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s-*cis*-(*Z*,*Z*) Structure of 1,2-Bis(2-pyridyl)ethylene Dianion in Solution

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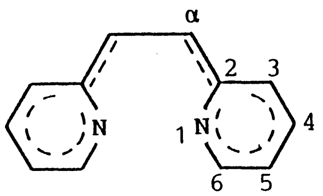
The ^1H, ^7Li and ^{13}C NMR spectra have been observed for the dilithium salt of 1,2-bis(2-pyridyl)ethylene in solution. The dianion in solution exists only one species with fixed s-*cis*-(*Z*,*Z*) configuration in contrast to stilbene dianion.

The structures of delocalized hydrocarbon anions have been extensively studied.1) A little is known, however, concerning the structure and behavior of 1,2-diarylethylene dianions in solutions. In previous papers, we reported that in stilbene and triphenylethylene dianions the configurations around the ethylenic bonds of the dianions are not fixed but the rotations about the bonds occur at room temperature.2) Little information is also available about structures of heteroatom containing analog dianions. In the alkali metal salts of 2-ethylpyridine the partial double bond character of the Cα-C2 bond leads to the occurrence of *E* and *Z* isomers.3c) Thus, we attempt to study the structure of 2-pyridyl containing 1,2-diarylethylene dianions by NMR spectroscopy. The preparation of the dilithium salt of 1,2-bis(2-pyridyl)ethylene **1** and procedures employed in this study are similar to those described in the previous papers.2b,c)

Typical ^1H and ^{13}C NMR spectra of the dianion **1** are shown in Fig. 1. There are five and six signals for **1** in the ^1H and ^{13}C NMR spectra, respectively. The 2-pyridyl ring proton signals have fine structures with the coupling constants of 4.6 - 9.0 Hz. The NMR parameters for the dianion **1** are compiled in Tables 1 and 2 together with the data of the precursor, *trans*-1,2-bis(2-pyridyl)ethylene **1a**. The assignments were confirmed by the 2D NMR spectra observed at several temperatures.



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The tendency of upfield shift changes caused by conversion of neutral precursor into dianion is consistent with the general trend observed in 2-picolyl type carbanions.3) It should be noted, however, that the charge demand of 2-pyridyl group in the dianion **1** is larger than that in lithio-2-ethylpyridine.3b,c) The excess charge on $C\alpha$ at 27 ℃ is estimated from ^{13}C chemical shifts to be 0.276*e* for **1** but for the stilbene dianion, 0.436*e*.2c,4) In addition, the $C\alpha$-$H\alpha$ coupling constants of 144-146 Hz indicate sp^2 hybridization for $C\alpha$.3c) These facts suggest that the double-bond character between the benzylic carbon and 2-pyridyl group is significantly large, and the rotation about the bond is restricted on the NMR time scale as well as picolyl type carbanions.3)

As for the dianion **1**, there are six possible isomers; i.e., *cis*- and *trans*-(*E*,*E*), (*E*,*Z*) and (*Z*,*Z*) geometries. It can be understood directly from the

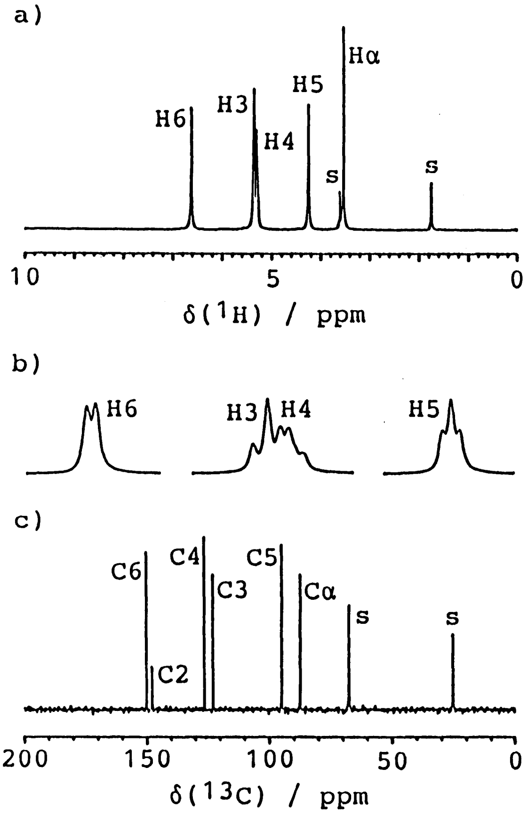

Fig. 1. NMR spectra of **1**: a,b) ^1H spectra at -30 ℃; c) ^{13}C spectrum at 27 ℃.

Table 1. ^1H NMR Data of The Dianion **1** and Its Precursor **1a**

			Chemical Shifts/ ppm a)					Couplings/ Hz b)
Compd.	Solvent	Temp /℃	H3	H4	H5	H6	$H\alpha$	$^3J_{\alpha\alpha'}$
1	THF-d_8	26	5.47	5.47	4.38	6.71	3.61	7.7
		0	5.43	5.43	4.34	6.68	3.59	8.0
		-30	5.41	5.37	4.30	6.65	3.56	8.2
		-70	5.37	5.31	4.25	6.62	3.53	8.4
	THF	26	5.47	5.47	4.38	6.67	c)	c)
1a	THF-d_8	26	7.49	7.70	7.18	8.61	7.81	15.6
	$CDCl_3$	26	7.42	7.66	7.15	8.62	7.71	15.6

a) The chemical shifts were measured for 0.3 mol dm^{-3} solutions in THF-d_8 or THF relative to the more shielded residual solvent peak, which is taken as 1.75 or 1.79 ppm from TMS, respectively. b) Measured from the ^{13}C satellite spectra with accuracy of ±0.3 Hz. c) Not available due to overlapping with a large solvent peak.

Table 2. ^{13}C NMR Data of The Dianion 1 and Its Precursor 1a

			Chemical Shifts/ ppm[a]						Couplings/ Hz[b]
Compd.	Solvent	Temp/℃	C2	C3	C4	C5	C6	Cα	$^1J(C\alpha H\alpha)$
1	THF-d_8	27	147.8	122.8	126.3	95.0	150.1	87.5	146
		-30	145.8	124.2	125.5	94.8	150.2	89.5	145
		-70	143.7	124.0	124.0	93.7	149.3	89.4	144
	THF	27	147.7	122.7	126.3	95.0	150.0	87.5	146
1a	THF-d_8	27	156.3	123.7	137.1	123.2	150.7	132.8	158
	$CDCl_3$	27	155.0	123.3	136.7	122.6	149.7	131.7	158

a) The chemical shifts were measured in THF-d_8 or THF relative to the more shielded solvent peak, which is taken as 25.4 or 26.4 ppm from TMS, respectively. b) With accuracy of ±1 Hz.

NMR spectra, however, that the dianion has either a symmetrical configuration (*E*,*E*) or (*Z*,*Z*). In order to determine the configuration about the C2-Cα bond, the spin-decoupling $^1H\{H\alpha\}$[3b,c] and the NOE experiments were carried out at -48.9 ℃, because at this temperature the H3 and H4 signals in the carbanion separated out. The homo-spin-decoupling experiments showed that H4 is not coupled to Hα in the dianion **1**. The NOE experiment was performed by irradiating Hα; there was a clear enhancement of the H3 (13%). The value of NOE corresponds to the interatomic distance between Hα and H3 by 2.7 Å.[5] These results support that the configuration of the C2-Cα bonds is a *Z*-geometry.

As shown in Table 1, the vicinal coupling constant $^3J_{\alpha\alpha'}$ of the neutral precursor **1a** is 15.6 Hz and confirms that **1a** has a *trans* configuration. For the dianion **1**, on the other hand, the coupling is about 8 Hz over the temperature range -70 to 27 ℃, suggesting that the configuration around the central Cα-Cα' bond of **1** is s-*cis*. Therefore, we conclude that configurations of both C2-Cα and Cα-Cα' bonds in **1** are fixed at least below room temperature, and that the structure of the dianion in solution has the s-*cis*-(*Z*,*Z*) geometry.

The *Z*-configuration around the partial double bond between the carbanionic carbon and the 2-pyridyl ring in the dianion **1** is opposite to that of the carbanion of 2-ethylpyridine,[3b,c] but consistent with that of the carbanion of 2-benzylpyridine.[3a] The s-*cis*-geometry of the central bond in **1** is similar to the Cβ-Cβ' bond for 1,4-diphenyl-1,3-butadiene dianion.[6] Further, comparison with the structure of stilbene dianion[2c] leads to the idea which the characteristic structural feature of **1** is caused by the presence of two nitrogen atoms in the 2-pyridyl groups.[7] It can therefore be presumed that the dianion **1** possesses the doubly bridging interactions between the 2-pyridyl nitrogen atoms and the lithium cations.

Although the ^{7}Li signal of 1 moved slightly upfield by 0.31 ppm in the temperature range from +50 to -70 ℃, no splitting of the signal was observed. This is considered to indicate that the dilithium salt 1 prefers C_2-symmetry, and that the nature of the bonding between nitrogens and lithium atoms of 1 is essentially ionic. MNDO calculations have also predicted that the twisted s-*cis*-(*Z*,*Z*) structure is the most stable among the four C_2 symmetrical isomers. The interatomic distance between Hα and H3 for the calculated structure is 2.63 Å, showing good agreement with the evaluated distance from the NOE experiments.

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