		5.96	6.24	6.37		6.52	6.28	2.87	3.09	2.07	
III[d)]		5.29		7.36	6.41	6.79	6.70	3.36	3.76	c)	
VI1	4.10	5.21	6.17	6.45	5.76	6.57	6.08	1.37[e)]			0.93
VI2	c)	5.11		6.71	5.79	6.59	6.08	c)		c)	0.91
VI3	4.10	5.32	6.20	6.39		6.49	6.10	1.38[e)]		2.08	0.94
VI4	4.11	5.25	6.18	6.41	5.71		6.00	1.39[e)]		2.10	0.93
VI5	4.08	5.13	6.13	6.34	5.62	6.46		1.38[e)]		2.05	0.91

a) Errors are estimated to be within ± 0.03 ppm. b) These values should be adopted, though they are partly different from the corresponding values in Table 1 of Ref. 4. c) Chemical shifts are not available because of overlapping of the large solvent peak. d) Measured at 200 MHz. e) Center peak of complex multiplet.

Table 2. The carbon chemical shifts of the anions, in ppm[a)]

Anion	Solvent	Assignment 1-C	2-C	3-C	4-C	5-C	6-C	7-C	8-C	9-C	10-C	CH_2			CH_3	
I[b)]	THF		164.2	116.1	131.6	97.3	148.7					57.0				
	HMPA		161.3	113.6	129.8	92.2	149.8					62.6				
III[b)]	THF		159.0	126.0	128.6	126.3	111.8	128.2	117.7	155.8	122.7	70.2				
	HMPA		159.0	125.0	127.9	125.5	108.7	127.7	119.0	156.5	121.9	70.7				
II3	THF		159.5	125.9	128.9	126.7	120.3	129.5	118.1	153.4	122.4	68.2			20.9	
III	THF		149.5	103.1	152.7	123.9	116.5	126.7	123.1	145.5	124.2	72.5			24.8	
IV	THF	158.0		146.6	93.3	120.9	127.2	123.2	124.3	130.4	140.2	68.7				
V	THF		57.2	97.9	126.4	90.8	150.2					34.7	28.5	24.4		15.0
	HMPA		58.0	92.3	127.0	85.2	151.4					35.8	28.5	24.1		15.0
VI1	THF		57.7	120.5	127.9	127.8	107.6	128.6	115.0	159.5	122.0	42.6	27.7	24.4		14.9
	HMPA		58.7	117.8	127.6	126.7	101.8	128.1	116.8	159.9	118.5	43.0	27.5	24.1		14.9
VI2	THF		57.5	119.0	131.2	124.1	107.4	128.3	114.7	159.3	122.9	42.5	27.8	24.3	19.6	14.8
VI3	THF		57.4	121.2	127.5	128.4	116.3	129.4	114.5	157.1	122.3	42.3	27.8	24.3	20.8	14.9
VI4	THF		57.6	120.2	127.7	127.3	109.6	137.2	114.7	159.1	120.0	42.6	27.8	24.4	22.2	14.9
VI5	THF		58.1	118.8	127.7	125.8	105.3	128.9	122.6	158.3	120.7	41.4	28.1	24.3	20.0	15.0
VII1	THF	62.7		151.7	88.2	118.0	125.7	118.4	126.3	126.9	139.9	34.5	29.5	24.2		14.9
VII2	THF	59.0		150.6	85.6	117.1	124.4	117.8	125.1	127.5	141.2	41.8	29.9	24.8	28.2	15.0
VII3	THF	63.3		157.7	85.5	116.0	125.3	117.3	125.6	126.3	141.3	35.2	29.5	24.3	25.1	15.0
	HMPA	62.7		157.8	83.0	113.7	124.7	115.7	125.0	125.8	142.5	35.1	28.9	23.9	25.2	14.9

a) Errors are estimated to be within ± 0.3 ppm. b) From the data in Table 2 of Ref. 1.

pyridines,[3)] the exchange reaction occurred at the 2-methyl group, and the anion formed, II2, isomerized to III. Similar isomerizations were reported previously.[3)] Next, 1-methylisoquinoline underwent both exchange and addition to give IV and VII2 simultaneously, but 3-methylisoquinoline did only addition at the 1-position to give VII3. These reaction sites were confirmed by ^1H and ^{13}C chemical-shift considerations.

As can be seen from these results, two kinds of anionic species are formed by exchange and addition. In the case of quinoline and isoquinoline, having no methyl group, the addition reaction can be expected to occur at a specific position. In fact, quinoline, isoquinoline, and, furthermore, pyridine react with butyllithium to give anionic σ-complexes, VI1, VIII1, and V.

Charge Distributions and Characteristics on the Anions. Typical ^1H NMR spectra of III1 and VI1 are shown in Figs. 1(a) and 1(b). The signals in the region of aromatic protons of both anions are present in higher fields than those of their starting materials. This upfield shift is ascribed to the excess-charge delocalization into the aromatic ring.[7)] Further, the 4-, 5-, and 7-proton signals of both anions appear at comparable fields, but the 3-, 6-, and 8-signals of VI1 do at a higher field than those of III1 respectively. This may arise from an increase of the negative charge in the aromatic ring except for the 2-position. The same tendencies are observed in the spectra of II2 and VI2, and II3 and VI3. Next, a typical spectrum of a mixture of IV and VII2 formed simultaneously is shown in Fig. 1(c). The signals, appearing as doublets, at δ 4.49 and 5.01 are attributable to the 4-protons of VII2 and IV respectively. The ratio of the two peak areas is about 1 : 1, indicating that IV and VII2 are present in this ratio. The signals at δ 3.28 and 3.68 are attributable to each of the methylene protons of IV. In III, the signals at δ 3.36 and 3.76 are also attributable to the methylene protons. The two protons of each anion, as well as those of II,[4)] show magnetic nonequivalence at room temperature. This nonequivalence is explained by the inhibited rotation around the bond between the ring and the methylene carbon, caused by the resonance stabilization in a molecular plane. Therefore, the methylene carbons of III—IV, as well as I—II, are virtually sp^2-hybridized.

The charge distributions in I, III1, IV, V, VI1, and VIII1 are discussed on the basis of the relationship between the carbon(^{13}C) chemical shifts and the total electron densities. In Fig. 3, the total electron densities calculated by the method described before are plotted

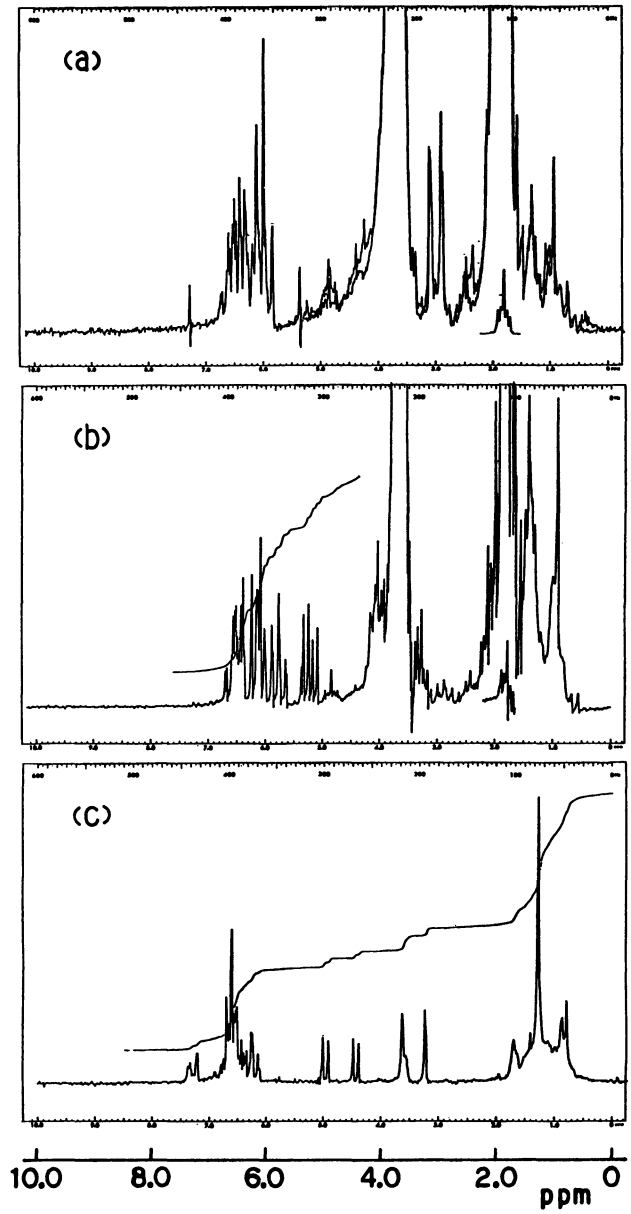


Fig. 1. ^{1}H spectra of the anions in THF at 60 MHz; (a) III, (b) VII, and (c) IV and VII2.

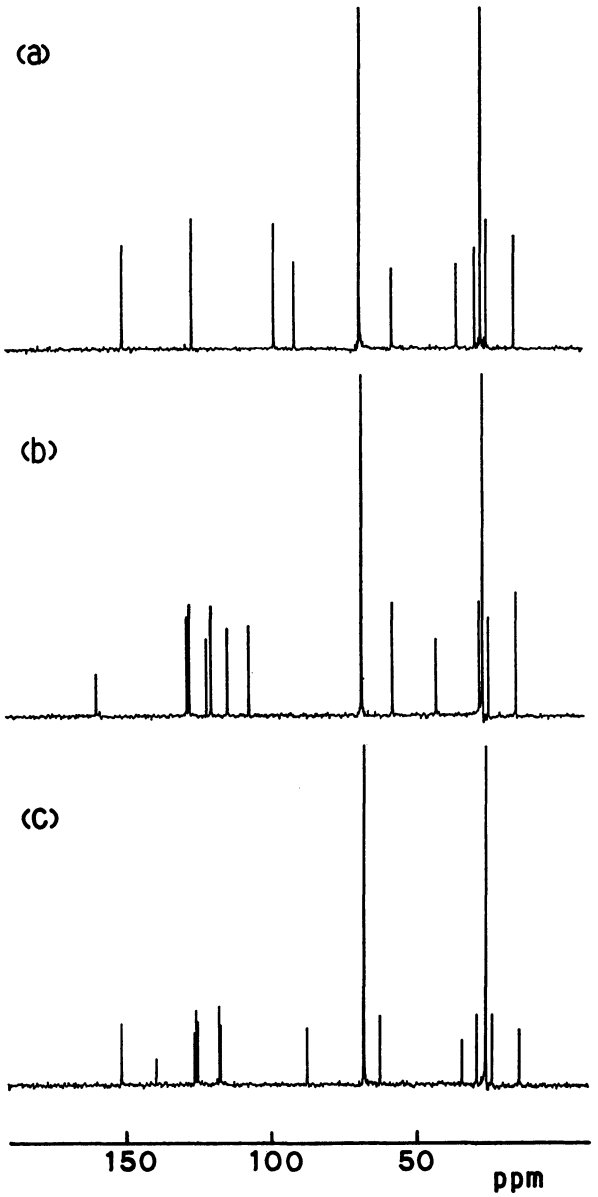


Fig. 2. ^{13}C spectra of the anions in THF at 25 MHz; (a) V, (b) VII, and (c) VIII.

against the carbon chemical shifts, except for the 2-carbons of V and VII, the 1-carbon of VIII, and the butyl carbons, having no π-electron. A good correlation exists between them, with a correlation coefficient of -0.981. Thus, these chemical shifts are linearly related to the total electron densities at the carbons in question, with a slope of -149 ppm electron^{-1}. This relationship implies that the total electron densities on the carbons of six different anions can be estimated from the observed carbon chemical shifts with an identical scale. The δ_c values of the aromatic carbons of I and V increase in the order 5-, 3-, 4-, and 6-carbons, showing that the total electron densities decrease in the same order. The δ_c values for III and VII, and for IV and VIII also increase in almost the same order respectively. In the aromatic rings of two kinds of anions, I, III, and IV, and the corresponding V, VII, and VIII, the

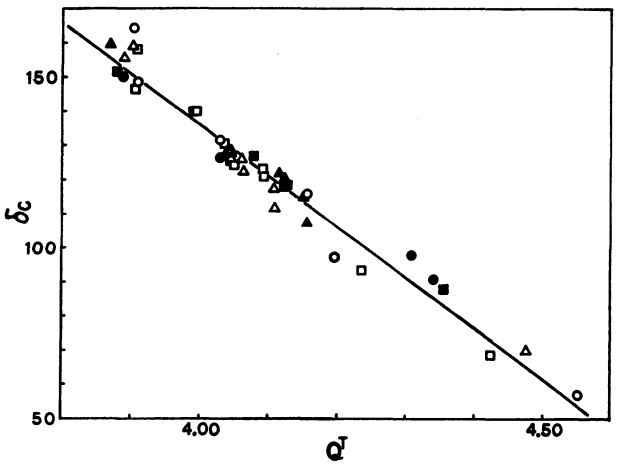


Fig. 3. ^{13}C chemical shifts *vs.* total electron densities. ○: I, △: III, □: IV, ●: V, ▲: VII, and ■: VIII in THF.

TABLE 3. THE TOTAL ($\sigma+\pi$) ELECTRON DENSITIES CALCULATED BY THE σ-INCLUDED ω-HMO METHOD (ω''-METHOD) FOR THE ANIONS

Anion Atom	I	III	V	VII	Atom	IV	VIII
1-N	5.486	5.568	5.681	5.775	1-C	3.908	
2-C	3.903	3.902			2-N	5.524	5.690
3-C	4.156	4.060	4.308	4.123	3-C	3.906	3.879
4-C	4.028	4.044	4.029	4.044	4-C	4.235	4.354
5-C	4.196	4.044	4.341	4.043	5-C	4.093	4.122
6-C	3.909	4.108	3.888	4.155	6-C	4.043	4.044
7-C		4.037		4.041	7-C	4.092	4.127
8-C		4.107		4.150	8-C	4.049	4.044
9-C		3.889		3.870	9-C	4.036	4.077
10-C		4.063		4.115	10-C	3.994	3.989
2-CH_2	4.552	4.476			1-CH_2	4.424	

charge-distribution patterns are clearly analogous respectively.

The carbon chemical shifts of I, III, V, VII, and VIII3 in THF and HMPA are given in Table 2. In the aromatic carbon shifts, the effect of a change in solvent from THF to HMPA, that is, the upfield shift induced by a change to a more polar solvent, is large on the 5-carbons of I and V, the 6-carbons of III and VII, and the 4-carbon of VIII3. The variation in the shift of V is similar to that of I, and those of VII and VIII3 are larger than and similar to that of III respectively. In addition, the ^{7}Li resonances for V, VII, and VIII3 in THF and HMPA are found in a range (0—$\pm$0.5 ppm) similar to those for I and III.[1] Therefore, two kinds of anions with lithium as a counter ion have essentially the same ion-pair structure, that is, V—VII, as well as I—II,[1] are present in THF as tight ion pairs in which the anion-cation interaction takes place mainly at the ring nitrogen and so are III—IV. In the case of V—VII, it is reasonable to regard the ring nitrogen as the site where the anion-cation interaction takes place mainly in view of the process of formation.

In conclusion, a series of anions, termed picolyl-type carbanions, with lithium as a counter ion in THF have basically three characteristics as follows: (1) This ionic species is formed by metal-proton exchange at a specific methyl group of the starting material and its methylene carbon is virtually sp^2-hybridized; (2) this ionic species is a charge-delocalized one and the total electron densities on the carbons can be estimated from the ^{13}C chemical shifts, that is, the observed chemical shifts are linearly related to the calculated electron densities; and (3) this ionic species is present as a tight ion pair in which the anion-cation interaction takes place mainly at the ring nitrogen. In view of these characteristics, I—IV can be regarded as picolyl-type carbanions, but V—VII are ionic species having the second and the third terms of the characteristics on picolyl-type carbanions.

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