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A Direct NMR Observation of Stilbene Dianion in Solution

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The NMR spectra of stilbene dianion have been observed in solution. The dianions derived from cis- and trans-stilbene are identical and only one species exists in solution even at -70℃. From the vicinal coupling constant $^3J_{\alpha\alpha'}$, it is concluded that the configuration around the central bond C_α-$C_{\alpha'}$ of the dianions is not fixed at the trans-form but the rotation about the bond occurs.

Stilbene is a representative aryl ethylene and its dianion is one of the interesting species from its electronic and structural view points. Stilbene dianion has been studied by electronic spectra[1,2] and X-ray.[3] The X-ray studies of dilithium salts solvated by tetramethylethylenediamine and pentamethyldiethylenetriamine claimed that the anions in these salts are planar and have trans configurations. From their electronic spectra, it has been deduced that the geometry of stilbene dianion is in a trans-form with coplanar phenyl rings in solution. The stilbene dianion has been considered as an intermediate in the cis-trans isomerization in stilbene catalyzed by electron transfer agents.[2,4]

Recently, Schenk et al. reported on the NMR parameters of 3,5-di-tert-butylstilbene dianion.[5] However, no direct NMR study of stilbene dianion itself has been performed yet. We have succeeded, more recently, in the NMR observation of the spectra of stilbene dianion S^{2-} in solution.

The dianions were prepared as follows. The starting hydrocarbon, cis- **CS** or trans-stilbene **TS**, dissolved in dried and degassed THF-d_8 was contacted with lithium metal in a vacuum at room temperature. After standing for one or two days at room temperature, the dark red solution was filtered and sealed in an NMR tube. The solutions appear to be stable for a long time in a freezer. In order to identify chemically the species in the solution, the lithium salts were quenched by water and D_2O. The quenched product was shown to have a structure consistent with 1,2-diphenylethane, based on its NMR parameters($CDCl_3$,TMS): $\delta_C(CH_2)=37.8$, $\delta_H(CH_2)=2.87$; $\delta_C(CHD)=37.6$, $^1J_{CD}=20.3$, $\delta_H(CHD)=2.88$.

Table 1. ^{1}H NMR Data of Stilbene Dianions and Their Precursors at 400 MHz

		Chemical shifts/ppm[a)]				Coupling/Hz[b)]
Compd.	Temp/℃	ortho	meta	para	α	$^3J_{\alpha\alpha'}$
TS^{2-}	27[c)]	5.02	5.88	4.71	2.96	--[d)]
		5.73	6.21			
	-50	4.96	5.73	4.52	3.06	11.0
		5.55	6.06			
CS^{2-}	27	5.02	5.88	4.72	2.96	10.2
		5.73	6.21			
	-50	4.95	5.73	4.52	3.05	10.9
		5.55	6.06			
TS	27	7.57	7.35	7.24	7.21	16.4
CS	27	(7.18	-	7.29)	6.63	12.4

a) The chemical shifts were measured for ca. 0.1 mol dm^{-3} solutions in THF-d_8 relative to the more shielded residual solvent peak, which is taken as 1.75 ppm from TMS. b) Measured from the ^{13}C satellite spectra with accuracy of ±0.3 Hz. c) Broad signals at this temperature due to existence of trace amount of radical species. d) Not available because of broad signals.

Table 2. ^{13}C Chemical Shifts of Stilbene Dianions and Their Precursors[a)]

		Assignments				
Compd.	Temp/℃	ipso	ortho	meta	para	α
TS^{2-}	27	140.7	103.0 117.9	127.7 131.6	97.7	59.7
CS^{2-}	27	140.7	103.0 117.8	127.7 131.6	97.6	59.8
TS	27	138.6	127.4	129.4	128.3	129.5
CS	27	138.3	129.7	129.0	127.9	131.1

a) The chemical shifts were measured for ca. 0.1 mol dm^{-3} solutions in THF-d_8 relative to the more shielded residual solvent peak, which is taken as 25.4 ppm from TMS.

The NMR data of the dianions are given in Tables 1 and 2 together with the data of their precursors. Important aspects on the configuration and electronic structure of stilbene dianion S^{2-} have been derived from the NMR parameters in Tables 1 and 2. First, the dianions resulting from the reduction of the cis and the trans isomer, CS^{2-} and TS^{2-} respectively, are identical. Only one species S^{-2} exists in the solution, even at -70 ℃. The vicinal coupling constant of this dianion $^3J_{\alpha\alpha'}$ is about 11 Hz and very close to the average of cis (8.6 Hz) and trans (15.2 Hz) vicinal couplings of allyl anions.[6)] It is concluded that in solution the configuration around the central bond of S^{2-} is not fixed at the trans-form but the rotation occurs about the C_α-$C_{\alpha'}$ bond in the NMR time scale. Second is on the conformation of phenyl rings. The proton and carbon chemical shifts of two ortho and meta positions of a phenyl ring of S^{2-} are nonequivalent, indicating that the rotation about the C_α-C_{ipso} bond is restricted even at room temperature. This fact shows that the rotational barrier is higher than those of the related carbanions, such as 1,4-diphenyl-1,3-butadiene dianion.[7a,c)] Third point is tendency of carbon shift changes caused by the conversion of hydrocarbons into dianions. This tendency of the upfield shift changes except for the downfield shift changes of ipso-carbon, is consistent with the general trend observed in other carbanions.[6,7] It should be noted, however, that the downfield shift changes of ipso-carbons (ca. 2 ppm) significantly differ from those of benzyl anion (ca. 20 ppm)[8] and 1,4-diphenyl-1,3-butadiene dianion (ca. 8 ppm).[7a,c]

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