

Registry No. 1a, 88730-05-6; 1b, 88730-06-7; 1c, 92472-05-4; 1d, 92472-06-5; 2a, 92472-07-6; 2b, 92472-08-7; 2c, 92472-09-8; 2d, 92472-10-1; 3a, 92472-11-2; 3b, 92472-12-3; 3c, 92472-13-4; 3d, 92472-14-5; 4a, 24104-20-9; 4b, 75750-06-0; 4c, 92472-15-6; 4c (dinitrophenylhydrazone), 92472-19-0; 4d, 92472-16-7; DMSO, 67-68-5; Ph₂C=CH₂, 612-00-0; PhC(Me)=CH₂, 98-83-9; 1,1-diphenylcyclopropane, 3282-18-6; 1-methyl-1-phenylcyclopropane, 2214-14-4; *cis*-1,2-dimethyl-1-phenylcyclopropane, 77422-55-0; *trans*-1,2-dimethyl-1-phenylcyclopropane, 35496-06-1; 2,2-diphenyl-5-methoxytetrahydrofuran, 92472-17-8; 2,4-dimethyl-5-methoxy-2-phenyltetrahydrofuran, 92472-18-9; 5-methoxy-2-methyl-2-phenyltetrahydrofuran, 82194-21-6.

Supplementary Material Available: Table and figures on the synthesis and characterization of stereotagged derivatives (4 pages). Ordering information is given on any current masthead page.

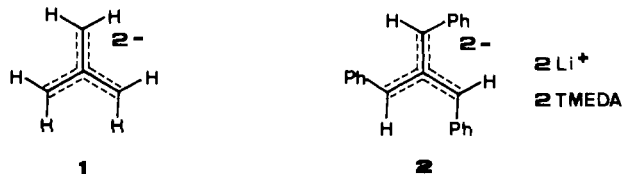
Dilithium Tribenzylidenemethane-2TMEDA: The First X-ray Structure of a Y-Conjugated Trimethylenemethane Dianion Derivative

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Klein's¹ recognition of the "Y-conjugated"² nature of the trimethylenemethane dianion (**1**) has led to widespread appreciation



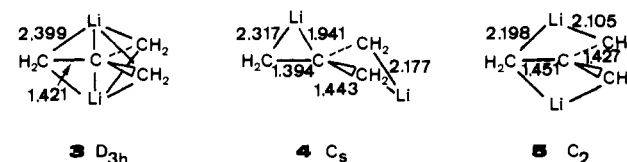
of the general importance of these species.¹⁻⁵ Such "dianions" owe their remarkable stabilities, relative to alternative linear and even cyclic 6 π -electron topographies, to the favorable charge distributions which reduce electrostatic repulsions.⁴ However, so-called "dianions" are better regarded as dimetallo compounds; their structures and stabilities may depend largely on the counterion interactions.⁵⁻⁷ We now report the first⁸ X-ray structure

of a trimethylenemethane dianion dilithium salt, the symmetrically substituted dilithium tribenzylidenemethane-2TMEDA (TMEDA = tetramethylethylenediamine) (**2**).^{3b}

The X-ray structure of **2**⁹ (Figures 1 and 2) does not, however, show the 3-fold symmetry indicated by MNDO calculations on the tribenzylidenemethane dianion itself;^{3b} one of the three bonds to the central carbon atom is considerably shorter (1.388 (4) Å) than the other two (1.433 (3) and 1.460 (3) Å). This asymmetry is larger than would be expected from the perturbation of the two TMEDA ligands and must be caused by interactions with the two lithiums. One cation, Li(4), favors an allyl lithium-like¹⁰ bridging position between C(17) and C(27). The asymmetry of this bridge (Li(4)-C(17) = 2.304 (5), Li(4)-C(27) = 2.234 (5) Å) can be attributed to the conformations of the phenyl groups on C(17) and C(27). The other lithium, Li(3), bridges the short C(7)-C(8) bond, and longer C-Li contacts to C(17) and the *ortho* carbon of one ring C(12) also are present. Why is this structure preferred? Consideration of the parent system provides some insights.

Calculations confirm the qualitative theoretical expectations:^{1,4} the trimethylenemethane dianion (**1**) prefers *D*_{3h} symmetry. However, as an isolated entity, this species is unrealistic, since the second "anionic" electron will not be bound. The counterions are *required* for stability, and their presence controls the geometric preference.⁵⁻⁸

Ab initio calculations (3-21G basis set)¹¹ on various C(CH₂)₃Li₂ geometries reveal 3-5 to be the most favorable alternatives. The



most symmetrical *D*_{3h} form (**3**), with the lithiums imposed to lie along the 3-fold axis, is *not* lowest in energy. On average, the lithium atoms are farther from the anion-bearing CH₂ carbons, and electrostatic interactions with the small lithium cations are not optimal. If the symmetry is reduced to *C*_s, a structure (**4**) is obtained which is only 0.1 kcal/mol more stable than **3**, and a doubly 1,3-lithium-bridged form (**5**, *C*₂) is 4.2 kcal/mol lower in energy. However, **5** has nearly equal C-C bond lengths and does not conform to the experimentally observed structure of the triphenyl derivative, **2**. The X-ray structure of **2** (Figures 1 and 2) corresponds more closely to that of **4**, which has two longer (1.443 Å) and one short (1.394 Å) C-C bonds. The potential energy surface is rather flat, and the further interactions of the lithium atoms with the phenyl groups are responsible for the structural preference observed in **2**.

The C(7)-C(8) distance in **2** (Figures 1 and 2) is similar to that found for one of the disordered forms of the dilithiated stilbene

(8) Structures of tricarbonyl(trimethylenemethane)iron and related complexes are distantly related. For references and discussion, see: Chandrasekhar, J.; Schleyer, P. v. R.; Schlegel, H. B. *Tetrahedron Lett.* **1978**, 3393. Albright, T. A. *Acc. Chem. Res.* **1982**, *15*, 149. Jones, M. D.; Kemmitt, R. D. W.; Platt, A. W. G.; Russell, D. R.; Sherry, L. J. S. *J. Chem. Soc., Chem. Commun.* **1984**, 673.

(9) Triclinic (from hexane), space group *P* $\bar{1}$, *Z* = 2, *a* = 8.627 (6) Å, *b* = 11.867 (4) Å, *c* = 17.026 (9) Å, α = 72.51 (4)°, β = 83.88 (6)°, γ = 76.84 (5)°, *V* = 1617 Å³, *d*_c = 1.085 g/cm³, λ = 0.71069 Å, 2° < θ < 27°; 63 292 reflection profiles were averaged to a set of 7039 structure factors (*F*²), 3900 of which were stronger than 2 σ . The structure was solved with MULTAN 76 and refined by X-RAY 76. The final *R* values based on the 3900 *F*_o²2 σ are *R*(*F*²) = 0.152 and *R*_w(*F*²) = 0.147. These relatively poor values are partly due to disorder in the TMEDA moieties (a number of similar cases are known^{6a}). The structure of the rest of the system is considered to be significantly better. Further details of the crystal structure investigation are available on request from the Cambridge Crystallographic Data Center, University Chemical Laboratory, Cambridge CB2 1EW, England.

(10) Clark, T.; Rohde, C.; Schleyer, P. v. R. *Organometallics* **1983**, *2*, 1344.

(11) The GAUSSIAN 82 program, release A (Binkley, J. S.; Frisch, M. J.; Raghavachari, K.; De Fries, D. J.; Schlegel, H. B.; Whiteside, R. A.; Fluder, E.; Seeger, R.; Pople, J. A. Carnegie-Mellon University, Pittsburgh, PA, 1983), adapted to CDC computers by A. Sawaryn, was employed. The 3-21G//3-21G energies of **3**, **4**, and **5** (in au) are, respectively, -168.851 18, -168.851 35, and -168.857 88.

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(1) Klein, J.; Medlik, A. *J. Chem. Soc., Chem. Commun.* **1973**, 275. For citations to earlier syntheses of **1** and a detailed discussion, see: Klein, J. *Tetrahedron* **1983**, *39*, 2733.

(2) Gund, P. *J. Chem. Educ.* **1972**, *49*, 100.

(3) (a) Mills, N. S.; Shapiro, J.; Hollingsworth, M. *J. Am. Chem. Soc.* **1981**, *103*, 1263. (b) Wilhelm, D.; Clark, T.; Schleyer, P. v. R.; Buckl, K.; Boche, G. *Chem. Ber.* **1983**, *116*, 1669. (c) Wilhelm, D.; Clark, T.; Schleyer, P. v. R. *Tetrahedron Lett.* **1983**, *24*, 3985. (d) Wilhelm, D.; Clark, T.; Schleyer, P. v. R. *J. Chem. Soc., Perkin Trans 2* **1984**, 915.

(4) Clark, T.; Wilhelm, D.; Schleyer, P. v. R. *Tetrahedron Lett.* **1982**, *33*, 3547.

(5) First example: Brooks, J. J.; Rhine, W.; Stucky, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 7346.

(6) (a) Schubert, W.; Neugebauer, W.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1982**, 1184. (b) Streitwieser, A., Jr.; Swanson, J. T. *J. Am. Chem. Soc.* **1983**, *105*, 2502.

(7) Schleyer, P. v. R. *Pure Appl. Chem.* **1983**, *55*, 355; *Ibid.* **1984**, *56*, 151 and references cited. Schleyer, P. v. R.; Kos, A. J.; Wilhelm, D.; Clark, T.; Boche, G.; Decker, G.; Etzrodt, H.; Dietrich, H.; Mahdi, W. *J. Chem. Soc., Chem. Commun.*, in press. For a review of the X-ray structures of lithium compounds, see: Setzer, W.; Schleyer, P. v. R. *Adv. Organomet. Chem.*, in press.

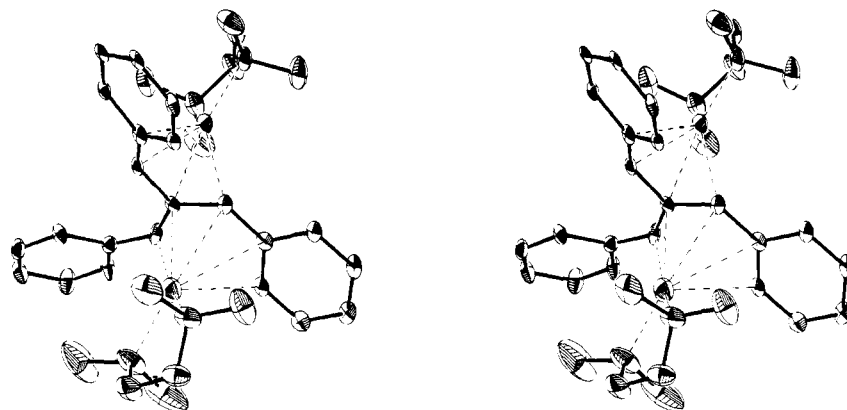


Figure 1. Stereoplots of the X-ray structure of dilithium tribenzylidenemethane-2TMEDA.

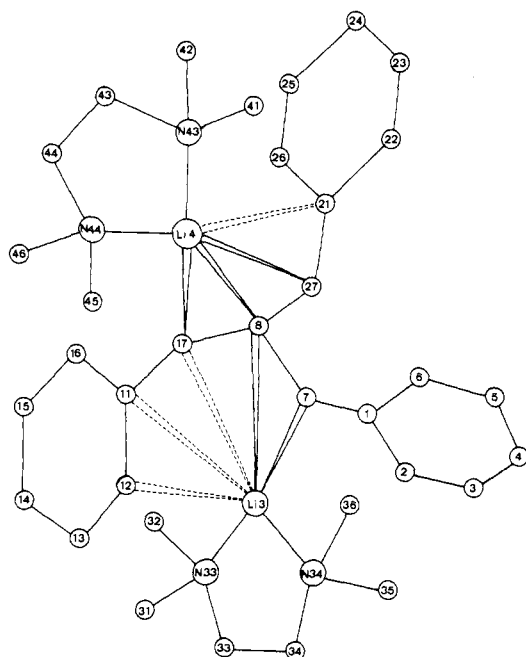


Figure 2. Schematic view of the structure in Figure 1. Important bond lengths in Å: C(8)–C(27) 1.460 (3), C(8)–C(17) 1.443 (3), C(8)–C(7) 1.388 (4), C(11)–C(17) 1.441 (3), C(7)–C(1) 1.420 (3), C(27)–C(21) 1.434 (4), Li(4)–C(21) 2.667 (4), Li(4)–C(27) 2.234 (5), Li(4)–C(8) 2.287 (6), Li(4)–C(17) 2.304 (5), Li(3)–C(7) 2.297 (5), Li(3)–C(8) 2.337 (6), Li(3)–C(17) 2.626 (6), Li(3)–C(11) 2.784 (6), Li(3)–C(12) 2.673 (5), C(1)–C(2) 1.395 (4), C(2)–C(3) 1.372 (4), C(3)–C(4) 1.437 (3), C(4)–C(5) 1.369 (4), C(5)–C(6) 1.371 (4), C(1)–C(6) 1.462 (3). Lithium–nitrogen distances vary between 2.025 and 2.118 Å.

dianion¹² and confirms this interpretation. The phenyl groups are twisted from the trimethylenemethane plane, as suggested by MNDO calculations on the dianion.³ The entire structure, with lithium atoms above and below the dianion plane in bridging positions between the carbon atoms with the highest negative charges, is electrostatically very favorable. The quinonoid distortions of the phenyl substituents (indicative of delocalization of the negative charge) are most pronounced for the ring bound to C(7), although the differences are not large. Finally, we note that the orientation of the TMEDA ligand coordinated to Li(4) is that expected from Stucky's orbital arguments^{5,12} but that the orientation of the other diamine moiety is consistent with an interaction with C(7) and C(12).¹³

The X-ray structure of a related Y-conjugated 1,3-acetone "dianion" derivative (dilithiated dibenzyl ketone) has just been reported.¹⁴ We have now been able to obtain the X-ray structure of another Y-conjugated system, dilithium dibenzylidene-ethylene-2-tetramethylpropanediamine.¹⁵ The geometry resembles **5** more closely than does **2**.

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Registry No. **1**, 13001-05-3; **2**, 92314-26-6.

(14) Dietrich, H.; Mahdi, W.; Wilhelm, D.; Clark, T.; Schleyer, P. v. R. *Angew. Chem.* **1984**, *96*, 623; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 621. Also see: Kos, A. J.; Clark, T.; Schleyer, P. v. R. *Angew. Chem.* **1984**, *96*, 622; *Angew. Chem., Int. Ed. Engl.*, **1984**, *23*, 620.

(15) Wilhelm, D.; Dietrich, H.; Mahdi, W.; Clark, T.; Schleyer, P. v. R., to be published.

¹³C, ¹H, and ²H NMR Observation of Trideuterated Cyclopropylmethyl-Cyclobutyl Carbocation: A Configurationally Stable Species^{1a}

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With the increasing power and sophistication of experimental and theoretical methods for assigning chemical structures, it seems almost incredible that the structure of any reasonably stable organic entity with a small number of carbons could remain enigmatic for very long. Nonetheless, this is true of C₄H₇⁺—one of the first "nonclassical" cations to be discovered, which has some of the characteristics expected for a very rapidly equilibrating mixture of classical cyclopropylmethyl, cyclobutyl, and 3-butenyl cations and yet other characteristics which wholly belie any description that implies conventional charge distributions or geometries derived from structural representations using solid lines representing two-electron bonds.²

(12) Walczak, M.; Stucky, G. J. *Am. Chem. Soc.* **1976**, *98*, 5531.

(13) See Bushby et al. (Bushby, R. J.; Tytko, M. P. *J. Organomet. Chem.* **1984**, *270*, 265) for an electrostatic interpretation of lithiated π -carbanion structures.

(1) (a) Supported by the National Science Foundation. (b) NSF Fellow, 1979–1980.

(2) Staral, J. S.; Roberts, J. D.; Prakash, E. K. S.; Donovan, D. J.; Olah, G. A. *J. Am. Chem. Soc.* **1978**, *100*, 8016, 8018.