(4) E. C. Ashby, F. R. Dobbs, and H. P. Hopkins, *J. Am. Chem. Soc.*, **95**, 2823 (1973); and unpublished results.
(5) T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **88**, 318 (1966).
(6) (a) E. L. Eliel and Y. Senda, *Tetrahedron*, **26**, 2411 (1970), and references therein; (b) D. C. Wigfield and D. J. Phelps, *Can. J. Chem.*, **50**, 388 (1972), and references therein; (c) P. Geneste, G. Lamaty, C. Moreau, and J. P. Roque, *Tetrahedron Lett.*, 5011 (1970), and references therein; (d) K. Bowden and M. Hardy, *Tetrahedron*, **22**, 1169 (1966); (e) J. A. Perry and K. D. Warren, *J. Chem. Soc.*, 4049 (1965) (f) G. G. Smith and R. P. Bayer, *Tetrahedron*, **18**, 323 (1962); (g) H. C. Brown and K. Ichikawa, *J. Am. Chem. Soc.*, **83**, 4372 (1961); (h) H. C. Brown, O. H. Wheeler, and K. Ichikawa, *Tetrahedron*, **1**, 214 (1957); (i) E. R. Garrett and D. A. Lyttle, *J. Am. Chem. Soc.*, **75**, 6051 (1953); (j) D. C. Ayers, D. N. Kirk, and R. Sawdaye, *J. Am. Chem. Soc. B*, 1133 (1970); (k) J. Klein, E. Dunkelblum, E. L. Eliel, and Y. Senda, *Tetrahedron Lett.*, 6127 (1968).
(7) (a) H. C. Brown, E. J. Mead, and B. C. Subba Roa, *J. Am. Chem. Soc.*, **77**, 6209 (1955); (b) H. C. Brown and K. Ichikawa, *J. Am. Chem. Soc.*, **83**, 4372 (1961); (c) P. T. Lansbury, R. E. MacLeay, and J. O. Peterson, *Tetrahedron Lett.*, 311 (1964); (d) P. T. Lansbury and R. E. MacLeay, *J. Am. Chem. Soc.*, **87**, 831 (1965).
(8) (a) P. Geneste and G. Lamaty, *Bull. Soc. Chim. Fr.*, 669 (1968); (b) D. C. Wigfield and D. J. Phelps, *Chem. Commun.*, 1152 (1970); (c) H. M. Cense, *Tetrahedron Lett.*, 2153 (1972).
(9) (a) H. C. Brown and R. F. McFarlin, *J. Am. Chem. Soc.*, **80**, 5372 (1958); (b) H. Haubenstock and E. L. Eliel, *J. Am. Chem. Soc.*, **84**, 2363 (1962).
(10) H. C. Brown, E. J. Mead, and C. J. Shoaf, *J. Am. Chem. Soc.*, **78**, 3515 (1956).
(11) H. C. Brown and H. R. Deck, *J. Am. Chem. Soc.*, **87**, 5620 (1965).
(12) H. O. House, "Modern Synthetic Organic Reactions", W. A. Benjamin, New York, N.Y., 1972, p 49.
(13) E. C. Ashby, J. R. Boone, and J. P. Oliver, *J. Am. Chem. Soc.*, **95**, 5427 (1973).
(14) P. H. Gore, J. A. Hoskins, R. J. W. LeFevre, L. Radom, and G. L. D. Ritchie, *J. Chem. Soc. B*, 741 (1967).
(15) E. C. Ashby and R. D. Schwartz, *J. Chem. Educ.*, **51**, 65 (1974).
(16) A. Mannschreck and L. Ernst, *Chem. Ber.*, **104**, 228 (1971).
(17) T. Holm and I. Crossland, *Acta Chem. Scand.*, **25**, 59 (1971).
(18) E. C. Ashby, Frank R. Dobbs, and H. P. Hopkins, Jr., *J. Am. Chem. Soc.*, **95**, 2823 (1973).
(19) E. C. Ashby and J. R. Boone, unpublished work.
(20) A. Langer, *Adv. Chem. Ser.*, 130 (1974).
(21) D. C. Wigfield and D. J. Phelps, *Can. J. Chem.*, **50**, 388 (1972).
(22) R. E. Davis, R. E. Kenson, C. L. Kibby, and H. H. Lloyd, *Chem. Commun.*, 593 (1965).
(23) R. E. Davis, E. Bromels, and C. L. Kibby, *J. Am. Chem. Soc.*, **84**, 885 (1962).

Effects of Reduction on the Olefinic Bond in Two Stilbene Dilithium Complexes

Michael Walczak and Galen Stucky*

*Contribution from the School of Chemical Sciences,
Department of Chemistry, and the Materials Research Laboratory,
University of Illinois, Urbana, Illinois 61801. Received June 20, 1975*

Abstract: Two complexes containing a dilithiated stilbene fragment have been prepared and isolated from the reactions of 1,2-diphenylethane with N-chelated butyllithium reagents. The molecular and crystal structures of these compounds, stilbene bis(lithium tetramethylethylenediamine) and stilbene bis(lithium pentamethyldiethylenetriamine), have been determined by x-ray diffraction techniques. Each structure contains two amine-solvated lithium atoms located above and below the olefinic bond of a stilbene molecule. The compound containing tetramethylethylenediamine exhibits crystallographic $2/m$ symmetry, and the stilbene group is thus required by symmetry to be planar. The pentamethyldiethylenetriamine complex has crystallographic $\bar{1}$ symmetry; however, the stilbene group is also planar. In both structures, the stilbene molecule is in a trans configuration about the $C(7)-C(7)'$ bond. The planar configuration is in contrast to results from solution studies of disproportionation of arylethylene anions and the photochemistry of stilbene, where a twisted structure was proposed. The planar dianion allows the maximum amount of electron density around each lithium atom. The stilbene group is disordered in each structure, occupying either of two orientations about the crystallographic inversion center. The $C(7)-C(7)'$ distance has increased in each structure by ~ 0.1 Å compared with the distance in *trans*-stilbene. Stilbene bis(lithium tetramethylethylenediamine) crystallizes in the monoclinic space group $C2/m$ with two molecules in a unit cell of dimensions $a = 12.613$ (7) Å, $b = 13.899$ (6) Å, $c = 8.179$ (5) Å, and $\beta = 105.89$ (3)°. Stilbene bis(lithium pentamethyldiethylenetriamine) crystallizes in the monoclinic space group $P2_1/c$ with two molecules in a unit cell of dimensions $a = 10.387$ (5) Å, $b = 11.531$ (6) Å, $c = 15.470$ (5) Å, and $\beta = 113.07$ (2)°. Full-matrix least-squares refinement of each structure has given final R_w factors of 0.064 for stilbene bis(lithium tetramethylethylenediamine), based on 1260 observations, and 0.064 for stilbene bis(lithium pentamethyldiethylenetriamine), based on 2547 observations.

Introduction

There has been extensive speculation concerning the geometry of the stilbene molecule in its reduced form as the mono- or dianion. Garst and Szwarc have observed that the metal cation, solvent, aggregation, and steric effects are important in determining the equilibrium position in the disproportionation of arylethylene radical anions.[1-2] Studies of monoanions of the sterically strained hydrocarbons tetraphenylethylene[2-4] and α-methylstilbene[5] show that they disproportionate much more readily than the stilbene monoanion, suggesting a relief of steric strain upon disproportionation. A change in structural geometry on formation of the dianion would relieve steric strain, assuming the monoanions were required to be planar, but the dianion could twist by 90° about the ethylenic carbon-carbon bond.[5] Szwarc recently reported the existence of distinct *cis*- and *trans*-stilbene dianions in the

electron transfer induced cis-trans isomerization of stilbene.[7] He proposed that cations associated with both phenyl groups in the cis dianion stabilized the cis configuration to rotation of one phenyl group with the other.

As pointed out by Walsh[8] and more recently Pearson,[9] there is a direct correspondence between the excited state and anion geometry, if the extra one or two electrons of the mono- or dianion are in the same molecular orbital as the one which is populated in the excited state. The point group symmetries of the two systems should be the same, and information about the geometry of one species can be obtained from studies of the other. In particular, Garst has observed that photochemical studies of the cis-trans conversion of stilbene are related to the question of the dianion's geometry.[5] Results from several photochemical studies have been interpreted in terms of the lowest energy excited state of stilbene being a twisted triplet configuration.[10,11] Calculations[12,13] have also shown a twisted

relaxed triplet configuration to be the lowest energy state, and the calculated energy difference between the ground and excited state agreed well with the energy difference obtained from sensitizer experiments.[10] Thus, the existing evidence points to arylethylene dianions, and the stilbene dianion specifically, existing in a twisted geometry in solution.

In view of the above, and as a continuation of our investigations of complexes containing π delocalized carbanions and amine-solvated lithium cations,[14] we were interested in examining the molecular configuration of arylethylene dianions. Two specific items of interest were to determine the structural effects associated with the formal addition of two electrons to the hydrocarbon and to ascertain the specific lithium–carbanion interaction and its relation to that observed in other π-carbanion complexes.[14-16]

While the first ethylenic system to be examined, $\Delta^{9,9'}$-bifluorene,[15c] is formally an arylethylene, neither this olefin nor its dianion is probably representative of what occurs in other arylethylenes. The C(11)–C(12) bond in each fluorenyl ring of the bifluorenyl skeleton confers on each half of the molecule a rigidity which is not present in arylethylenes such as tetraphenylethylene or stilbene. We, therefore, elected to examine another arylethylene; in view of the great interest shown in stilbene, we have investigated the solid state structure of the dilithium complex of stilbene. In order to prepare these complexes, we chose to use the 1,2 dimetallation of dibenzyl using amine-solvated n-butyllithium, a synthetic route to the dianion not previously reported. A similar approach was used in the synthesis of (TMEDLi)₂naphthalene from 1,4-dihydronaphthalene.[15d] Harvey has since reported the preparation of the dianion by this route in conjunction with his oxidation studies.[17] We now report the x-ray structural determinations of stilbene bis(lithium tetramethylethylenediamine) and stilbene bis(lithium pentamethyldiethylenetriamine).

Experimental Section

I. Synthesis. (1) $C_{14}H_{12}(N_2C_6H_{16}Li)_2$. A 2.73-g (15 mmol) sample of 1,2-diphenylethane was placed in a 100-ml three-necked flask under a nitrogen atmosphere, and 50 ml of dry benzene was added. To this was added 4 ml (30 mmol) of N,N,N',N'-tetramethylethylenediamine (TMEDA). A 20-ml (30 mmol) sample of n-butyllithium in hexane was added to the flask via syringe while stirring at room temperature; the resulting solution was red After addition of the n-butyllithium, stirring was stopped, and the reaction mixture was brought inside an argon-filled drybox and allowd to stand for 24 h. Concentration of the deep-red solution under reduced pressure inside the drybox yielded dark-green crystals which were collected by filtration, dried, and used for x-ray analysis without further purification.

(2) $C_{14}H_{12}(N_3C_9H_{23}Li)_2$. The same procedure as above was used to prepare stilbene bis(lithium PMDTA). Addition of n-butyllithium to the reaction mixture gave an orange solution which slowly turned red-brown. Concentration of the solution under reduced pressure inside the drybox yielded dark green crystals which were isolated by filtration, dried, and used in the x-ray analysis without further purification.

II. Data Collection. Crystals of $C_{14}H_{12}(N_2C_6H_{16}Li)_2$ and $C_{14}H_{12}(N_3C_9H_{23}Li)_2$ used for x-ray analysis were sealed in thin-walled glass capillaries in an argon atmosphere because of their sensitivity to oxygen and moisture. Preliminary precession photographs of $C_{14}H_{12}(N_2C_6H_{16}Li)_2$ showed the crystals to be monoclinic with systematic absences on hkl for $h + k = 2n + 1$, indicating the space group was $C2$, Cm, or $C2/m$. The space group $C2/m$ was subsequently used in the refinement on the basis of statistical tests and the successful solution and refinement in the centric space group. An irregularly shaped crystal of approximate dimensions 0.4 × 0.5 × 0.4 mm, mounted so that the $\overline{2}10$ axis was coincident with the ϕ axis of the diffractometer, was used for data collection. Thirteen reflections centered on a Picker four-circle diffractometer were used in a least-squares refinement of the lattice parameters and the following cell constants obtained (T = 20 °C, $\lambda = 0.71069$ Å): $a = 12.613$ (7) Å, $b = 13.899$ (6) Å, $c = 8.179$ (5) Å, and $\beta = 105.89$ (3)°. The measured density, obtained by flotation in a bromobenzene–hexane

mixture, was 0.99 (5) g/cm³. The calculated density was 1.027 g/cm³ for two molecules per unit cell.

Preliminary precession photograph of $C_{14}H_{12}(N_3C_9H_{23}Li)_2$ showed the crystals to be monoclinic with systematic absences on $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$, uniquely determining the space group as $P2_1/c$. An irregularly shaped crystal of approximate dimensions 0.4 × 0.4 × 0.6 mm was used for data collection. The crystal was mounted so that the rotation axis was coincident with the c^* axis. Fifteen reflections centered on the diffractometer were used in a least-squares refinement of the lattice parameters and the following cell constants obtained (T = 20 °C, $\lambda = 0.71069$ Å): $a = 10.387$ (5) Å, $b = 11.531$ (6) Å, $c = 15.470$ (5) Å, and $\beta = 113.07$ (2)°. No density was measured; the calculated density for two molecules per unit cell was 1.053 g/cm³, a reasonable value for an aryllithium compound.

Intensity data for both compounds were measured using Mo $K\alpha$ radiation on an automated Picker four-circle diffractometer equipped with a graphite single-crystal monochromator. Data were collected using θ–2θ scan technique with a scan rate of 1.0°/min. Stationary crystal-stationary counter background counts of 10 s were taken at the beginning and end of each scan. For $C_{14}H_{12}(N_2C_6H_{16}Li)_2$, a scan width of 2.0° and a take-off angle of 1.6° were employed for data collection, while for $C_{14}H_{12}(N_3C_9H_{23}Li)_2$, a scan width of 1.8° and take-off angle of 1.5° were used. Several ω scans showed the typical full peak width at half-height to be less than 0.18° for $C_{14}H_{12}(N_2C_6H_{16}Li)_2$ and 0.14° for $C_{14}H_{12}(N_3C_9H_{23}Li)_2$, indicating the mosaicity was acceptably low for each compound for data collection. No trends were noted in either compound in the three standard reflections monitored after every 60 reflections in each data collection to insure crystal and counter stability.

For $C_{14}H_{12}(N_2C_6H_{16}Li)_2$, a full form of data ($\overline{h}kl$ and hkl) was measured to $2\theta_{max} = 50°$, giving 1351 reflections, of which 1260 were unique and 452 classified as observed using the criterion $I_{obsd} \geq 3\sigma_c(I)$ where $\sigma_c(I) = [T_c + 0.25(t_c/t_b)^2(B_1 + B_2)]^{1/2}$. T_c is the total integrated counts, t_c/t_b is the ratio of the time spent counting the peak intensity to the time spent counting the background intensities, and B_1 and B_2 are the background counts. For $C_{14}H_{12}(N_3C_9H_{23}Li)_2$, a full form of data ($\overline{h}kl$ and hkl) measured to $2\theta_{max} = 47°$ gave 2736 reflections, of which 2547 were unique and 955 classified as observed using the criterion above. Due to the irregular crystal shape of each compound and the small value for the linear absorption coefficients [$\mu = 0.64$ cm⁻¹ for $C_{14}H_{12}(N_2C_6H_{16}Li)_2$ and 0.67 cm⁻¹ for $C_{14}H_{12}(N_3C_9H_{23}Li)_2$], no absorption corrections were made. The remainder of the data collection details for each structure are the same as previously reported.[16]

III. Solution and Refinement. (1) $C_{14}H_{12}(N_2C_6H_{16}Li)_2$. The statistics from FAME[16] indicated the centric space group $C2/m$ as the correct choice. Furthermore, the $N(z)$ test[18] also indicated a centric distribution of data. Therefore, $C2/m$ was chosen as the space group in which to attempt solution and refinement. Many difficulties were encountered in solving this structure. Solution was first attempted by direct methods (symbolic addition procedure). However, no success was encountered using the programs MULTAN[19] and MAGIC-LINK-SYMPL.[16] Further attempts involved using the Patterson function, and essentially employing the benzene ring as a heavy atom. An ide-

Table I. Positional Parameters for the Nonhydrogen Atoms in Stilbene Bis(lithium TMEDA)

Atom	x	y	z
E1C(7)	0.0592 (10)	0.0000	0.0013 (32)
E2C(7)	0.0118 (41)	0.0000	0.0871 (26)
C(1)	0.1371 (6)	0.0000	0.1698 (9)
C(2)	0.1270 (5)	0.0000	0.3386 (13)
C(3)	0.2178 (8)	0.0000	0.4770 (8)
C(4)	0.3237 (6)	0.0000	0.4588 (10)
C(5)	0.3332 (5)	0.0000	0.2973 (11)
C(6)	0.2473	0.0000	0.1611 (8)
AC(1)	0.0300 (3)	0.2560 (2)	0.3041 (5)
AC(2)	0.1980 (3)	0.2507 (3)	0.2305 (4)
AC(3)	0.0516 (3)	0.3448 (2)	0.0613 (5)
N	0.0794 (2)	0.2566 (2)	0.1628 (3)
Li	0.0000	0.1464 (5)	0.0000

Table II. Anisotropic Thermal Parameters for the Nonhydrogen Atoms in Stilbene Bis(lithium TMEDA)

Atom	$\beta_{11}{}^a$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
E1C(7)	0.0060 (12)	0.0035 (4)	0.0221 (33)	0.0000	0.0065 (21)	0.0000
E2C(7)	0.0088 (24)	0.0087 (11)	0.0229 (48)	0.0000	−0.0001 (41)	0.0000
C(1)	0.0144 (8)	0.0036 (3)	0.0325 (20)	0.0000	−0.0050 (11)	0.0000
C(2)	0.0087 (5)	0.0049 (3)	0.0520 (21)	0.0000	0.0035 (10)	0.0000
C(3)	0.0192 (8)	0.0063 (4)	0.0311 (16)	0.0000	0.0044 (12)	0.0000
C(4)	0.0147 (8)	0.0067 (4)	0.0310 (17)	0.0000	−0.0086 (11)	0.0000
C(5)	0.0097 (6)	0.0056 (3)	0.0435 (20)	0.0000	0.0001 (10)	0.0000
C(6)	0.0157 (7)	0.0054 (3)	0.0287 (16)	0.0000	0.0029 (9)	0.0000
AC(1)	0.0130 (4)	0.0090 (3)	0.0351 (9)	0.0002 (3)	0.0084 (5)	−0.0016 (5)
AC(2)	0.0125 (3)	0.0089 (3)	0.0272 (8)	0.0001 (3)	0.0047 (4)	−0.0020 (4)
AC(3)	0.0164 (5)	0.0053 (2)	0.0352 (11)	0.0002 (2)	0.0002 (5)	−0.0009 (4)
N	0.0098 (2)	0.0052 (2)	0.0211 (5)	0.0012 (2)	0.0020 (3)	−0.0008 (3)
Li	0.0097 (7)	0.0055 (5)	0.0209 (16)	0.0000	0.0037 (8)	0.0000

^{a} The form of the anisotropic ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

alized geometry for a benzene ring having carbon–carbon bond distances of 1.40 Å and angles of 120° was used, and it was assumed that the ring was in the crystallographic mirror plane at $y = 0$. A set of positions for the seven unique stilbene carbon atoms was found in the Patterson map, giving an $R_1 = \Sigma F_o - F_o / \Sigma F_o$ of 0.654. After location of the one unique nitrogen atom on the subsequent Fourier map, a second Fourier revealed the positions of the lithium atom and two of the three unique TMEDA carbon atoms; R_1 was 0.498. The remaining TMEDA carbon atom was then located on a Fourier based on these eleven atoms. Full-matrix least-squares refinement of all atomic positions, using the program ORFLSD,[16] with isotropic temperature factors for all atoms fixed at 4.5, lowered R_1 to 0.212. Further refinement varying both thermal and positional parameters for all atoms lowered R_1 to 0.189.

Further problems now appeared—the C(7)–C(7)′ and C(7)–C(1) distances were not chemically reasonable, and the isotropic thermal parameter for C(7) was larger than those for the ring carbons. A difference Fourier calculated at this time revealed a rather poorly defined alternate position for the ethylenic carbon atom, but gave no evidence for disorder in the ring. Partial occupancy was assumed, and the carbon atoms placed at each position were given equal isotropic thermal parameters. The occupancy factor for each ethylenic carbon atom was then refined, assuming that the thermal parameters for each carbon atom should be equal. Normalization of the occupancy factors to unity gave carbon E1C(7) an occupancy factor of 0.62 while that for E2C(7) was 0.38. Hydrogen atoms were then added at calculated positions 1.0 Å from the carbon atom to which each was bonded and given an isotropic thermal parameter equal to that of the carbon atom. Continued refinement on all nonhydrogen atom parameters using all the data and a counting statistics weighting scheme ($k = 0.03$)[16] gave at isotropic convergence an $R_2 = \{\Sigma w(F_o - F_c)^2 / \Sigma w F_o^2\}^{1/2}$ of 0.137. After conversion to anisotropic thermal parameters for all nonhydrogen atoms, refinement of all nonhydrogen atom thermal and positional parameters was continued, giving at final convergence an R_1 (observed reflections only) of 0.062 and R_2 (all data) of 0.064 and $erf = [\Sigma w(F_o - F_c)^2 / (NO - NV)]^{1/2}$ of 1.81, where NO = number of observations and NV = number of variables.

A final difference Fourier, calculated to check the correctness of the disordered model, showed only small two peaks of 0.35 e/Å^3 each. One was next to the TMEDA methylene carbon atom and suggested some electron density outside the final refined carbon atom position, which would result in a slightly larger carbon–carbon bond length. The other peak was in a potential TMEDA methylene hydrogen position. There were no other peaks over 0.20 e/Å^3, and no evidence suggestive of disorder in the ring carbon atoms.

The final positional and thermal parameters for the nonhydrogen atoms are contained in Tables I and II, respectively. Table III gives the hydrogen atom positions and thermal parameters. Bond distances and angles are given in Tables IV and V, respectively. Table VI gives the root mean square amplitudes of displacement for the nonhydrogen atoms and F_{obsd} and F_{calcd} values are listed in Table VII (see Supplementary Material section).

(2) $C_{14}H_{12}(N_3C_9H_{23}Li)_2$. The structure of $C_{14}H_{12}(N_3C_9H_{23}Li)_2$ was solved using direct methods (symbolic addition procedure) using the program package MULTAN.[19] The E map generated from the set of phases with the highest figure of merit yielded the positions of seven

Table III. Positional Parameters and Isotropic Thermal Parameters for the Hydrogen Atoms in Stilbene Bis(lithium TMEDA)

Atom	x	y	z	B^a
E1H(7)	0.0845	0.0000	−0.1036	3.82
E2H(7)	−0.0480	0.0000	0.1491	3.93
H(2)	0.0520	0.0000	0.3577	6.46
H(3)	0.2075	0.0000	0.5940	6.53
H(4)	0.3901	0.0000	0.5592	6.25
H(5)	0.4087	0.0000	0.2797	6.49
H(6)	0.2608	0.0000	0.0462	6.65
AH(11)	0.0505	0.1951	0.3705	7.47
AH(12)	0.0577	0.3124	0.3796	7.47
AH(13)	−0.0520	0.3600	0.2594	7.47
AH(21)	0.2177	0.1908	0.2998	6.66
AH(22)	0.2330	0.2493	0.1346	6.66
AH(23)	0.2252	0.3081	0.3037	6.66
AH(31)	0.0523	0.3994	0.1412	7.42
AH(32)	0.1097	0.3553	0.0012	7.42

^{a} The form of the isotropic thermal parameter is $\exp[-B(\sin^2 \theta/\lambda^2)]$.

Table IV. Interatomic Distances (Å) for the Nonhydrogen Atoms in Stilbene Bis(lithium TMEDA)

Atoms	Distance	Atoms	Distance
Li–E1C(7)	2.166 (8)^a	C(1)–C(6)	1.410 (7)
Li–E2C(7)	2.147 (9)	C(2)–C(3)	1.372 (8)
Li–C(1)	2.783 (6)	C(3)–C(4)	1.384 (7)
Li–N	2.096 (6)	C(4)–C(5)	1.358 (7)
E1C(7)–E1C(7)′	1.487 (21)	C(5)–C(6)	1.325 (7)
E2C(7)–E2C(7)′	1.373 (43)	N–AC(1)	1.455 (4)
E1C(7)–C(1)	1.458 (24)	N–AC(2)	1.449 (4)
E2C(7)–C(1)	1.540 (47)	N–AC(3)	1.468 (4)
C(1)–C(2)	1.421 (8)	AC(3)–AC(3)′	1.408 (6)

^{a} Errors in the lattice parameters are included in the estimated standard deviations.

stilbene carbon atoms (some were poorly defined), two PMDTA nitrogen atoms and six PMDTA carbon atoms. A Fourier map based on these 15 atoms revealed the positions of the lithium atom and the remaining PMDTA atoms. The R factor was $R_1 = 0.365$. Full-matrix least-squares refinement gave at isotropic convergence an R factor of $R_1 = 0.178$. Since the C(7)–C(7)′ and C(7)–C(1) distances were chemically unreasonable at this time, and the isotropic thermal parameter for C(7) was much larger than those for the ring carbon atoms, a difference Fourier was calculated to check for possible disorder of the ethylene carbon atom. The features in refinement here were reminiscent of those previously observed in the stilbene bis(li-

Table V. Bond Angles (deg) for the Nonhydrogen Atoms in Stilbene Bis(lithium TMEDA)

Atoms	Angle
N–Li–N'	86.1 (3)[a]
E1C(7)'–E1C(7)–C(1)	115.3 (24)
E1C(7)–C(1)–E2C(7)	40.4 (8)
E2C(7)'–E2C(7)–C(1)	111.1 (55)
E1C(7)–C(1)–C(6)	111.8 (9)
E2C(7)–C(1)–C(2)	94.2 (14)
C(2)–C(1)–C(6)	113.6 (5)
C(1)–C(2)–C(3)	121.7 (6)
C(2)–C(3)–C(4)	121.5 (7)
C(3)–C(4)–C(5)	116.7 (6)
C(4)–C(5)–C(6)	123.2 (6)
C(1)–C(6)–C(5)	123.3 (6)
AC(1)–N–AC(2)	108.6 (3)
AC(1)–N–AC(3)	111.5 (3)
AC(2)–N–AC(3)	108.9 (3)
N–AC(3)–AC(3)'	115.7 (2)

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

Table VI. Root Mean Square Amplitudes of Vibration (Å) Along the Principal Axes R_i for Stilbene Bis(lithium TMEDA)

Atom	R_1	R_2	R_3
E1C(7)	0.175 (20)	0.186 (12)	0.272 (21)
E2C(7)	0.231 (39)	0.291 (20)	0.309 (44)
C(1)	0.188 (8)	0.251 (10)	0.422 (9)
C(2)	0.220 (7)	0.254 (8)	0.414 (8)
C(3)	0.249 (8)	0.311 (9)	0.388 (9)
C(4)	0.220 (9)	0.257 (8)	0.447 (11)
C(5)	0.233 (7)	0.260 (9)	0.398 (9)
C(6)	0.231 (7)	0.295 (9)	0.359 (8)
AC(1)	0.281 (6)	0.304 (5)	0.341 (4)
AC(2)	0.273 (5)	0.304 (4)	0.316 (5)
AC(3)	0.227 (4)	0.303 (5)	0.400 (5)
N	0.215 (4)	0.248 (3)	0.295 (4)
Li	0.232 (10)	0.256 (10)	0.270 (10)

thium TMEDA) structure. The difference Fourier revealed the presence of a second ethylene carbon atom position. Inclusion of carbon atoms at each position, with equal occupancy factors, lowered R_1 to 0.158. The hydrogen atoms were then added at the calculated positions using the program HYGEN.[16] Each hydrogen atom was given an isotropic thermal parameter equal to that of its parent carbon atom and placed 1.0 Å from the atom. Further isotropic refinement of the nonhydrogen atoms and conversion from unit weights to a statistical weighting scheme ($k = 0.03$) previously defined,[16] gave an $R_2 = 0.126$. Continued refinement of all nonhydrogen atom thermal and positional parameters after conversion to anisotropic thermal parameters for all nonhydrogen atoms led to final values of R_1 and R_2: $R_1 = 0.054$ (observed data), $R_2 = 0.064$ (all data) and $erf = 1.36$.

A final difference Fourier again showed only small peaks with intensities less than 0.36 e/Å³. A peak of 0.27 e/Å³ was close to the final calculated position of AH(51), while two peaks of 0.36 and 0.27 e/Å³ were each approximately 1 Å from C(17) and C(19), respectively. A fourth peak of 0.30 e/Å was approximately 1 Å away from Li. Because of the small electron densities, no further investigation of any possible disorder was made. A test of the weighting scheme showed no significant variations of $w(F_o - F_c)^2$ with the magnitudes of the F_{obsd} or increasing $\sin \theta/\lambda$.

The final positional and thermal parameters for the nonhydrogen atoms are contained in Tables VIII and IX, respectively. Table X gives the hydrogen atom positions and thermal parameters. Bond distances and angles are given in Tables XI and XII, respectively. Table XIII gives the root mean square amplitudes of displacements for the nonhydrogen atoms, and F_{obsd} and F_{calcd} values are listed in Table XIV (see Supplementary Material section).

Table VIII. Positional Parameters for the Nonhydrogen Atoms in Stilbene Bis(lithium PMDTA)

Atom	x	y	z
E1C(7)	−0.0456 (9)	0.0288 (16)	0.0156 (14)
E2C(7)	−0.0174 (21)	0.0436 (13)	−0.0365 (9)
C(1)	−0.1219 (4)	0.1292 (4)	−0.0283 (4)
C(2)	−0.1439 (5)	0.1881 (6)	−0.1082 (4)
C(3)	−0.2293 (6)	0.2924 (6)	−0.1288 (3)
C(4)	−0.2977 (5)	0.3255 (4)	−0.0757 (6)
C(5)	−0.2807 (6)	0.2617 (6)	0.0023 (5)
C(6)	−0.1964 (6)	0.1680 (5)	0.0248 (3)
AC(1)	0.3531 (3)	0.1141 (3)	0.0074 (2)
AC(2)	0.4707 (4)	0.0182 (3)	0.1516 (2)
AC(3)	0.4350 (3)	0.2224 (3)	0.1505 (2)
AC(4)	0.3294 (4)	0.3178 (3)	0.1206 (2)
AC(5)	0.0873 (4)	0.3652 (3)	0.0761 (3)
AC(6)	0.2249 (4)	0.3048 (3)	0.2340 (3)
AC(7)	0.1413 (4)	0.2248 (5)	0.2637 (2)
AC(8)	0.0609 (5)	0.0381 (4)	0.2736 (2)
AC(9)	0.3040 (5)	0.0668 (5)	0.3269 (3)
N(1)	0.3748 (2)	0.1125 (2)	0.1060 (2)
N(2)	0.2013 (3)	0.2898 (2)	0.1353 (2)
N(3)	0.1715 (4)	0.1000 (3)	0.2568 (2)
Li	0.1661 (5)	0.1034 (5)	0.1090 (3)

The scattering factors for C°, N°, and Li° used in each refinement were taken from the compilation of Hanson et al.,[20] and those for hydrogen are the best spherical form factors of Stewart et al.[21]

Discussion

General Description of Each Molecular Structure. The structure of stilbene bis(lithium TMEDA), illustrated in Figure 1, consists of two lithium–TMEDA groups located at equal distances above and below the midpoint of the ethylenic carbon–carbon bond of a planar stilbene fragment having a trans configuration. The entire molecule exhibits crystallographic $2/m$ symmetry. The stilbene portion lies in a crystallographic mirror plane and is, therefore, required by symmetry to be planar. Only one-half of the stilbene is crystallographically unique, as a twofold axis passes through the midpoint of the C(7)–C(7)' bond relating the two halves. The two lithium atoms lie on the twofold axis and are related by the mirror plane symmetry operation. The twofold axis also bisects the AC(3)–Ac(3)' bond in each TMEDA, so that only one TMEDA nitrogen atom and the three carbon atoms bonded to it are crystallographically unique. The LiN_2 fragments above and below the stilbene plane are required by symmetry to be oriented in the same direction with respect to the carbon atoms of the stilbene portion. Although there is disorder present in the molecule (see discussion below), for clarity, only one of the two ethylene carbon positions, labeled C(7), has been shown in Figure 1.
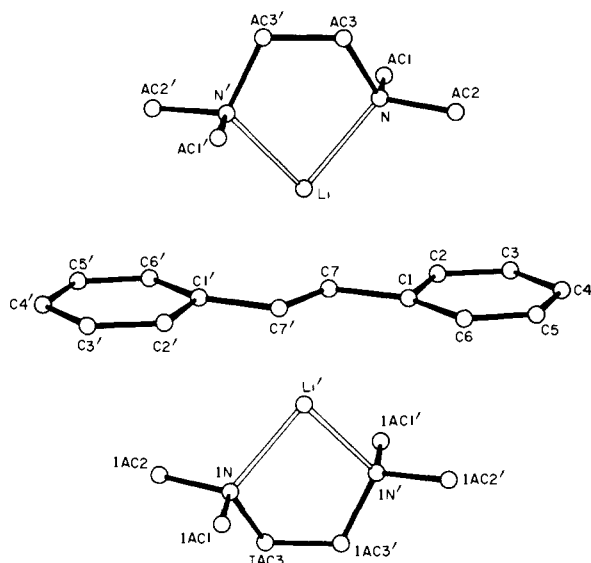
The molecular structure of stilbene bis(lithium PMDTA), illustrated in Figure 2, consists of two lithium–PMDTA moieties bonded to a stilbene group exhibiting a trans configuration about the C(7)–C(7)' bond. The amine-solvated lithium atoms lie above and below the nearly planar stilbene fragment. The molecule lies on a crystallographic inversion center, so that only half of the stilbene portion and one lithium–PMDTA group are crystallographically unique. All three PMDTA nitrogen atoms are coordinated to the lithium atom. This is the first π delocalized carbanion complex to be isolated and structurally characterized that contains other than a disolvated lithium atom.

Disorder in the Stilbene Group. Any discussion of the geometry of the stilbene fragment is somewhat clouded by the fact that it is disordered in each structure. The nature of the disorder in each structure is the same as that observed by

Table IX. Anisotropic Thermal Parameters for the Nonhydrogen Atoms in Stilbene Bis(lithium PMDTA)
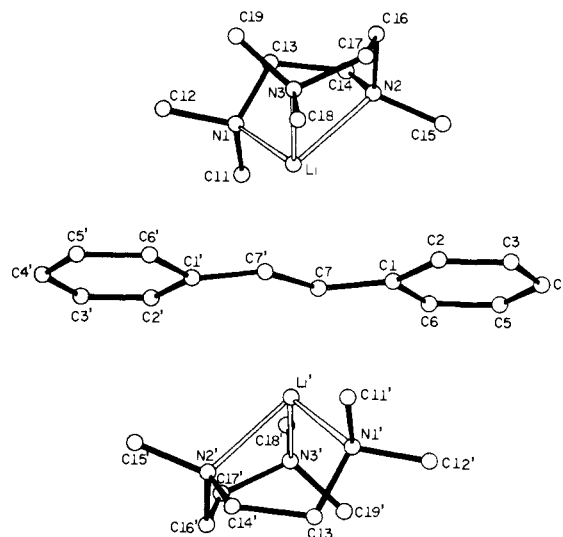
Atoms	$\beta_{11}{}^a$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
E1C(7)	0.0111 (11)	0.0058 (12)	0.0045 (7)	−0.0006 (10)	0.0015 (8)	0.0005 (6)
E2C(7)	0.0188 (20)	0.0084 (15)	0.0051 (8)	−0.0043 (17)	0.0034 (10)	0.0007 (8)
C(1)	0.0126 (6)	0.0087 (5)	0.0103 (4)	−0.0009 (4)	−0.0007 (4)	−0.0038 (4)
C(2)	0.0145 (7)	0.0184 (7)	0.0094 (4)	−0.0029 (5)	0.0039 (4)	−0.0047 (4)
C(3)	0.0159 (8)	0.0183 (8)	0.0102 (4)	−0.0041 (6)	−0.0009 (4)	0.0036 (4)
C(4)	0.0114 (6)	0.0095 (5)	0.0217 (7)	0.0010 (4)	0.0047 (6)	−0.0007 (5)
C(5)	0.0239 (9)	0.0117 (6)	0.0159 (5)	−0.0063 (6)	0.0128 (6)	−0.0052 (4)
C(6)	0.0247 (9)	0.0090 (5)	0.0096 (3)	−0.0051 (5)	0.0033 (5)	−0.0010 (3)
AC(1)	0.0182 (6)	0.0110 (4)	0.0065 (2)	−0.0021 (4)	0.0046 (3)	−0.0003 (3)
AC(2)	0.0183 (6)	0.0136 (5)	0.0084 (3)	0.0042 (4)	0.0034 (3)	0.0001 (3)
AC(3)	0.0118 (5)	0.0125 (4)	0.0075 (2)	−0.0027 (4)	0.0038 (3)	−0.0013 (3)
AC(4)	0.0134 (5)	0.0083 (4)	0.0084 (3)	−0.0028 (4)	0.0024 (3)	−0.0010 (2)
AC(5)	0.0150 (5)	0.0096 (4)	0.0104 (3)	−0.0003 (4)	0.0028 (3)	−0.0006 (3)
AC(6)	0.0196 (6)	0.0107 (4)	0.0098 (3)	−0.0021 (4)	0.0064 (4)	−0.0033 (3)
AC(7)	0.0297 (8)	0.0207 (6)	0.0081 (3)	−0.0083 (6)	0.0102 (4)	−0.0060 (4)
AC(8)	0.0307 (8)	0.0208 (6)	0.0082 (3)	−0.0081 (6)	0.0099 (4)	−0.0017 (3)
AC(9)	0.0249 (8)	0.0342 (9)	0.0078 (3)	−0.0003 (7)	0.0049 (4)	0.0026 (4)
N(1)	0.0124 (4)	0.0089 (3)	0.0053 (2)	0.0003 (3)	0.0026 (2)	−0.0006 (2)
N(2)	0.0125 (4)	0.0084 (3)	0.0059 (2)	−0.0004 (3)	0.0024 (2)	−0.0014 (2)
N(3)	0.0240 (6)	0.0117 (4)	0.0061 (2)	−0.0054 (4)	0.0068 (3)	−0.0020 (2)
Li	0.0125 (7)	0.0101 (6)	0.0061 (3)	−0.0022 (5)	0.0035 (4)	−0.0008 (4)

^{a} The form of the anisotropic thermal ellipsoid is exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Figure 1. The molecular structure of stilbene bis(lithium TMEDA).

Figure 2. The molecular structure of stilbene bis(lithium PMDTA).

Brown in the structure of p-azotoluene.[22] The atomic coordinates determined for the carbon atoms in the phenyl ring are the resultant of two sets of atomic parameters for the two superpositioned stilbene molecules. Here, only separate positions for the ethylenic carbon atoms could be located. Furthermore, the resultant isotropic thermal parameters for comparable atoms in the stilbene portion and in p-azotoluene are similar. The values of 3.82 (25) and 3.93 (35) for E1C(7) and E2C(7), respectively, in stilbene bis(lithium TMEDA), and 3.08 (30) and 3.70 (32) for E1C(7) and E2C(7), respectively, in stilbene bis(lithium PMDTA) are comparable with values for all of the nonhydrogen atoms in the two separated molecules of p-azotoluene. The value of 6.59 for the average isotropic thermal parameter for the hydrogen atoms in the refined p-azotoluene molecule is also comparable with values of 6.48 (30) and 7.33 (28) found in stilbene bis(lithium TMEDA) and stilbene bis(lithium PMDTA), respectively.

Only the ethylene carbon atoms appear to be disordered in the x-ray analysis. In stilbene bis(lithium TMEDA), it was assumed that the isotropic thermal parameters for each eth-

ylene carbon atom should be equal, but that the occupancy factors for each position need not necessarily be equal. This has resulted in final occupancies of 0.62 for E1C(7) and 0.38 for E2C(7). A similar nonstatistical occupancy ratio also seems to be present in the improved crystal structure of $trans$-stilbene recently reported by Allinger and co-workers.[23] Furthermore, in the structure of stilbene bis(lithium TMEDA), there appear to be some differences in the relative orientation of the LiN_2 fragment with respect to each set of ethylene carbon atom positions, and this would lead to unequal occupancy factors if one LiN_2-carbanion orientation were slightly preferred. In stilbene bis(lithium PMDTA), equal occupancy factors were chosen for the two ethylene carbon atom positions, based on the results of Fourier and difference Fourier calculations which indicated approximately equal populations at each site. Brown's determination of the structure of p-azotoluene[22] was not found until both stilbene dianion structures had been fully refined. The time, effort, and cost involved do not justify either attempting to resolve the two separate ring orientations or refining again using different sets of occupancy factors. Also, refinement of stilbene bis(lithium TMEDA) was not attempted

Table X. Positional Parameters and Isotropic Thermal Parameters for the Hydrogen Atoms in Stilbene Bis(lithium PMDTA)

Atom	x	y	z	B^a
E1H(7)	−0.0601	−0.0022	0.0751	3.08
E2H(7)	0.0195	0.0501	−0.0848	3.70
H(2)	−0.0963	0.1767	−0.1512	6.95
H(3)	−0.2424	0.3403	−0.1877	7.83
H(4)	−0.3631	0.3932	−0.0938	7.78
H(5)	−0.3319	0.2879	0.0426	7.28
H(6)	−0.1843	0.1234	0.0840	7.02
AH(11)	0.3134	0.0380	−0.0218	5.81
AH(12)	0.2881	0.1780	−0.0253	5.81
AH(13)	0.4456	0.1265	0.0019	5.81
AH(21)	0.4301	−0.0583	0.1204	6.97
AH(22)	0.5634	0.0295	0.1468	6.97
AH(23)	0.4860	0.0126	0.2197	6.97
AH(31)	0.5153	0.2440	0.1346	5.73
AH(32)	0.4685	0.2130	0.2211	5.73
AH(41)	0.3038	0.3326	0.0529	5.16
AH(42)	0.3726	0.3891	0.1579	5.16
AH(51)	−0.0010	0.3466	0.0856	6.40
AH(52)	0.1115	0.4483	0.0913	6.40
AH(53)	0.0698	0.3510	0.0081	6.40
AH(61)	0.1999	0.3868	0.2443	6.29
AH(62)	0.3249	0.2903	0.2737	6.29
AH(71)	0.0380	0.2391	0.2222	8.27
AH(72)	0.1540	0.2444	0.3301	8.27
AH(81)	0.0765	−0.0474	0.2689	8.89
AH(82)	0.0611	0.0581	0.3346	8.89
AH(83)	−0.0308	0.0597	0.2215	8.89
AH(91)	0.3172	−0.0166	0.3177	9.75
AH(92)	0.3770	0.1144	0.3177	9.75
AH(93)	0.3017	0.0812	0.3894	9.75

^{a} The form of the isotropic thermal parameter is exp $[-B(\sin^2\theta/\lambda^2)]$.

Table XI. Interatomic Distances (Å) for the Nonhydrogen Atoms in Stilbene Bis(lithium PMDTA)

Atoms	Distance	Atoms	Distance
E1C(7)–E1C(7)′	1.389 (22)^a	Li–N(1)	2.189 (6)
E1C(7)–C(1)	1.417 (22)	Li–N(2)	2.192 (6)
E2C(7)–E2C(7)′	1.447 (20)	Li–N(3)	2.265 (6)
E2C(7)–C(1)	1.509 (28)	N(1)–AC(1)	1.453 (4)
C(1)–C(2)	1.417 (6)	N(1)–Ac(2)	1.457 (4)
C(1)–C(6)	1.404 (6)	N(1)–AC(3)	1.460 (4)
C(2)–C(3)	1.351 (6)	N(2)–AC(4)	1.472 (4)
C(3)–C(4)	1.335 (6)	N(2)–AC(5)	1.465 (4)
C(4)–C(5)	1.365 (6)	N(2)–AC(6)	1.458 (4)
C(5)–C(6)	1.348 (6)	N(3)–AC(7)	1.485 (5)
Li–E1C(7)	2.274 (9)	N(3)–AC(8)	1.452 (4)
Li–E2C(7)	2.411 (11)	N(3)–AC(9)	1.431 (5)
Li–E1C(7)′	2.391 (9)	AC(3)–AC(4)	1.493 (4)
Li–E2C(7)′	2.271 (10)	AC(6)–AC(7)	1.459 (5)
Li–C(1)	2.927 (7)		

^{a} Errors in the lattice parameters are included in the estimated standard deviations.

in *Cm*. In view of the results from stilbene bis(lithium PMDTA), where only a crystallographic inversion center was present, but the disorder problem was the same, it does not appear that inclusion of the twofold axis has caused the observed disorder. The position for E1C(7) in stilbene bis(lithium TMEDA) is probably close to correct, and most discussions of the lithium-carbanion orientation in stilbene bis(lithium TMEDA) will involve only this carbon atom and not E2C(7). General features in both stilbene dianion structures, such as the lithium coordination sphere and the overall carbanion geometry, would not change in any further refinements of the structure.

Unlike stilbene bis(lithium TMEDA), there are no symmetry restrictions in stilbene bis(lithium PMDTA) which require that the molecules lie in the same plane. Calculations (see Table XV) show that, except for the ethylene carbon atoms, no carbon atom is more than 0.013 (5) Å away from the plane of the superpositioned molecule so that each separated stilbene molecule is planar. The disorder present in both structures does not affect the fact that a trans geometry about the C(7)–C(7)′ bond is observed in both. Furthermore, neither dianion structure exhibits a 90° twist about the C(7)–C(7)′ bond. The stilbene molecule is required by symmetry to be planar in stilbene bis(lithium TMEDA) and does not show any statistically significant deviation from planarity in stilbene bis(lithium PMDTA).

Stilbene Geometry. In each stilbene dianion structure, only the positions for the ethylene carbon atoms of the separated molecules could be observed. The two C(7)–C(7)′ distances in stilbene bis(lithium TMEDA) are 1.487 (21) Å for E1C(7)–E1C(7)′ and 1.373 (43) Å for E2C(7)–E2C(7)′, while

for stilbene bis(lithium PMDTA), they are 1.389 (22) Å for E1C(7)–E1C(7)′ and 1.447 (20) Å for E2C(7)–E2C(7)′. The estimated standard deviations for these bond lengths may be underestimated, due to the fact that the harmonic displacement assumptions inherent to the anisotropic model used for refinement may not accurately represent the disorder. The average C(7)–C(7)′ bond length for the four disordered structures is 1.42 (5) Å. This is an increase of 0.10 (Å) over the C(7)–C(7)′ distance observed in *trans*-stilbene[23] and is consistent with the highest occupied molecular orbital of the dianion being antibonding with respect to the C(7)–C(7)′ bond. For comparison, the olefinic bond length is also increased by 0.10 (2) Å upon reduction in $\Delta^{9,9'}$-bifluorene.[15c]

Lithium Geometry in $(C_{14}H_{12})(LiN_2C_6H_{16})_2$. The coordination sphere around each lithium atom in stilbene bis(lithium TMEDA) consists of two tertiary amine nitrogen atoms and the unsaturated organic group. Each lithium atom is 2.166 (8) Å away from E1C(7) and E1C(7)′ and 2.034 (6) Å away from the stilbene plane. This is the shortest lithium-carbon distance observed to date in complexes containing an amine-solvated lithium cation and a π delocalized carbanion.[14] Figure 3 shows the orientation of the LiN₂ fragment with respect to the two different orientations of the C(7)–C(7)′ bond, as viewed down the twofold axis, where only one LiN₂ fragment has been shown for clarity. The two relative orientations of the LiN₂ fragments are slightly different. A vector drawn perpendicular to the LiN₂ plane is roughly parallel to the E2C(7)–E2H(7) bond in the stilbene molecule containing E2C(7), but the same vector intersects the E1C(7)–E1H(7) bond in the molecule containing E1C(7). As in all the unsaturated organolithium structures which have been studied to date, each lithium atom is in a position corresponding to a nodal surface of the highest occupied molecular orbital of the dianion. Unlike the previous organolithium structures,[14] however, the orientation of the LiN₂ frament does not favor the use of an empty lithium p orbital parallel to the stilbene molecule. Apparently, the σ interaction between the C(7)–C(7)′ carbon atoms and each lithium atom is of such magnitude that the lithium atoms do not move to locations where a carbanion p_π-lithium p orbital interaction is favored, but where close proximity to both ethylenic carbon atoms would be lost. The lithium-nitrogen bond distance is 2.096 (6) Å and the nitrogen-lithium-nitrogen bond angle is 86.1 (3) Å; these values are typical for lithium-TMEDA groups previously studied.[14,15a-d]

Lithium Geometry in $(C_{14}H_{12})(LiN_3C_9H_{23})_2$. The coordination sphere around the lithium atom in stilbene bis(lithium

Table XII. Bond Angles (deg) for the Nonhydrogen Atoms in Stilbene Bis(lithium PMDTA)

Atoms	Angle	Atoms	Angle
C(1)–E1C(7)–E1C(7)'	123.7 (29)[a]	AC(1)–N(1)–AC(2)	108.2 (3)
C(1)–E2C(7)–E2C(7)'	110.9 (28)	AC(1)–N(1)–AC(3)	110.3 (3)
C(6)–C(1)–E1C(7)	108.3 (10)	AC(2)–N(1)–AC(3)	109.5 (3)
C(6)–C(1)–E2C(7)	146.8 (8)	AC(4)–N(2)–AC(5)	109.3 (3)
C(2)–C(1)–E1C(7)	138.7 (10)	AC(4)–N(2)–AC(6)	110.2 (3)
C(2)–C(1)–E2C(7)	100.0 (8)	AC(5)–N(2)–AC(6)	110.3 (3)
C(2)–C(1)–C(6)	113.0 (4)	AC(7)–N(3)–AC(8)	105.1 (3)
C(1)–C(2)–C(3)	121.7 (4)	AC(7)–N(3)–AC(9)	111.9 (3)
C(3)–C(4)–C(5)	122.8 (5)	AC(8)–N(3)–AC(9)	109.3 (3)
C(4)–C(5)–C(6)	118.3 (5)	AC(1)–N(1)–Li	106.0 (2)
C(1)–C(6)–C(5)	120.4 (5)	AC(2)–N(1)–Li	116.7 (3)
AC(4)–AC(3)–N(1)	123.8 (4)	AC(3)–N(1)–Li	106.0 (2)
AC(3)–AC(4)–N(2)	111.5 (3)	AC(4)–N(2)–Li	106.3 (2)
AC(7)–AC(4)–N(2)	112.9 (3)	AC(5)–N(2)–Li	115.5 (2)
AC(7)–AC(6)–N(2)	112.2 (3)	AC(6)–N(2)–Li	104.9 (2)
AC(6)–AC(7)–N(3)	114.9 (3)	AC(7)–N(3)–Li	97.7 (3)
N(1)–Li–N(2)	82.1 (2)	AC(8)–N(3)–Li	118.0 (3)
N(2)–Li–N(3)	83.9 (2)	AC(9)–N(3)–Li	113.9 (3)
N(1)–Li–N(3)	112.9 (2)		

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

Table XIII. Root Mean Square Amplitudes of Vibration (Å) Along the Principal Axes R_i for Stilbene Bis(lithium PMDTA)

Atom	R_1	R_2	R_3
E1C(7)	0.191 (20)	0.206 (11)	0.255 (14)
E2C(7)	0.194 (18)	0.235 (13)	0.327 (22)
C(1)	0.187 (6)	0.252 (6)	0.397 (6)
C(2)	0.244 (6)	0.284 (6)	0.390 (7)
C(3)	0.237 (6)	0.300 (6)	0.439 (7)
C(4)	0.221 (7)	0.257 (6)	0.494 (8)
C(5)	0.237 (6)	0.272 (7)	0.436 (7)
C(6)	0.217 (6)	0.314 (6)	0.381 (6)
AC(1)	0.253 (5)	0.259 (5)	0.304 (5)
AC(2)	0.254 (5)	0.296 (5)	0.345 (5)
AC(3)	0.219 (5)	0.272 (5)	0.306 (5)
AC(4)	0.204 (5)	0.272 (5)	0.315 (5)
AC(5)	0.251 (5)	0.263 (5)	0.350 (5)
AC(6)	0.235 (6)	0.290 (5)	0.343 (5)
AC(7)	0.212 (6)	0.307 (6)	0.442 (6)
AC(8)	0.240 (5)	0.316 (6)	0.432 (5)
AC(9)	0.277 (6)	0.345 (6)	0.484 (7)
N(1)	0.227 (4)	0.238 (4)	0.259 (4)
N(2)	0.214 (4)	0.244 (4)	0.275 (4)
N(3)	0.223 (4)	0.247 (5)	0.360 (4)
Li	0.222 (8)	0.248 (7)	0.277 (7)

Table XV. Best Weighted Least-Squares Planes for Stilbene Bis(lithium PMDTA)

Plane	Atoms in plane	Equation of plane[a,b]
1	E1C(7), C(1), C(2), C(3), C(4), C(5), C(6), E2C(7)', C(1)', C(2)', C(3)', C(4)', C(5)', C(6)'	$-0.6047x -$ $0.5826y -$ $0.5431z = 0$
2	E2C(7), C(1), C(2), C(3), C(4), C(5), C(6), E2C(7)', C(1)', C(2)', C(3)', C(4)', C(5)', C(6)'	$-0.6047x -$ $0.5825y -$ $0.5431z = 0$

Deviations of unique atoms from planes (Å)

Atom	Plane 1	Plane 2
E1C(7)	0.032 (18)	
E2C(7)		−0.032 (18)
C(1)	0.013 (5)	0.013 (5)
C(2)	0.005 (6)	0.006 (6)
C(3)	−0.002 (6)	−0.001 (6)
C(4)	−0.010 (6)	−0.010 (6)
C(5)	−0.005 (6)	−0.005 (6)
C(6)	0.004 (5)	0.005 (5)
N(1)	−3.538 (2)	−3.538 (2)
N(2)	−3.761 (2)	−3.761 (2)
N(3)	−2.792 (3)	−2.792 (3)
Li	−2.180 (5)	−2.180 (5)

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

PMDTA) consists of three tertiary amine nitrogen atoms from one PMDTA molecule and one carbanion; the geometry around the lithium atom is roughly tetrahedral. The relative orientation of the two lithium–PMDTA groups with respect to the carbanion is the same for each of the two separated stilbene molecules. This is illustrated in Figure 4, where the stilbene portion lies in the plane of the page, with lithium atoms above and below the plane, and where all of the PMDTA carbon atoms have been omitted for clarity. The coordinative unsaturation of the lithium atom in stilbene bis(lithium TMEDA) is emphasized by the fact that the lithium atom is 2.180 (5) Å from the stilbene plane in the PMDTA complex, but only 2.034 (6) Å in the TMEDA complex. The average Li–C(7) distances are 2.34 (7) Å (PMDTA) and 2.16 (3) Å (TMEDA).

The previously proposed bonding model for π carbanion complexes[14-16] suggests that a trisolvated lithium atom should be located at a position predicted by an electrostatic model.[24]

For the stilbene dianion, this position should be on a vector through the midpoint of the C(7)–C(7)' bond and perpendicular to the stilbene plane. In fact, the lithium atom is not above the midpoint of the C(7)–C(7)' bond, as can be seen in Figure 4. However, the dipole of the PMDTA–Li fragment is directed toward the midpoint of the C(7)–C(7)' bond, in agreement with an ion–dipole model. It appears that the lithium–PMDTA group has shifted slightly from the predicted position so that N(3) is closer to the stilbene plane, while still maintaining the orientation of the lithium dipole toward the midpoint of the C(7)–C(7)' bond. This shift thus leads to the molecule oc-
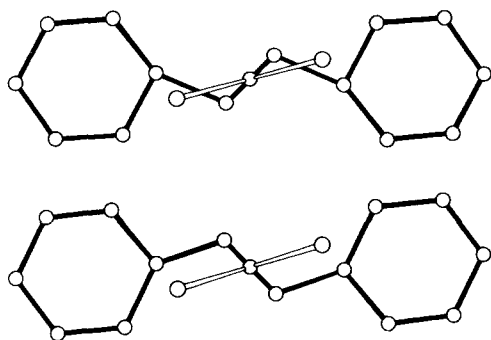
Figure 3. Orientation of the LiN$_2$ plane with respect to the two different orientations of the ethylene carbon–carbon bond, as viewed down the twofold axis.

cupying a slightly smaller volume in the unit cell than would otherwise be the case and helps to eliminate possible nonbonded intermolecular contacts in packing.

The lithium–nitrogen atom bond distances and angles in stilbene bis(lithium PMDTA) are not similar to those previously observed in lithium–TMEDA systems.[14,15a-d] The N(1)–Li–N(2) and N(2)–Li–N(3) angles of 82.1 (2)° and 83.9 (2)°, respectively, are smaller than those seen in the lithium–TMEDA group, while the lithium–nitrogen bond lengths—2.189 (6) Å for Li–N(1), 2.192 (6) Å for Li–N(2), and 2.265 (5) Å for Li–N(3)—are all longer. Addition of the third nitrogen atom coordinated to the lithium atom has a pronounced effect on the lithium–base interaction. The three lithium–PMDTA nitrogen distances average 0.12 Å longer than the lithium–nitrogen distance in stilbene bis(lithium TMEDA). While the increase may be due to steric factors, more likely it is an electronic effect, showing the coordinated base acts as a variable electron density source so that the same charge on the lithium atom is maintained in each of the complexes.

PMDTA Geometry. Since the PMDTA portion of stilbene bis(lithium PMDTA) was found to be well behaved, and no structural information on the PMDTA ligand in organolithium compounds had been previously reported, its structure will be described in some detail. The carbon–carbon distances between PMDTA methylene carbon atoms are 1.493 (4) Å for AC(3)–AC(4) and 1.459 (5) Å for AC(6)–AC(7). The carbon–nitrogen bond lengths in stilbene bis(lithium PMDTA) average 1.457 (4) Å around N(1), 1.465 Å around N(2), and 1.456 (4) Å around N(3). The similar average in stilbene bis(lithium TMEDA) is 1.457 (4) Å. In stilbene bis(lithium PMDTA), the carbon–nitrogen–carbon angles average 109.3 (3)° around N(1), 109.9 (3)° around N(2), and 108.9 (3)° around N(3), while the carbon–nitrogen–lithium angles average 109.6 (3) around N(1), 108.9 (3)° around N(2), and 109.9 (3)° around N(3).

Comparison of X-Ray and Solution Studies of the Stilbene Dianion. A tight contact ion pair consisting of amine-solvated lithium cations above and below a planar stilbene dianion and exhibiting a substantial interaction between the cations and the ethylenic carbon atoms was found in each structure. This geometry is in contrast to the solution studies involving disproportionation of arylethylene monoanions and the photochemical behavior of *cis*- and *trans*-stilbene, which were explained using a twisted structure. This apparent disagreement may at first seem somewhat surprising, as several previously determined crystal structures of π delocalized carbanions have been found to be good models for interpreting solution results (see, for example, the results from dilithionaphthalene,[15d] the NMR studies of the methylnaphthalene anions[25] and the structure of benzyllithium,[15e] and the recently reported x-ray structure of an ion pair containing the hexatriene group[26]).
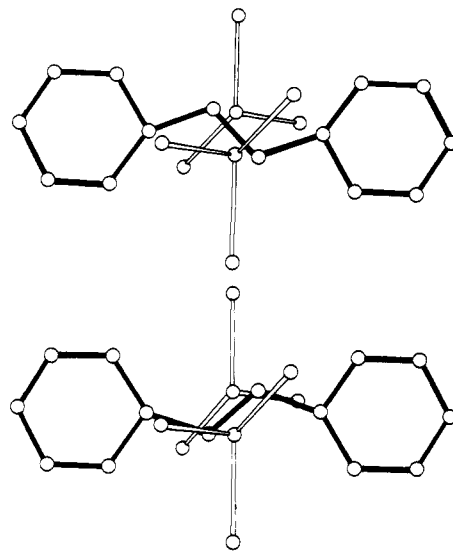

Figure 4. Orientation of the two LiN$_3$ groups with respect to the two different orientations of the ethylene carbon–carbon central bond.

However, the solution structures of the stilbene dianion and other more highly substituted arylethylenes, such as the α-methylstilbene or tetraphenylethylene dianion, need not be the same. The steric strain present in highly substituted planar arylethylene monoanions is negligible in a planar stilbene monoanion. Thus, there is not the driving force in the stilbene system for the dianion to adopt a twisted geometry to relieve the steric crowding, as is the case in more congested systems. Furthermore, the photochemical behavior of stilbene may not provide a good model for describing the dianion's structure in solution. The twisted triplet photochemical intermediate is analogous to a solvent separated dianion in solution, insulated from immediate contact with any partially solvated cations. However, the solution studies have involved contact ion pairs, with at least one solvated cation interacting with the stilbene dianion. Since the cation(s) in the ion pair will play a part in determining the structure of the stilbene dianion, predictions based on the photochemical results may not be valid.

The photochemical results can be used to obtain some information about the free dianion in the planar and twisted geometries. Molecular orbital calculations had previously predicted an energy difference between the two lowest energy triplet configurations of approximately 5 kcal/mol, with the twisted structure lower in energy than the trans planar geometry.[13b] Recent photochemical results have suggested a much larger energy gap exists, as it was found that essentially all of the stilbene triplets were twisted.[11a] Assuming equal energies for association of the cations with either form, this would then suggest that the trans planar contact ion pair would not be energetically accessible in solution from the twisted ion pair. Under such circumstances, it is then difficult to envision how the planar trans form would be the structure isolated from the reaction. The above assumption of equal cation association energies with either configuration is, therefore, probably not correct. Previous calculations have indicated that significant charge transfer from π delocalized anion to lithium cation occurs in the contact ion pair.[14] This effect should be more important in reducing Coulombic interactions resulting from negative charge residing on the adjacent ethylenic carbon atoms in the planar trans dianion than in the twisted geometry. The increase in Coulombic interactions on dissociation of one or more cations from the dianion thus should have a greater effect in the planar species, and, therefore, the energy necessary for dissociation of a lithium cation should be greater in the planar form. Here, in the ion pair, the planar dianion allows

the maximum interaction of each lithium atom with the π charge density of the stilbene molecule and for this reason is favored over the twisted structure. Intramolecular nonbonded interactions are negligible in the planar trans dianion, so that twisting need not occur, unlike other more sterically crowded systems, such as the tetraphenylethylene dianion, where such interactions are present. Even in the ion pair containing tri-solvated lithium cations, the planar dianion is still present. Thus, the planar structure can provide a good model for the ion-paired stilbene dianion in solution.

Features observed in the two crystal structures presented here are helpful in explaining the results Szwarc obtained in his electron transfer induced cis–trans isomerization studies of stilbene.[7] The rate-determining step in the isomerization was found to be conversion of the *cis*-stilbene dianion to the *trans*-stilbene dianion. Because of the presence of excess cation in solution inhibiting dissociation, the dianionic species existed predominantly as contact ion pairs. In the cis dianion, place-ment of metal cations above and below the stilbene molecule, with each cation associated with both ethylenic carbon atoms, would lead to hindered rotation about the formally reduced carbon–carbon double bond, since the interaction of the metal cation with the π charge density between the ethylenic carbon atoms would have to be decreased before rotation could occur. The trans dianion formed in the isomerization step would then resemble the structures observed here in the solid state.

Supplementary Material Available: A listing of the observed and calculated factor amplitudes in electrons for stilbene bis(lithium TMEDA) (Table VII) and stilbene bis(lithium PMDTA) (Table XIV) (26 pp). Ordering information is given on any current masthead page.

References and Notes

(1) J. F. Garst, *J. Am. Chem. Soc.*, **93**, 6312 (1971).
(2) (a) J. F. Garst, E. R. Zabolotny, and R. S. Cole, *J. Am. Chem. Soc.*, **86**, 2257 (1964); (b) J. F. Garst and E. R. Zabolotny, *ibid.*, **87**, 495 (1965).
(3) (a) R. C. Roberts and M. Szwarc, *J. Am. Chem. Soc.*, **87**, 5542 (1965); (b) A. Cserhegyi, J. Jagur-Grodzinski, and M. Szwarc, *ibid.*, **91**, 1892 (1969); (c) B. Lundgren, G. Levin, S. Claesson, and M. Szwarc, *ibid.*, **97**, 262 (1975).
(4) J. F. Garst and E. R. Zabolotny, *J. Am. Chem. Soc.*, **86**, 1645 (1964), and references therein.
(5) J. F. Garst, J. G. Pacifici, and E. R. Zabolotny, *J. Am. Chem. Soc.*, **88**, 3872 (1966).
(6) S. Sorensen, G. Levin, and M. Szwarc, *J. Am. Chem. Soc.*, **97**, 2341 (1975).
(7) (a) G. Levin, T. A. Ward, and M. Szwarc, *J. Am. Chem. Soc.*, **96**, 270 (1974); (b) T. A. Ward, G. Levin, and M. Szwarc, *ibid.*, **97**, 258 (1975).
(8) A. D. Walsh, *J. Chem. Soc.*, 2296, 2325 (1953).
(9) R. G. Pearson, *Chem. Phys. Lett.*, **10**, 31 (1971).
(10) (a) J. Saltiel and G. S. Hammond, *J. Am. Chem. Soc.*, **85**, 2515 (1963); (b) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *ibid.*, **86**, 3197 (1964); (c) W. G. Herkstroeter and G. S. Hammond, *ibid.*, **88**, 4769 (1966).
(11) (a) J. Saltiel and B. Thomas, *J. Am. Chem. Soc.*, **96**, 5660 (1974); (b) J. Saltiel, D. W. L. Chang, and E. D. Megarity, *ibid.*, **96**, 6521 (1974); (c) J. Saltiel, J. D Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton, and O. C. Zafiriou, *Org. Photochem.*, **3**, 1 (1973); (d) J. Saltiel and J. T. D'Agostino, *J. Am. Chem. Soc.*, **94**, 6445 (1972); (e) J. Saltiel, J. T. D'A-gostino, W. G. Herkstroeter, G. Saint-Ruf, and N. P. Buu-Hoi, *ibid.*, **95**, 2543 (1973).
(12) A. Bylina and Z. R. Grabowski, *Trans. Faraday Soc.*, **65** 458 (1969).
(13) (a) N. C. Baird, *Mol. Photochem.*, **2**, 53 (1970); (b) N. C. Baird and R. M. West, *J. Am. Chem. Soc.*, **93**, 4427 (1971).
(14) G. Stucky, *Adv. Chem. Ser.*, **130**, 56 (1974).
(15) (a) W. Rhine and G. Stucky, *J. Am. Chem. Soc.*, **97**, 737 (1975); (b) W. Rhine, J. Davis, and G. Stucky, *ibid.*, **97**, 2079 (1975); (c) M. Walczak and G. D. Stucky, *J. Organomet. Chem.*, **97**, 313 (1975); (d) J. J. Brooks, W. Rhine, and G. D. Stucky, *J. Am. Chem. Soc.*, **94**, 7346 (1972); (e) S. P. Patterman, I. L. Karle, and G. D. Stucky, *ibid.*, **92**, 1150 (1970).
(16) J. J. Brooks, W. Rhine, and G. D. Stucky, *J. Am. Chem. Soc.*, **94**, 7339 (1972).
(17) (a) R. G. Harvey, L. Nazarene, and H. Cho, *J. Am. Chem. Soc.*, **95**, 2376 (1973); (b) R. G. Harvey and H. Cho, *ibid.*, **96**, 2434 (1972).
(18) E. R. Howells, D. C. Philips, and D. Rogers, *Acta Crystallogr.*, **3**, 210 (1950).
(19) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. B*, **26**, 274 (1970).
(20) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).
(21) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(22) C. J. Brown, *Acta Crystallogr.*, **21**, 153 (1966).
(23) C. J. Finder, M. G. Newton, and N. L. Allinger, *Acta Crystallogr., Sect. B*, **30**, 411 (1974).
(24) I. B. Goldberg and J. R. Bolton, *J. Phys. Chem.*, **74**, 1965 (1970).
(25) F. J. Kronzer and V. R. Sandel, *J. Am. Chem. Soc.*, **94**, 5750 (1972).
(26) S. K. Arora, R. B. Bates, W. A. Beavers, and R. S. Cutler, *J. Am. Chem. Soc.*, **97**, 6271 (1975).

Halogen Cleavage Reactions of
threo-PhCHDCHDFe(CO)$_2$(η^5-C$_5$H$_5$)

D. A. Slack and M. C. Baird*

Contribution from the Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6. Received December 8, 1975

Abstract: Halogen cleavage reactions of the metal–carbon bond of the compound *threo*-PhCHDCHDFe(CO)$_2$(η^5-C$_5$H$_5$) have been studied under a variety of conditions. The major product in most cases is the *threo*-α,β-dideuteriophenethyl halide, al-though *threo*-α,β-dideuteriophenethyl methyl ether is produced when reactions are carried out in methanol. Analogous cleav-age reactions of samples labeled with ^{13}C at the α-carbon atom show that, in most cases, the methylene carbon atoms become equivalent at some point along the reaction pathway. A mechanism is proposed which involves initial oxidation of the metal to give the fluxional intermediate [η^5-C$_5$H$_5$Fe(CO)$_2$X(CHDCHDPh)]$^+$ (rather than direct attack of halogen on the α-carbon atom), followed by reductive elimination of *threo*-phenethyl halide. The intermediate also yields *erythro*-phenethyl halide, not by nucleophilic attack on the intermediate by halide ion, but more probably via nonchain radical processes. It is proposed that halogen cleavage of transition metal alkyl complex containing nonbonding d electrons may generally proceed via initial oxidation of the metal, and that the long-accepted S_E2 (cyclic) mechanism for the cleavage of main group metal alkyl com-pounds is a symmetry-forbidden process.

Electrophilic cleavage of transition metal–carbon σ bonds by reagents as diverse as protic acids, halogens, and mercu-ry(II) salts has long been used for synthetic purposes as well as an aid in the identification of organometallic compounds;[1] in the case of halogens, cleavage normally results in the for-mation of metal halide and alkyl halide, i.e.