

Preliminary communication

2,6-BIS(LITHIUMTRIMETHYLSILYLMETHYL)PYRIDINE · 2TMEDA: A MONOMERIC DILITHIO COMPOUND EXHIBITING ELECTROSTATIC CHARGE COMMUNICATION

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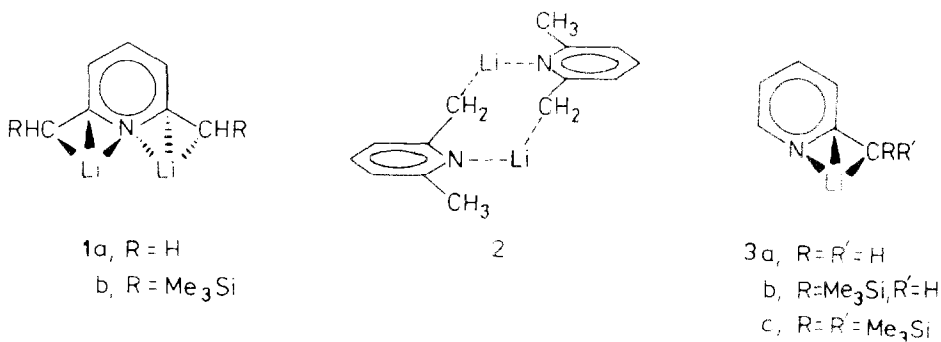
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Summary

The crystal structure of 2,6-bis(lithiumtrimethylsilylmethyl)pyridine · 2TMEDA, which is readily obtained by metallation of 2,6-(Me₃SiCH₂)₂C₅H₃N, exhibiting double (η^3 -aza-allyl)-lithium bonding, represents a beautiful example of C⁻Li⁺N⁻Li⁺C⁻ charge communication, and confirms the predictions of theory.

The predominately ionic character of lithium and other alkali metal compounds often permits their structures to be predicted on the basis of simple electrostatic considerations [1]. When two such electropositive metals are present in the same molecule, geometries in which the charges alternate, e.g. -/+ / + / - / + / - , may be favoured [2]. On the basis of such charge communication, α,α' -dilithio-2,6-dimethylpyridine can be expected to have structure **1a**, with one lithium above and one



below the ring plane. MNDO calculations [3] support this prediction. We now report the experimental verification.

In the crystal the corresponding monolithiated derivative, (α -lithio-2,6-dimethylpyridine \cdot TMEDA)₂ (**2**), prefers a dimeric eight-membered ring structure, which is an ideal compromise permitting simultaneous charge delocalization and N–Li chelation [4]. In monomers of this type, MNDO calculations [4] indicate aza-allyl coordination (**3a**) to be favoured over involvement of the N-lone pair. Such arrangements are exhibited experimentally in the X-ray structures of the lithium derivatives of the α -silylated compounds, **3b** and **3c** [5].

In order to obtain a crystalline derivative of **1**, we first dimetallated 2,6-lutidine with a 1/1/1 mixture of butyllithium-tetramethylethylenediamine (TMEDA)/potassium t-amylate (or potassium t-butylate) [6] in hexane [7]. Addition of THF and trimethylchlorosilane gave a yield of more than 60% of 2,6-bis(trimethylsilylmethyl)pyridine after distillation. Further metallation of this silylated lutidine by n-butyllithium/TMEDA in hexane at room temperature afforded orange crystals of **1b** as the TMEDA complex.

The crystal structure of this complex * does indeed confirm the expected charge communication. As shown in Fig. 1, the two lithium cations occupy η^3 -aza-allylic positions on different sides of the pyridine ring. This minimizes their dipolar repulsion and results in an electrostatically favorable C[−]Li⁺N[−]Li⁺C[−] sequence. The geometry largely precludes Li⁺ interactions with the in-plane lone pair on nitrogen. Additional complexation of the lithiums by TMEDA molecules affords coordination numbers of five in essential C₂ symmetry. The trimethylsilyl groups are only slightly twisted out of the pyridine plane. Since the silyl groups stabilize carbanions largely by polarization [8], the structure of **1b** should be similar to that of its parent **1a**. In the aza-allylic moiety of **1b**, the Li–N distances, (2.015(6) and 1.998(7) Å), are nearly equal, and are shorter than the Li–C distances (2.254(7), 2.276(7) and 2.264(7) Å). This is general behavior [1b,c], and is found, e.g., in the dimeric monolithium compound **2** [4] and the lithiated picoline structures **3b** and **3c** [5].

A model MNDO calculation, with α -SiH₃ substituents on **1** and NH₃ ligands (in place of TMEDA) (Fig. 2), shows excellent overall agreement with the crystal structure. However, the Li–C distances are shorter than the Li–N distances owing

* *Crystal structure data:* C₂₅H₅₅Li₂N₅Si₂, *M_r* = 495.80, triclinic, space group $\bar{P}1$, *a* 9.621(1), *b* 11.617(2), *c* 15.753(2) Å, α 97.15(1), β 90.71(1), γ 99.27(1)°, *U* 1723.21 Å³, *D_c* = 0.955 g cm^{−3} for *Z* = 2, *F*(000) = 548, μ (Mo-*K α*) 1.2 cm^{−1}. 5362 unique reflections were collected on an automated four-circle diffractometer (ω -scans, $\Delta\omega$ 0.9°, $1 \leq \vartheta \leq 24^\circ$, $+h, \pm k, \pm l$, Mo-*K α* radiation, λ 0.71069 Å, graphite monochromator, *T* −40°C, Syntex P2₁). After Lorentz polarization corrections 3941 structure factors with $|F_0| \geq 4.0\sigma(F_0)$ were deemed "observed" and used in all further calculations. The structure was solved by direct methods (MULTAN 80) [12] and completed by difference-Fourier syntheses. 49 out of a total of 55 hydrogen atoms could be located, and the remainder were placed at calculated positions. Full-matrix least-squares of 349 parameters converged at *R* = 0.064, *R_w* = 0.068, $w = 1/\sigma^2(F_0)$ (non-H atoms anisotropic, CH₃ as rigid groups, all other hydrogens fixed, SHELX-76 [13]. A final difference map indicated slight disorder of the TMEDA methylene groups C(31)/C(32) but was featureless otherwise, $\Delta\rho_{\text{max/min}}$ 0.57/−0.37 e/Å³. The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

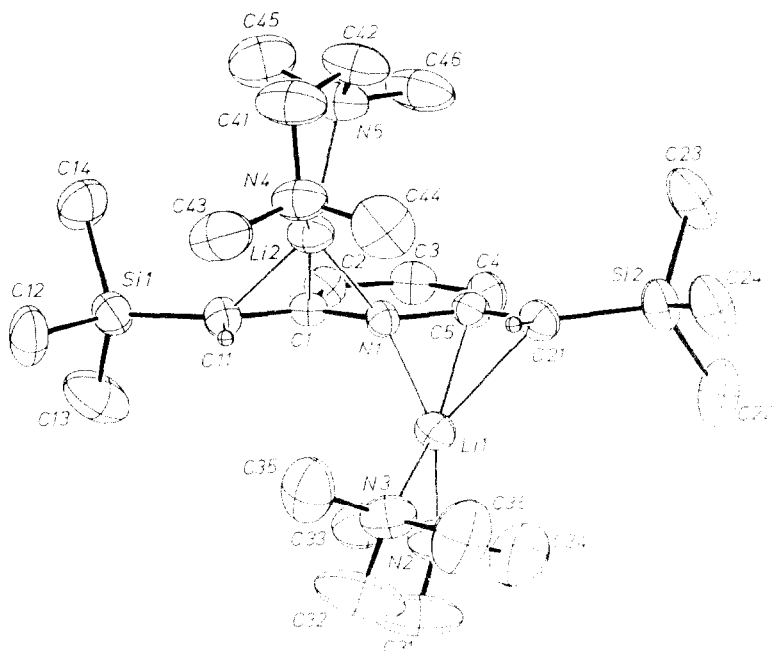
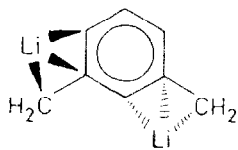


Fig. 1. Molecular structure of **1b** (ORTEP, thermal ellipsoids at the 50% probability level, H atoms omitted for clarity except those at the α -carbon atoms which were drawn with arbitrary radii). Principal distances (Å) and angles ($^\circ$) are: N(1)–C(1) 1.402(4), N(1)–C(5) 1.389(4), C(1)–C(2) 1.413(5), C(2)–C(3) 1.379(5), C(3)–C(4) 1.391(5), C(4)–C(5) 1.425(5), C(1)–C(11) 1.413(5), Si(1)–C(11) 1.819(4), C(5)–C(21) 1.417(5), Si(2)–C(21) 1.816(4), Li(1)–N(1) 2.015(6), Li(1)–C(5) 2.254(7), Li(1)–C(21) 2.276(7), Li(1)–N(2) 2.062(7), Li(1)–N(3) 2.103(7), Li(2)–N(1) 1.998(7), Li(2)–C(1) 2.264(7), Li(2)–C(11) 2.264(7), Li(2)–N(4) 2.106(7), Li(2)–N(5) 2.084(7); Si(1)–C(11)–C(1) 128.3(3), C(11)–C(1)–N(1) 115.4(3), C(11)–C(1)–C(2) 125.7(3), N(1)–C(1)–C(2) 118.8(3), C(1)–N(1)–C(5) 122.0(3), Si(2)–C(21)–C(5) 128.6(3), C(21)–C(5)–N(1) 116.3(3), C(21)–C(5)–C(4) 125.3(3), N(1)–C(5)–C(4) 118.4(3). The entire arrangement Si(1),C(11),C(1),N(1),C(5),C(21),Si(2) is marginally skewed: Si(1),C(11),C(21),Si(2) deviate by 0.10, 0.01, –0.06, –0.23 Å, respectively, from the best plane through the pyridine ring.

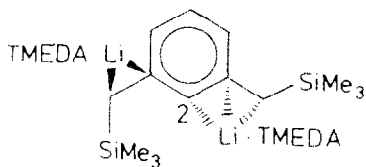
to the known deficiencies in the MNDO Li-parametrization [3]. Nevertheless, the correspondence of the experimental and the calculated geometries once again shows MNDO to be an efficient tool for predicting the structures of lithium compounds [1a,2,4].

Substitution of the electronegative pyridine nitrogen in **1** by a CH group changes the electron distribution in the ring and results in a different geometry. For α,α' -dilithio-*m*-xylene, MNDO now favours structure **4**, with separated cations, over the C_2 geometry corresponding to **1a** (with CH in place of N), by 3.5 kcal/mol [9].



(4) ΔH_f° (MNDO)

3.4 kcal/mol



(5)

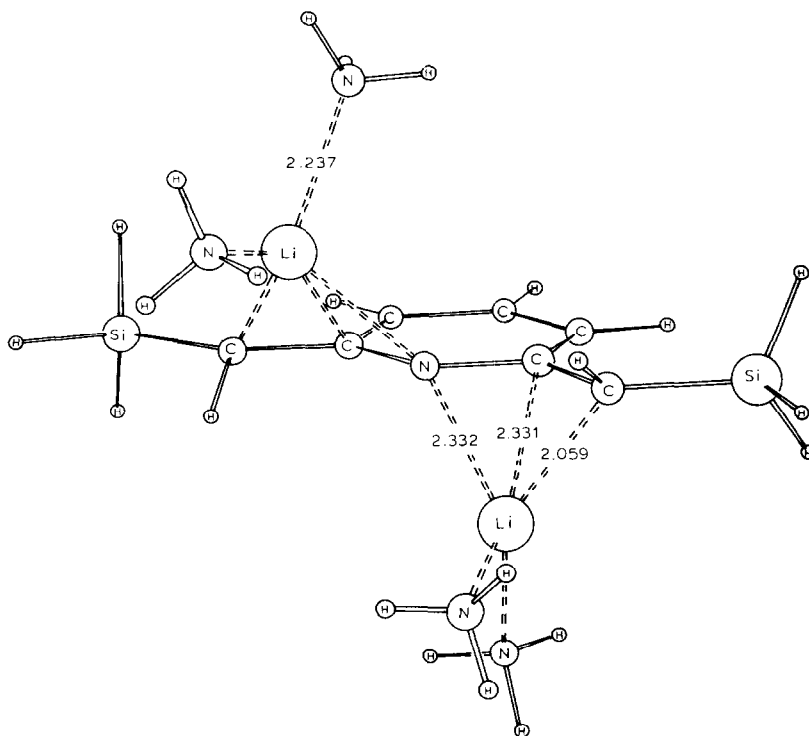


Fig. 2. The MNDO structure of 2,6-(H₃SiCH₂)₂C₅H₃N[Li(NH₃)₂]₂, a model for **1b** with H₃Si substituents (in place of Me₃Si) and NH₃ ligands (in place of TMEDA). Compare with Fig. 1.

The crystal structure of the bis(trimethylsilyl) derivative **5** [10] shows features similar to **4**. As in benzyl lithium [11], both lithiums are closest to the α - (2.14 ± 0.01 Å) and to the *ipso* carbons (2.26 ± 0.02 Å). Only one lithium is coordinated to the central carbon, C(2) (2.44 Å); the distance from C(2) to the other Li is 2.97 Å. This contrast with the essentially symmetrical structure of **1b** may be partly due to the different orientation of the SiMe₃ groups, but probably reflects the more even π -electron distribution in **5**. The lithium counterions provide electrostatic balance [2] rather than communication because an electronegative central atom (as N in **1**) is not present.

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References

- (a) P.v.R. Schleyer, *Pure and Appl. Chem.*, **56** (1984) 151 and refs. cited. (b) W. Setzer and P.v.R. Schleyer, *Adv. Organometal. Chem.*, **24** (1985) 353. (c) C. Schade and P.v.R. Schleyer, *ibid.*, **25** (1986) in press.
- (a) J.J. Stezowski, H. Hoier, D. Wilhelm, T. Clark, and P.v.R. Schleyer, *J. Chem. Soc., Chem. Commun.*, (1985) 1263. For additional examples of quasi-linear C-Li-C-Li-C or

- C. Li, O. Li, C. communication, see: (b) P.v.R. Schleyer, A.J. Kos, and E. Kaufmann, *J. Am. Chem. Soc.*, 105 (1983) 7617; (c) G. Boche, G. Decher, A. Etzrodt, H. Dietrich, W. Mahdi, A.J. Kos, and P.v.R. Schleyer, *J. Chem. Soc., Chem. Commun.*, (1984) 1493; (d) P.v.R. Schleyer, A.J. Kos, D. Wilhelm, T. Clark, G. Boche, G. Decher, H. Etzrodt, H. Dietrich, and W. Mahdi, *ibid.*, (1984) 1495; (e) A.J. Kos, T. Clark, and P.v.R. Schleyer, *Angew. Chem. Int. Ed. Engl.*, 23 (1984) 620; (f) H. Dietrich, W. Mahdi, D. Wilhelm, T. Clark, and P.v.R. Schleyer, *ibid.*, 23 (1984) 621; (g) D. Wilhelm, H. Dietrich, T. Clark, W. Mahdi, A.J. Kos, and P.v.R. Schleyer, *J. Am. Chem. Soc.*, 106 (1984) 7279; (h) C. Schade, P.v.R. Schleyer, H. Dietrich, and W. Mahdi, *ibid.*, 108 (1986) in press and lit. cited.
- 3 M.J.S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 99 (1977) 4899, 4907; Lithium parametrization by W. Thiel and T. Clark, QCPE newsletter, submitted.
 - 4 P.v.R. Schleyer, R. Hacker, H. Dietrich, and W. Mahdi, *J. Chem. Soc., Chem. Commun.*, (1985) 622. Cf., M.H. Chisholm, K. Folting, J.C. Huffman and I.P. Rothwell, *Inorg. Chem.*, 20 (1981) 1496-1500.
 - 5 D. Colgan, R.I. Papasergio, C.L. Raston and A.H. White, *J. Chem. Soc., Chem. Commun.*, (1984) 1708.
 - 6 L. Brandsma, H.D. Verkruijse, C. Schade and P.v.R. Schleyer, *J. Chem. Soc., Chem. Commun.*, (1986) 260; L. Brandsma and H.D. Verkruijse, *Preparative Polar Organometallic Chemistry*, Vol. 1, Springer-Verlag, Heidelberg, 1986; L. Brandsma, H.D. Verkruijse, R.L.P. de Jong, P.A.A. Klusener, C. Schade, R. Hacker, and P.v.R. Schleyer, to be published.
 - 7 Other procedures are much less satisfactory. Cf., F. Bergmann and W. Rosenthal, *J. Prakt. Chem.*, 135 (1932) 267; E.D. Bergmann and S. Pinchas, *J. Org. Chem.*, 15 (1950) 1184.
 - 8 P.v.R. Schleyer, T. Clark, A.J. Kos, G.W. Spitznagel, C. Rohde, D. Arad, K.N. Houk and N.G. Rondan, *J. Am. Chem. Soc.*, 106 (1984) 6467; 107 (1985) 1457.
 - 9 D. Wilhelm and P.v.R. Schleyer, unpublished calculations. See: D. Wilhelm, T. Clark, P.v.R. Schleyer, J.L. Courtneidge, and A.G. Davies, *J. Am. Chem. Soc.*, 106 (1984) 361.
 - 10 L.M. Engelhardt, W.-P. Leung, C.L. Raston and A.H. White, *J. Chem. Soc., Dalton Trans.*, (1985) 337.
 - 11 S.P. Patterman, I.L. Karle and G.D. Stucky, *J. Am. Chem. Soc.*, 92 (1970) 1150.
 - 12 P. Main, S.J. Fiske, S.E. Hull, I. Lessinger, G. Germain, J.-P. Declercq, M.M. Woolfson, MULTAN 80, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data, Universities of York, England, and Louvain, Belgium, 1980.
 - 13 G.M. Sheldrick, SHELX-76, Program for Crystal Structure Determination, University of Cambridge, England, 1976.