$(CH_3)_3$ in benzene, relative to the aqueous LiBr external standard, are −1.36, −1.00, and −0.53 p.p.m., respectively.

The molecular weight of lithiomethyltrimethylsilane in benzene was determined by freezing point lowering.[6] The results are as follows, where $\bar{n}$ represents apparent degree of association.

m (as monomer)	$\bar{n}$	m (as monomer)	$\bar{n}$
0.0566	3.91	0.360	4.05
0.145	3.98	0.489	4.28

It is apparent that the compound is highly associated in benzene at about 6°, even to fairly low concentrations. There is some evidence in the data for a concentration dependence of $\bar{n}$, but the predominant species in solution is probably tetramer.

The discrepancy between these data and the result reported by Connolly and Urry might be due to a temperature difference; their isopiestic measurement was performed at room temperature.[8] The ^{7}Li n.m.r. results reported above were obtained at room temperature, however, and the concordance of the ^{7}Li chemical shifts for lithiomethyltrimethylsilane and n-butyllithium are an indication that the lithium atoms are in similar chemical environments.[9] It is our conclusion, therefore, that lithiomethyltrimethylsilane behaves normally, *i.e.*, that it forms electron-deficient polymeric species as do other alkyllithium compounds. At the same time, the steric effect of the trimethylsilyl group is evident, in that a tetramer rather than hexamer predominates in solution.

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(8) Dr. G. Urry, private communication.

(9) Ebulliometric measurements also indicate a tetrameric association: R. H. Baney and R. J. Krager, *Inorg. Chem.*, **3**, 1657 (1964).

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RECEIVED JUNE 29, 1964

The Nature of Lithiomethyltrimethylsilane in Hydrocarbon Solvents

Sir:

Recently Connolly and Urry[1] reported that lithiomethyltrimethylsilane was monomeric in 2-methylpentane. Their finding is in contrast to those for other alkyllithium compounds, which are tetrameric or hexameric in benzene or n-hexane.[2–5] Since this apparently abnormal behavior might be explained by some unusual stabilization of the carbanion portion by $(d\pi-p\pi)$ bonding with the adjacent silicon atom, thus reducing the tendency to associate, we undertook to re-examine these results.

TABLE I

Benzene (b.p. 80°)			2-Methylpentane (b.p. 60°)		
Molality (as monomer)	Molality (measured)	App. deg. of assn.	Molality (as monomer)	Molality (measured)	App. deg. of assn.
0.58	0.166	3.5	0.20	0.047	4.3
0.79	0.193	3.9	0.39	0.094	4.1
1.45	0.355	4.1	0.44	0.145	3.0
1.75	0.438	4.0	0.76	0.184	4.1
1.82	0.436	4.2	0.80	0.195	4.1
2.78	0.637	4.3	0.84	0.229	3.7
	Av.	4.0	0.87	0.210	4.1
			1.04	0.270	3.9
			1.10	0.291	3.8
			1.23	0.324	3.8
				Av.	3.9

Crystalline lithiomethyltrimethylsilane was prepared by the reaction of chloromethyltrimethylsilane with lithium in 2-methylpentane under an argon atmosphere by a procedure similar to that of Connolly and Urry.[1] The compound was then isolated from solution and purified by vacuum sublimation.

The ultraviolet spectrum of a dilute isooctane solution of $LiCH_2Si(CH_3)_3$ examined on a Cary Model 14 recording spectrophotometer revealed no absorption maxima above 200 mμ. This lack of any significant bathochromic shift suggests that there is no extensive delocalization of the electron pair on the carbanion.

The molecular weight of $LiCH_2Si(CH_3)_3$ was determined ebulliometrically in benzene and 2-methylpentane following the procedure of Weiner, Vogel and West.[2] Table I summarizes the results.

It is evident that lithiomethyltrimethylsilane is highly associated in both benzene and 2-methylpentane at their boiling points. Results by Hartwell and Brown on freezing-point lowering of benzene solutions confirm the tetrameric association.[6] The change in polarity in going from benzene to 2-methylpentane has little effect upon the degree of association. The apparent slight concentration dependence of the degree of association in benzene most likely is coincidental, since the same degree of association is observed at the boiling and freezing points of benzene. The trend, even if real, would not account for the results of Connolly and Urry[1] at 0.24 m (as monomer) since extrapolation to infinite dilution gives a degree of association still considerably greater than three. Likewise, the apparent discrepancy cannot be explained by a temperature difference since the isopiestic measurements of Connolly and Urry[1] were made at room temperature, intermediate between the ebulliometric and cryoscopic measurements. It seems evident that if $(d\pi-p\pi)$ bonding between the carbanion and silicon atom in lithiomethyltrimethylsilane does exist, it has little effect on the ultraviolet spectrum or on the degree of association in hydrocarbon solvents.

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(1) (a) J. W. Connolly and G. Urry, *Inorg. Chem.*, **2**, 645 (1963); (b) J. W. Connolly, Ph.D. Thesis, Purdue University, 1963.

(2) M. Weiner, G. Vogel, and R. West, *Inorg. Chem.*, **1**, 654 (1962).

(3) T. L. Brown, D. W. Dickerhoof, and D. A. Bafus, *J. Am. Chem. Soc.*, **84**, 1371 (1962).

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(5) T. L. Brown, R. L. Gerteis, D. A. Bafus, and J. A. Ladd, *J. Am. Chem. Soc.*, **86**, 2135 (1964).

(6) G. E. Hartwell and T. L. Brown, *Inorg. Chem.*, **3**, 1656 (1964).

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RECEIVED AUGUST 10, 1964