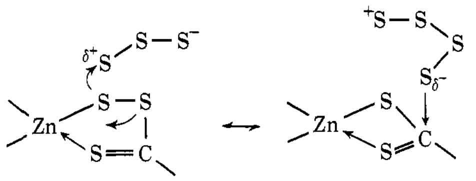
zinc dithiolates generally function as accelerators for sulfur addition to olefins by creating labile, nucleophilic (or electrophilic), active disulfide sulfur. While "sulfur-rich" metal xanthates or dithiocarbonates have not been isolated to date, there is no reason to believe that such materials cannot be formed.

As a final point, it is possible that the mass spectral results are directly related to the nmr kinetic data in the zinc dithiolate system. If the rapid sulfur atom exchange between ligands also produces the sulfur atom scrambling, it is apparent that the activation energy associated with the insertion of sulfur into the C–S bond of the dithiolate ligand is very small. The activation energy of ~5 kcal/mol for the exchange process is not very different from the activation energy of the reaction of NiL_2S with triphenylphosphine (~8 kcal/mol). This latter process requires P–S bond formation as well as C–S and S–S bond rupture leading to the transition state. The low activation energy suggests that C–S bond formation also occurs (eq 9). A related type of mechanism is possible for the sulfur atom exchange (eq 10), although the exchange may be intramolecular at low concentrations.



(10)

Acknowledgments. The support of the National Science Foundation, GP-11701, the National Institutes of Health, AM-13558, and the donors of the Petroleum Research Fund, PRF-3201-AC3, is gratefully acknowledged for various parts of this study. James A. Smith, Dominic Hunt, and Alex Avdeef also are recognized for their contributions to some of these studies.

π Groups in Ion Pair Bonding. Triphenylmethyllithium Tetramethylethylenediamine

J. J. Brooks and G. D. Stucky*

Contribution from the School of Chemical Sciences,
Department of Chemistry, and the Materials Research Laboratory,
University of Illinois, Urbana, Illinois 61801. *Received January 10, 1972*

Abstract: The stereochemistry of the triphenylmethyl carbanion has been determined in the crystalline complex, triphenylmethyllithium tetramethylethylenediamine, $(C_6H_5)_3C^-Li^+(CH_3)_2N(CH_2)_2N(CH_3)_2$, from three-dimensional X-ray data collected by counter methods. The crystallographic parameters are: a = 8.546 (2), b = 16.171 (3), c = 16.999 (3) Å; β = 106.75 (2)° at 22°; $P2_1/c, Z = 4$ with a calculated density of 1.07 g/cc. Each lithium atom is coordinated to two nitrogen atoms of the bidentate chelate and to one π carbanion. The $(C_6H_5)_3C^-$ group has C_6H_5–C(1)–C_6H_5 bond angles of 117.0 (6), 122.8 (7), and 118.3 (6)°, suggesting predominantly sp^2 hybridization for the central carbon atom, C(1). The twist angles of the phenyl rings depend on their interaction with the lithium atom, with the smallest twist angle being observed for the phenyl ring with the closest lithium–carbon atom contacts. Geometrical features are consistent with greater π-electron delocalization between the benzylic carbon atom and the two phenyl groups which exhibit smaller twist angles. The lithium atom is not located directly over C(1) but has four close contacts to the carbanion, 2.23 Å to C(1), 2.49 and 2.51 Å to two carbon atoms on one phenyl group, and one close contact of 2.54 Å to one carbon atom of a second phenyl group. A correlation is noted between carbanion stability and metal–nitrogen atom distances in organometallic complexes containing coordinated nitrogen base molecules.

The triphenylmethyl moiety can be stabilized as a carbonium ion, radical, or carbanion. The stabilization of these species is the result of delocalization attained through π-type interactions, with the maximum delocalization being obtained when the phenyl groups are coplanar with the methyl carbon atom. However, it is sterically impossible for the triphenylmethyl group to attain a planar conformation. Lewis and coworkers[1] and Seel[2] were the first to suggest twisted phenyl rings in triphenylmethyl and diphenylmethyl molecules. Two types of twisted geometries were suggested:[1] (1) the symmetrical propeller geometry in which each of the phenyl rings is twisted by some angle θ from the mean plane of the four central carbons, and (2) the nonsymmetrical form in which one of the three rings is twisted in the opposite direction to the other two. The present consensus is that the propeller geometry is more favorable.

Calculations based on van der Waals radii[2,3] and spectral evidence[4] produced predictions of twist angles of from 20 to 30° for the radical species. Vapor-phase electron diffraction studies[5] of the triphenylmethyl radical showed a twist angle of approximately 45°. Crystallographic studies of the tri-*p*-nitrophenylmethyl radical[6] gave twist angles of 40, 30, and 30° for the phenyl rings.

---

(1) G. N. Lewis, T. M. Magel, and D. Lipkin, *J. Amer. Chem. Soc.*, **64**, 1774 (1942).

(2) F. Seel, *Naturwissenschaften*, **31**, 504 (1943).

(3) M. Szwarc, *Discuss. Faraday Soc.*, **2**, 39 (1947).

(4) F. C. Adam and S. I. Weissman, *J. Amer. Chem. Soc.*, **80**, 2057 (1958).

(5) P. Andersen, *Acta Chem. Scand.*, **19**, 629 (1965).

(6) P. Andersen and B. Klewe, *ibid.*, **21**, 2599 (1967).

The carbonium ion case has been equally well investigated. Calculations based on van der Waals radii[7-9] and nmr studies[10,11] predict twist angles of from 23 to 30°. Various crystal structures[12-14] have helped to confirm the predicted angles.

In contrast to the radical and carbonium ion species, the triphenylmethyl carbanion has received only sparing attention. An nmr study by Sandel and Freedman[13] offers no information on the twist angle. A recent study[14] based on extended Hückel calculations and potential energy curves predicts an equilibrium twist angle of 35 ± 2° for the phenyl rings in the triphenylmethyl carbanion. No structural information concerning the triphenylmethyl carbanion is available.

In addition, little is known about the coordination of a triphenylmethyl moiety with metals. King[15] has suggested that the nickel atom is coordinated in a π-benzylic fashion in bistriphenylmethylnickel. Sandel and Freedman[13] made no attempt to predict structures on the basis of their nmr studies of alkali metal–triphenylmethyl complexes. They did report that, unlike the fluorenyl spectrum, the triphenylmethyl spectrum is neither solvent nor cation sensitive. On this basis they concluded that in solution the alkali triphenylmethyls are completely ionized.

In an attempt to provide structural information about the triphenylmethyl carbanion and to examine the metal–triphenylmethyl interaction, the single-crystal X-ray analysis of triphenylmethyllithium *N,N,N′N′*-tetramethylethylenediamine was undertaken.

Experimental Section

Triphenylmethyllithium *N,N,N′,N′*-tetramethylethylenediamine was prepared in an argon atmosphere drybox by adding 2 mmol each of *n*-butyllithium and *N,N,N′,N′*-tetramethylethylenediamine to 30 ml of hexane containing 2 mmol of triphenylmethane.[16] The resulting dark-red solution was filtered and allowed to stand overnight. Large glistening red needles up to 1 cm in length grew from the solution and suitable single crystals were found for X-ray analysis without further purification. Preliminary precession photographs showed the crystals to be monoclinic with systematic absences $0k0$, $k = 2n + 1$ and $h0l$, $l = 2n + 1$. These absences uniquely determine the space group $P2_1/c$. A second crystal was chosen for data collection and aligned so that the crystal was rotated about the [102] direction which was an easily accessible zone axis in preliminary photographs. The crystal dimensions (0.99 × 0.36 × 0.29 mm) were large by ordinary X-ray standards, but since absorption corrections were not large for this system, we felt that the added intensity gained from a large crystal was advantageous. Care was taken to ensure that all the crystal was in the X-ray beam at all times. Several ω scans gave an average peak width at half-height of 0.15°, indicating that the mosaicity of the crystal was sufficiently small for data collection. Twelve reflections were carefully centered on a Picker four-circle diffractometer and used in a least-squares refinement of the lattice parameters ($T = 23°$, $\lambda = 1.54178$ Å). The values obtained were: $a = 8.546$ (2), $b = 16.171$ (3), $c = 16.999$ (3) Å; and $\beta = 106.75$ (2)°. No accurate density measurement could be obtained by the flotation method due to the sensitivity of the crystals to various solvent systems used. A density of 1.07 g/cc was calculated assuming four molecules of $(C_6H_5)_3CLi[(CH_3)_2N(CH_2)_2N(CH_3)_2]$ per unit cell and this is a reasonable value for the density based on our past experience with similar organolithium compounds.

Diffraction data were collected on a fully automated Picker four-circle diffractometer using Cu Kα radiation filtered by a 0.0005-in. nickel foil filter. Data were collected using the θ-2θ scan technique with a scan width of 1.3° and a scan rate of 1.0°/min. A takeoff angle of 2.7° and pulse height analyzer settings of 3.0 and 8.0 for the lower and upper level discriminators, respectively, were used. Stationary counter–stationary crystal background counts of 10 sec were taken before and after each peak. Crystal and diffractometer stabilities were monitored by measuring two standards every 40 reflections and no systematic drift was observed in these standards during data collection.

All the accessible copper sphere of data to $2\theta_{max} = 105°$ was collected in order to obtain four independent forms of data. A total of approximately 12,000 reflections were measured of which about 70% were observed. Lorentz–polarization corrections were made to the raw data and the observed structure factor amplitudes, F_o, were obtained using a local program, TPRD. An absorption calculation with the program ORABS[17] ($\mu = 4.68$ cm^{-1}) for reflections which represented the extremes of absorption revealed that the maximum variation in the transmission factors was about 5% and confirmed that no absorption correction was necessary.

For the initial structure solution and refinement, only the observed reflections of one form of data (hkl and $hk\bar{l}$) were used. An averaged data set (2066 independent reflections) of all the equivalent observed reflections in the copper sphere was used in the final refinement with a weighting scheme based on population statistics.[18] A test of the weights showed no systematic variation of $w(F_o - F_c)^2$ with either the magnitude of the structure factors or with $\sin \theta/\lambda$.

The scattering factors for C^0, N^0, and Li^0 were taken from the compilation of Hanson, *et al.*,[19] while the hydrogen scattering factors were those of Stewart, *et al.*[20] The structure was solved using the symbolic addition procedure.[21] A calculation based on the positions of the 13 atoms located from the first E map was used to calculate a Fourier map which subsequently revealed the positions of three of the carbon atoms of the third phenyl ring. A second Fourier calculation was used to locate seven atoms which constituted part of the *N,N,N′,N′*-tetramethylethylenediamine group. It was also noted at this point that the electron density defining the tetramethylethylenediamine (TMEDA) appeared to be smeared over a large region. The remaining three carbon atoms of the third phenyl ring were located by a reexamination of the original E map and the comparison of peaks on the two Fourier maps. The lithium atom, along with peaks which could be assigned to complete the TMEDA group, was located from a third Fourier synthesis and completed positional assignments for all 28 nonhydrogen atoms in the asymmetric unit. Several cycles of least-squares refinement of the positional parameters confirmed earlier problems with the TMEDA group indicating that the carbon atoms, but not the nitrogen atoms, were disordered, so that the disorder could be described in terms of a rotation about the two nitrogen atom–lithium atom vectors (Figure 1). This corresponds to an interconversion between the two puckered configurations of the *N,N,N′,N′*-tetramethylethylenediamine group.

A rigid group refinement of the TMEDA group was used in order to get the best fit of the data with reasonable bond lengths. Four groups were constructed using the averaged models of ethylenediamine groups taken from the bisethylenediamine lithium bromide and bisethylenediamine lithium chloride structures of Durant.[22] Each group consisted of the one methylene carbon atom and

---

(7) D. W. A. Sharp and N. Sheppard, *J. Chem. Soc.*, 675 (1957).

(8) N. C. Deno, J. J. Jaruzelski, and A. Schriescheim, *J. Org. Chem.*, **19**, 155 (1954).

(9) N. C. Deno, P. T. Groves, and G. Saines, *J. Amer. Chem. Soc.*, **81**, 5790 (1959).

(10) D. E. O'Reilly and H. P. Leftin, *J. Phys. Chem.*, **64**, 1555 (1960).

(11) R. S. Berry, R. Dehl, and W. R. Vaughan, *J. Chem. Phys.*, **34**, 1460 (1961).

(12) A. H. Gomes de Mesquita, C. H. MacGillavry, and K. Eriks, *Acta Crystallogr.*, **18**, 437 (1965).

(13) V. R. Sandel and H. H. Freedman, *J. Amer. Chem. Soc.*, **85**, 2328 (1963).

(14) R. Hoffmann, R. Bissell, and D. Farnum, *J. Phys. Chem.*, **73**, 1789 (1969).

(15) R. B. King, *Organometal. Chem. Rev., Sect. B*, **3**, 403 (1967).

(16) A. W. Langer, Jr., U. S. Patent 3,541,149 (Nov 17, 1970).

(17) D. J. Wehe, W. R. Busing, and H. A. Levy, "ORABS, A Fortran Program for Calculating Single Crystal Absorption Corrections," USAEC Report ORNL-TM-229, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(18) D. A. Matthews, Doctoral Dissertation, University of Illinois, 1971.

(19) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).

(20) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(21) W. H. Zachariesen, *Acta Crystallogr.*, **5**, 68 (1952).

(22) P. F. Durant, P. Piret, and M. Van Meerssche, *ibid.*, **23**, 780 (1967).

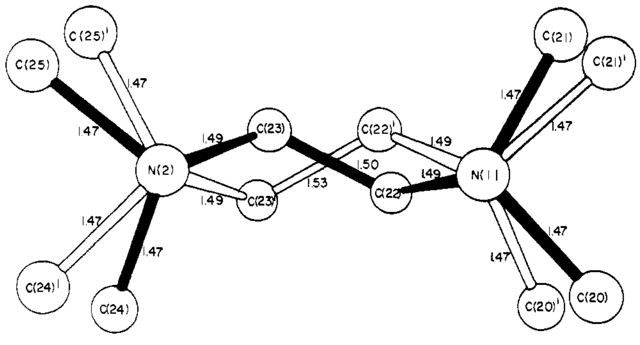


Figure 1. Disordered model of *N,N,N',N'*-tetramethylethylenediamine used in rigid group refinement of $(C_6H_5)_3CLi[(CH_3)_2N(CH_2)_2N(CH_3)_2]$.

the two methyl carbon atoms that are bonded to each of the nitrogen atoms in TMEDA and all the hydrogen atoms associated with these three carbon atoms. Each of these group atoms was given the weight of one-half of an atom. The nitrogen atoms were not placed in the rigid groups and the origins of the groups were fixed at the nitrogen atom positions during refinement so that only the Scheringer[23] angles were allowed to vary. Using this method, the methylene carbon atom–methylene carbon atom bond length was the only bonded-atom TMEDA distance which was free to refine. Repeated cycles of full anisotropic refinement of the triphenylmethyllithium moiety and the two nitrogen atoms and refinement of the Scheringer angles of the rigid groups gave $R_2 = 0.117$.

It was felt that disordering of the TMEDA group should not greatly affect the bond lengths and angles in the triphenylmethyllithium group. In order to test this hypothesis, a least-squares refinement of the positional and isotropic temperature parameters of the disordered TMEDA group was performed while the remainder of the structure was held constant. Three cycles of this refinement starting with the rigid body disordered model resulted in convergence at $R_2 = 0.076$. The remainder of the structure was then allowed to refine anisotropically (Tables I and II) and gave final values $R_1 = 0.063$ and $R_2 = 0.068$. A comparison of the bond distances (Table III) and bond angles (Table IV) of the tirphenylmethyllithium moiety for the group and nongroup refinements showed that the nongroup results are within two standard deviations of the group results with standard deviations on the order of 0.01 Å for the nongroup refinement. The chemically unreasonable bond lengths obtained for the TMEDA group (Table V) with the nongroup refinement suggests that little can be said about the bond lengths or angles in the TMEDA group. However, the nongroup refinement does give a better fit of the data and does allow an evaluation of the effect of the disorder on the geometry of the most interesting part of the molecule, the triphenylmethyl carbanion. The discussion of the structure will be based on the values of the standard deviations obtained from the nongroup refinement.[24]

Discussion

Triphenylmethyl Carbanion. The molecular structure (Figure 2) can be described as a contact ion pair consisting of the triphenylmethyl carbanion and a lithium cation coordinated to a TMEDA group. Each of the three phenyl rings of the triphenylmethyl carbanion is planar within experimental error (planes 2, 3, and 4, Table VI), although only one benzyl fragment is planar (plane 2, Table VI). The C(2)–C(1)–C(8), (C2)–C(1)–C(14), and C(8)–C(1)–C(14) angles of 117.0 (6), 122.8 (7), and 118.3 (6)° clearly indicate the sp^2 character of C(1) even though C(1) is 0.12 Å out of the plane of the three carbon atoms (C(2), C(8), and C(14) of the phenyl rings. The triphenylmethyl carbanion has the propeller geometry with the twist angles of the three phenyl rings from the plane of the three-point carbon atoms varying in order of their interaction with the lithium cation. The twist angles for the C(14), C(2), and C(8) phenyl rings are 19.7, 30.6, and 44.8°, respectively. As mentioned earlier, a theoretical value for the equilib-

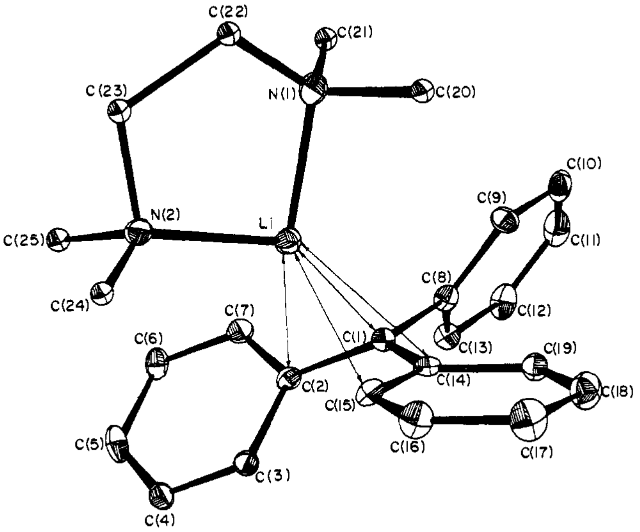


Figure 2. The molecular geometry of $(C_6H_5)_3CLi[(CH_3)_2N(CH_2)_2N(CH_3)_2]$.

Table I. Final Positional Parameters of the Nonhydrogen Atoms for the Nongroup Refinement of $(C_6H_5)_3CLi[(CH_3)_2N(CH_2)_2N(CH_3)_2]$

Atom	*x*	*y*	*z*
Li	0.4800 (6)	0.2692 (3)	0.4308 (3)
C(1)	0.7390 (3)	0.3095 (2)	0.4807 (2)
C(2)	0.7049 (3)	0.3528 (2)	0.4021 (2)
C(3)	0.7475 (4)	0.3222 (2)	0.3337 (2)
C(4)	0.7140 (4)	0.3657 (2)	0.2599 (2)
C(5)	0.6357 (5)	0.4409 (2)	0.2510 (2)
C(6)	0.5928 (4)	0.4732 (2)	0.3163 (2)
C(7)	0.6259 (4)	0.4305 (2)	0.3894 (2)
C(8)	0.7881 (3)	0.3611 (2)	0.5563 (2)
C(9)	0.7406 (4)	0.3425 (2)	0.6270 (2)
C(10)	0.7908 (5)	0.3885 (2)	0.6990 (2)
C(11)	0.8913 (5)	0.4562 (2)	0.7014 (2)
C(12)	0.9400 (5)	0.4764 (2)	0.6331 (2)
C(13)	0.8887 (4)	0.4299 (2)	0.5618 (2)
C(14)	0.7669 (3)	0.2212 (2)	0.4886 (2)
C(15)	0.6978 (4)	0.1648 (2)	0.4239 (2)
C(16)	0.7192 (5)	0.0802 (2)	0.4327 (2)
C(17)	0.8137 (6)	0.0465 (2)	0.5053 (3)
C(18)	0.8838 (5)	0.0993 (2)	0.5696 (3)
C(19)	0.8632 (4)	0.1839 (2)	0.5619 (2)
N(1)	0.3103 (3)	0.2500 (2)	0.4939 (2)
N(2)	0.2954 (3)	0.2472 (1)	0.3212 (1)
C(20)	0.2929 (17)	0.3402 (9)	0.5433 (9)
C(20)'	0.3475 (15)	0.1983 (7)	0.5552 (8)
C(21)	0.3687 (13)	0.1704 (6)	0.5496 (7)
C(21)'	0.2542 (15)	0.3036 (8)	0.5301 (8)
C(22)	0.1502 (10)	0.2561 (5)	0.4313 (5)
C(22)'	0.1718 (9)	0.2015 (5)	0.4261 (5)
C(23)	0.1732 (9)	0.2039 (5)	0.3616 (5)
C(23)'	0.1471 (9)	0.2529 (5)	0.3446 (5)
C(24)	0.3242 (11)	0.1961 (5)	0.2583 (5)
C(24)'	0.2898 (12)	0.3185 (6)	0.2600 (5)
C(25)	0.2349 (12)	0.3230 (6)	0.2833 (6)
C(25)'	0.3094 (11)	0.1683 (5)	0.2778 (5)

---

[23] C. Scheringer, *Acta Crystallogr.*, **16**, 546 (1963).

[24] Tables of the observed and calculated structure factor amplitudes, of the coordinates used for the rigid group refinements, and of the calculated hydrogen atom positions will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-7333. Remit check or money order for \$3.00 for photocopy of \$2.00 for microfiche.

Table II. Thermal Parameters of the Nonhydrogen Atoms for the Nongroup Refinement of $(C_6H_5)_3CLi[(CH_3)_2N(CH_2)_2N(CH_3)_2]$

Atom	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(20)	8.66 (50)[b,c]					
C(20)′	8.34 (32)					
C(21)	6.45 (27)					
C(21)′	8.61 (35)					
C(22)	6.31 (19)					
C(22)′	5.00 (16)					
C(23)	5.96 (19)					
C(23)′	5.37 (18)					
C(24)	5.55 (22)					
C(24)′	6.83 (25)					
C(25)	7.55 (26)					
C(25)′	5.55 (23)					
Li	0.0157 (11)	0.0060 (3)	0.0046 (3)	−0.0005 (4)	0.0024 (4)	−0.0008 (2)
C(1)	0.0141 (6)	0.0034 (1)	0.0037 (1)	−0.0004 (2)	0.0021 (2)	−0.0001 (1)
C(2)	0.0121 (6)	0.0034 (1)	0.0040 (2)	−0.0007 (2)	0.0013 (2)	−0.0002 (1)
C(3)	0.0155 (6)	0.0044 (2)	0.0041 (2)	−0.0004 (2)	0.0022 (3)	0.0000 (1)
C(4)	0.0221 (8)	0.0064 (2)	0.0037 (2)	−0.0016 (3)	0.0027 (3)	−0.0002 (2)
C(5)	0.0296 (10)	0.0059 (2)	0.0045 (2)	−0.0010 (4)	0.0006 (3)	0.0013 (2)
C(6)	0.0258 (9)	0.0046 (2)	0.0056 (2)	0.0013 (3)	0.0011 (3)	0.0008 (1)
C(7)	0.0200 (7)	0.0041 (2)	0.0046 (2)	0.0010 (3)	0.0019 (3)	−0.0002 (1)
C(8)	0.0139 (6)	0.0037 (1)	0.0037 (1)	0.0002 (2)	0.0016 (2)	−0.0002 (1)
C(9)	0.0194 (7)	0.0045 (2)	0.0049 (2)	−0.0006 (3)	0.0030 (3)	−0.0005 (1)
C(10)	0.0252 (9)	0.0064 (2)	0.0041 (2)	0.0034 (3)	0.0024 (3)	−0.0004 (1)
C(11)	0.0288 (10)	0.0052 (2)	0.0051 (2)	0.0027 (4)	−0.0012 (4)	−0.0018 (2)
C(12)	0.0253 (8)	0.0045 (2)	0.0063 (2)	−0.0018 (3)	0.0005 (4)	−0.0006 (2)
C(13)	0.0192 (7)	0.0041 (2)	0.0046 (2)	−0.0017 (3)	0.0020 (3)	−0.0008 (1)
C(14)	0.0129 (6)	0.0036 (1)	0.0040 (2)	−0.0002 (2)	0.0028 (2)	−0.0001 (1)
C(15)	0.0158 (7)	0.0036 (1)	0.0051 (2)	−0.0003 (3)	0.0020 (3)	−0.0006 (1)
C(16)	0.0266 (9)	0.0042 (2)	0.0068 (2)	−0.0005 (3)	0.0025 (4)	−0.0010 (2)
C(17)	0.0380 (12)	0.0035 (2)	0.0088 (3)	0.0008 (4)	0.0046 (5)	−0.0001 (2)
C(18)	0.0310 (10)	0.0050 (2)	0.0060 (2)	0.0029 (3)	0.0031 (4)	0.0016 (2)
C(19)	0.0179 (7)	0.0044 (2)	0.0041 (2)	0.0006 (3)	0.0017 (3)	0.0003 (1)
N(1)	0.0151 (5)	0.0130 (2)	0.0041 (1)	−0.0012 (3)	0.0017 (2)	0.0001 (1)
N(2)	0.0153 (5)	0.0065 (2)	0.0045 (1)	−0.0010 (2)	0.0025 (2)	−0.0015 (1)

[a] The form of the anisotropic ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] The thermal parameters for the carbon atoms of the disordered *N,N,N′,N′*-tetramethylethylenediamine groups were varied isotropically. [c] The form of the isotropic thermal parameters is $\exp[-\beta(\sin^2 \theta/\lambda^2)]$.

Table III. Interatomic Distances (Å) for the Nonhydrogen Atoms[a] in $(C_6H_5)_3CLi[(CH_3)_2N(CH_2)_2N(CH_3)_2]$

Atom	Nongroup distance	Group distance
Li–N(1)	2.060 (10)	2.061 (28)
Li–N(2)	2.096 (9)	2.096 (28)
Li–C(1)	2.227 (8)	2.236 (29)
Li–C(2)	2.511 (13)	2.516 (29)
Li–C(14)	2.488 (10)	2.496 (31)
Li–C(15)	2.541 (9)	2.549 (30)
C(1)–C(2)	1.462 (13)	1.455 (18)
C(1)–C(8)	1.488 (10)	1.500 (18)
C(1)–C(14)	1.448 (9)	1.450 (18)
C(2)–C(3)	1.405 (13)	1.407 (18)
C(2)–C(7)	1.413 (15)	1.411 (18)
C(3)–C(4)	1.393 (8)	1.390 (20)
C(4)–C(5)	1.375 (9)	1.364 (21)
C(5)–C(6)	1.371 (10)	1.364 (22)
C(6)–C(7)	1.378 (11)	1.381 (20)
C(8)–C(9)	1.406 (10)	1.400 (19)
C(8)–C(13)	1.393 (13)	1.396 (19)
C(9)–C(10)	1.391 (9)	1.386 (20)
C(10)–C(11)	1.384 (9)	1.385 (24)
C(11)–C(12)	1.381 (11)	1.386 (22)
C(12)–C(13)	1.385 (11)	1.395 (20)
C(14)–C(15)	1.419 (9)	1.403 (18)
C(14)–C(19)	1.417 (12)	1.420 (18)
C(15)–C(16)	1.383 (9)	1.386 (20)
C(16)–C(17)	1.377 (9)	1.360 (22)
C(17)–C(18)	1.381 (10)	1.385 (22)
C(18)–C(19)	1.379 (10)	1.390 (20)

[a] Errors in the lattice parameters are included in the estimated standard deviations.

Table IV. Bond Angles (deg) for the Nonhydrogen Atoms in $(C_6H_5)_3CLi[(CH_3)_2N(CH_2)_2N(CH_3)_2]$

Atoms	Nongroup angle	Group angle
N(1)–Li–N(2)	88.5 (4)[a]	89.9 (11)
C(1)–Li–C(2)	35.3 (3)	35.0 (6)
C(1)–Li–C(14)	35.2 (2)	35.1 (6)
C(1)–Li–C(15)	63.3 (3)	62.9 (8)
C(14)–Li–C(15)	32.8 (2)	32.3 (5)
C(2)–C(1)–C(8)	117.0 (6)	117.6 (11)
C(2)–C(1)–C(14)	122.8 (7)	122.7 (13)
C(8)–C(1)–C(14)	118.3 (6)	117.8 (12)
C(1)–C(2)–C(3)	123.9 (9)	123.5 (13)
C(1)–C(2)–C(7)	121.7 (9)	122.1 (14)
C(3)–C(2)–C(7)	114.4 (9)	114.3 (13)
C(2)–C(3)–C(4)	122.2 (7)	121.5 (14)
C(3)–C(4)–C(5)	120.8 (5)	121.8 (16)
C(4)–C(5)–C(6)	118.9 (5)	118.6 (16)
C(5)–C(6)–C(7)	120.4 (6)	120.5 (15)
C(6)–C(7)–C(2)	123.3 (8)	123.3 (14)
C(1)–C(8)–C(9)	122.6 (6)	123.0 (13)
C(1)–C(8)–C(13)	121.4 (8)	120.3 (14)
C(9)–C(8)–C(13)	116.0 (8)	116.7 (14)
C(8)–C(9)–C(10)	123.0 (7)	123.1 (15)
C(9)–C(10)–C(11)	118.8 (6)	118.7 (17)
C(10)–C(11)–C(12)	119.8 (6)	120.1 (17)
C(11)–C(12)–C(13)	120.7 (7)	120.3 (16)
C(12)–C(13)–C(8)	121.7 (9)	121.1 (15)
C(1)–C(14)–C(15)	122.8 (7)	123.3 (14)
C(1)–C(14)–C(19)	122.7 (7)	123.4 (13)
C(15)–C(14)–C(19)	114.5 (7)	114.3 (13)
C(14)–C(15)–C(16)	122.6 (6)	123.1 (15)
C(15)–C(16)–C(17)	120.9 (6)	121.4 (17)
C(16)–C(17)–C(18)	118.2 (6)	117.9 (16)
C(17)–C(18)–C(19)	121.6 (7)	121.5 (16)
C(18)–C(19)–C(14)	122.1 (8)	121.8 (14)

[a] Errors in lattice parameters are included in the estimated standard deviations.

rium twist angle in the triphenylmethyl carbanion is 35 ± 2°[14] assuming equal twist angles for all three phenyl

Table V. Interatomic Distances (Å) in Disordered *N,N,N',N'*-Tetramethylethylenediamine Groups

Atom	Nongroup distance	Group distance
N(1)–C(20)	1.71	1.47
N(1)–C(21)	1.59	1.47
N(1)–C(22)	1.47	1.49
C(22)–C(23)	1.51	1.50
N(2)–C(23)	1.57	1.49
N(2)–C(24)	1.43	1.47
N(2)–C(25)	1.41	1.47
N(1)–C(20)'	1.30	1.47
N(1)–C(21)'	1.24	1.47
N(1)–C(22)'	1.60	1.49
C(22)'–C(23)'	1.58	1.53
N(2)–C(23)'	1.44	1.49
N(2)–C(24)'	1.54	1.47
N(2)–C(25)'	1.50	1.47

Table VI. Best Weighted Least-Squares Planes for $(C_6H_5)_3CLi[(CH_3)_2N(CH_2)_2N(CH_3)_2]$

Plane	Atoms in plane	Equation of plane[a,b]
1	C(2), C(8), C(14)	$-0.9981x - 0.0594y - 0.0145z + 4.4808 = 0$
2	C(2), C(3), C(4), C(5), C(5), C(7)	$-0.8302x - 0.4584y - 0.3171z + 8.0580 = 0$
3	C(8), C(9), C(10), C(11), C(12), C(13)	$-0.7412x + 0.5862y - 0.3268z + 2.0653 = 0$
4	C(14), C(15), C(16), C(17), C(18), C(19)	$0.9443x + 0.0719y - 0.3209z - 1.6405 = 0$

	Deviations of atoms from planes, Å			
Atom	Plane 1	Plane 2	Plane 3	Plane 4
C(1)	0.117 (3)	−0.006 (3)	−0.052 (3)	−0.051 (3)
C(2)	0.000 (3)	0.001 (3)		
C(3)		0.000 (3)		
C(4)		−0.003 (3)		
C(5)		0.005 (4)		
C(6)		−0.002 (3)		
C(7)		0.000 (3)		
C(8)	0.000 (3)		−0.003 (3)	
C(9)			0.002 (3)	
C(10)			−0.001 (4)	
C(11)			0.000 (4)	
C(12)			−0.002 (4)	
C(13)			0.003 (3)	
C(14)	0.000 (3)			−0.006 (3)
C(15)				0.007 (4)
C(16)				−0.005 (4)
C(17)				0.004 (5)
C(18)				−0.003 (4)
C(19)				0.005 (4)
Li	2.133 (5)	2.185 (5)	1.290 (5)	−1.697 (5)

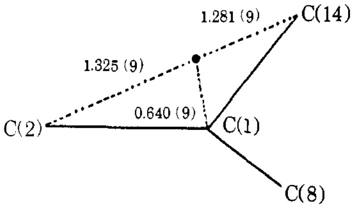
The dihedral angle between planes 1 and 2 is 30.6°
The dihedral angle between planes 1 and 3 is 44.8°
The dihedral angle between planes 1 and 4 is 19.7°

[a] The orthogonal unit cell vectors *x*, *y*, *z* are related to the monoclinic vectors *a*, *b*, *c* as follows: $(x, y, z) = (a + c \cos \beta, c \sin \beta)$. [b] The weight of each atom is inversely proportional to the mean variance of the positional parameters for that atom.

rings. The average observed twist angle of 31.7° is in reasonable agreement with this value. The degree of π-electron delocalization between the benzylic carbon atom and the phenyl groups might be expected to be dependent on the twist angle, with the most delocalization occurring when the phenyl ring is coplanar with the mean plane of the four central carbon atoms of the carbanion. Increasing π-electron delocalization with decreasing twist angle is suggested by C(1)–C(phenyl) bond distances of 1.448 (9), 1.462 (13), and 1.488 (10) Å for twist angles of 19.7, 30.6, and 44.8°. In benzyllithium, the smaller corresponding C(1)–C(phenyl) distance of 1.39 (1) Å is consistent with the predictions of simple Hückel theory. An increase in the C(1)–C(phenyl) bond order is expected to be accompanied by a decrease in the bond order of ring C–C bonds involving C(phenyl), *e.g.*, C(2)–C(3) and C(2)–C(7). The average distance in benzyllithium is 1.44 (1) Å, while the corresponding average distances in the C(14), C(2), and C(8) phenyl rings are 1.418 (8), 1.409 (10), and 1.399 (9) Å, respectively. Another geometrical feature which may reflect the C(1)–C(phenyl) π delocalization is the phenyl intra-ring angle characterized by C(15)–C(14)–C(19), C(3)–C(2)–C(7), and C(13)–C(8)–C(9). In order of decreasing twist angle, these angles for the triphenylmethyl carbanion are 116.0 (8), 114.4 (9), and 114.5 (7)°. The corresponding angle in benzyllithium is 112.8 (5)°.

Lithium Atom Environment. The interaction of the lithium cation with the triphenylmethyl carbanion closely resembles that in benzyllithium[25a] and fluorenyllithium.[25b] As in these systems, the closest approach of the lithium atom to any carbon atom in the triphenylmethyl group is to the benzylic carbon atom which, in every case, is predicted by simple Hückel theory to have the greatest electron density. The lithium atom is not, however, located in the position required for a two center Li–C(1) bond analogous to the H–C(1) bond in triphenylmethane. This is evident from the projection of lithium atom position onto the plane defined by C(2)–C(8)–C(14) (plane 1 of Table VI) as shown below.

(25) (a) S. P. Patterman, I. L. Karle, and G. D. Stucky, *J. Amer. Chem. Soc.*, **92**, 1150 (1970); (b) J. J. Brooks, W. Rhine, and G. D. Stucky, *ibid.*, **94**, 7339 (1972).



It is not possible to explain the above geometry or, for that matter, the stereochemistry of any of the unsaturated complexes of lithium that we have investigated by two-center σ and/or ionic interactions alone. The delocalized geometry of the carbanion and the "allylic" geometry described above suggest that a delocalized bonding mechanism which involves all the 2 s and 2 p orbitals of the lithium atom is utilized.

In an organometallic complex, RMX·NR′$_3$, the strength of the coordination bond formed between the tertiary amine, NR′$_3$, and the metal atom, M, might be expected to depend significantly upon the stability of the carbanion, R$^-$, with the more stable carbanion resulting in shorter M-N bond lengths. The relative stabilities of the benzyl, triphenylmethyl, and fluorenyl carbanions as indicated by the pK_a of the most acidic proton of toluene, triphenylmethane, and fluorene are 35, 31, and 27,[26] respectively. The average Li-N bond lengths observed for benzyllithium triethylenediamine, triphenylmethyllithium *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, and fluorenyllithium bisquinuclidine are 2.100 (7), 2.078 (12), and 2.031 (7) Å.

A similar correlation is observed with dimethylmagnesium bisquinuclidine,[27] bis[2-dimethylaminoethyl-(methyl)amino]di(methylmagnesium),[28] and ethylmagnesium bromide triethylamine.[29] The anionic species in these three molecules are CH_3^-, CH_3^-; CH_3^-, NR_2^-; and $C_2H_5^-$, Br$^-$. The Mg-N bond lengths are 2.239 (6), 2.182 (3), and 2.150 (10) Å, respectively, which again parallel the expected anion stabilities. In this example, carbanion stability is more important than the base strength of the tertiary amine, since quinuclidine is a stronger base than triethylamine. The same relation between bond lengths and expected carbanion stability is also evident in $(CH_3)_3Al$·quinuclidine,[30] $(CH_3)_2AlI·N(CH_3)_3$,[30] and $Cl_3AlN(CH_3)_3$[31] where Al-N distances of 2.06 (1), 2.01 (1), and 1.96 (1) Å again follow anionic stabilities. The variation of up to 0.1 Å in Al-N distances also points out the problems involved in using the additivity of atomic radii to predict metal-ligand interatomic distances even when the coordination number is constant.

Acknowledgment. The authors gratefully acknowledge the generous support of the Advanced Projects Research Agency under Contract No. HC 15-67CO221 and the National Science Foundation.

---

(26) R. E. Dessy, W. Kitching, T. Psarras, R. Salinger, A. Chen, and T. Chivers, *J. Amer. Chem. Soc.*, 88, 460 (1966).

(27) J. Toney and G. D. Stucky, *J. Organometal. Chem.*, **22**, 241 (1970).

(28) V. R. Magnuson, and G. D. Stucky, *Inorg. Chem.*, 8, 1427 (1969).

(29) J. Toney, and G. D. Stucky, *Chem. Commun.*, 1168 (1967).

(30) J. Atwood, private communication.

(31) D. F. Grant, R. C. Killean, and J. L. Lawrence, *Acta Crystallogr., Sect. B.*, **25**, 377 (1969).