The Eight-membered Ring Structure of an α-Lithio-2,6-dimethylpyridine–Tetramethylethylenediamine (TMEDA) Dimer

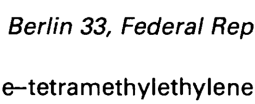
Paul von Ragué Schleyer,*[a] Roland Hacker,[a] Hans Dietrich,*[b] and Waruno Mahdi[b]

[a] *Institut für Organische Chemie der Friedrich-Alexander-Universität Erlangen-Nürnberg, Henkestrasse 42, D-8520 Erlangen, Federal Republic of Germany*

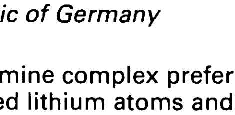
[b] *Fritz-Haber Institut der Max-Planck-Gesellschaft, Faradayweg 4–6 1 Berlin 33, Federal Republic of Germany*

Unlike monomeric benzyl-lithium, the α-lithiated 2,6-dimethylpyridine–tetramethylethylenediamine complex prefers a dimeric, chair-like, eight-membered ring arrangement involving two intermolecularly chelated lithium atoms and near ideal perpendicular conformations of the α-CH_2Li^+ groups, as shown by a crystal structure.

Synthetically useful 'carbanions' can be regarded as polar organometallic compounds[1] with interesting structures.[2] Reactions often begin at the metal cation centres and the locations of these gegenions influence the charge distribution and control stereochemistry.[3] As part of our studies to understand the structures of organolithium compounds,[2—4] we have investigated the effect on the structure of benzyl-lithium when a 2-pyridyl group replaces a phenyl group. From *X*-ray analysis, benzyl-lithium (**1**) is known to be a monomer and to have a bridging lithium.[5] However, the pyridine analogue is unlikely to be similar. While MNDO calculations[6]† indicate the benzyl-lithium-like structure (**2**), with a N–C–C–Li dihedral angle of 134.5°, to be a local minimum ($\Delta H_f° = 20.9$ kcal/mol)‡, the CH_2Li group prefers a configuration (**3**) with the much smaller N–C–C–Li dihedral angle of 25.2°, $\Delta H_f°$(MNDO) = 13.2 kcal/mol. The computed energies of equations (1)—(3) show that the metallation of α-picoline is much more favourable than that of toluene, but only if structure (**3**), rather than (**2**), is adopted. The MNDO potential energy surface of (**3**) is very flat; if a 0° N–C–C–Li dihedral angle is imposed (C_s symmetry) the energy is only increased by 0.1 kcal/mol. N → Li Chelation is thus indicated to be more important energetically than benzyl-type resonance, since benzyl type resonance is present in (**2**) but is excluded in (**3**). However, such competition between the two stabilizing effects can hardly be ideal.



(**1**) X = CH, $R^1 = R^2 = H$
(**2**) X = N, $R^1 = R^2 = H$
(**4**) X = N, $R^1 = SiMe_3$, $R^2 = H$
(**5**) X = N, $R^1 = R^2 = SiMe_3$



(**3**)

$MePh + LiMe \rightarrow (1) + CH_4$ (1) −11.2 kcal/mol(MNDO)
$\alpha\text{-}MeC_5NH_5 + LiMe \rightarrow (2) + CH_4$ (2) −9.5 kcal/mol(MNDO)
$\alpha\text{-}MeC_5NH_5 + LiMe \rightarrow (3) + CH_4$ (3) −17.2 kcal/mol(MNDO)

---

† Lithium parametrization, W. Thiel and T. Clark, unpublished results. The $\Delta H_f°$(MNDO) values (in kcal/mol) for the reference compounds in equations (1)—(3) are: toluene (+13.5), α-picoline (+19.9), methyl-lithium (−1.4), and methane (−11.9).

‡1 kcal = 4.184 kJ.

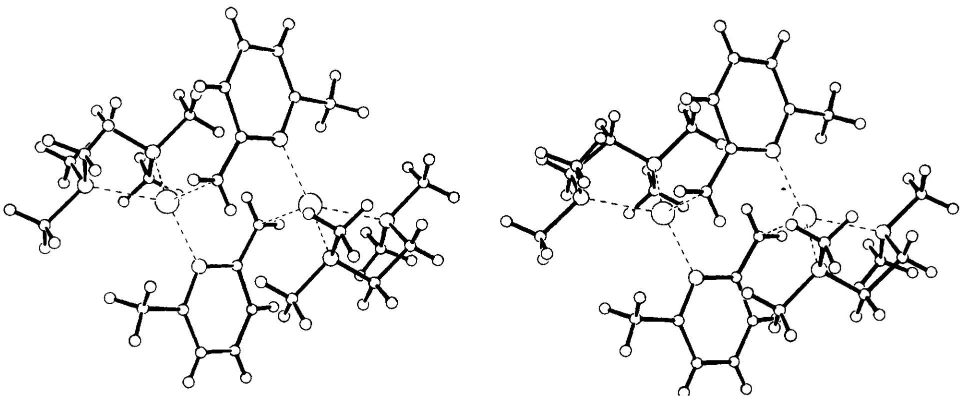


Figure 1. Stereodiagram of the X-ray structure of the α-lithio-2,6-dimethylpyridine–tetramethylethylenediamine dimer. Selected geometrical parameters (in Å and degrees) are [the ring is numbered conventionally; C(α2) and C(α6) are the benzylic and the methyl carbons respectively, Li' is the lithium co-ordinated to nitrogen, and N(2) and N(3) are TMEDA nitrogens]: Li'–N(1) 2.080(1), Li–C(α2) 2.351(1), Li–N(2) 2.166(1), Li–N(3) 2.307(1), C(2)–N(1) 1.382(1), C(2)–C(α2) 1.379(1), C(2)–C(3) 1.450(1), C(3)–C(4) 1.353(1), C(4)–C(5) 1.389(1), C(5)–C(6) 1.373, C(6)–C(α6) 1.488(1), C(6)–N(1) 1.364(1), C(2)–C(α2)–Li 105.35(5), C(α2)–Li'–N(1) 99.68(4), C(2)–N(1)–Li' 119.32(5), C(6)–N(1)–Li' 121.96(5), Li'–N(1)–C(2)–C(α2) −10.5, N(1)–C(2)–C(α2)–Li −76.9, C(6)–N(1)–C(2)–Li' 178.6, C(3)–C(2)–N(1)–Li' 170.5, C(2α')–Li'–N(1)–C(2) 88.0, C(6)–N(1)–C(2)–C(2α) 168.2, C(6)–N(1)–C(2)–C(3) −10.9.

Nature prefers another way out of this dilemma. As shown by the crystal structure of the tetramethylethylenediamine (TMEDA) adduct (Figure 1),§ it is possible in the dimer (with a crystallographic inversion centre) to have an almost perfect combination of both chelation and resonance stabilization simultaneously. Both lithium cations extend from the α-carbon atoms in nearly ideal perpendicular conformations relative to the planes of the aromatic rings. This is one of the rare cases in such π-systems where each lithium has only one carbon contact.[2] The very slight twistings of the CH_2 groups entail no significant loss of resonance energy. At the same time, each intermolecular pyridine N → Li interaction also has a nearly perfect linear geometry. The lithium atoms ignore their intramolecular nitrogen neighbours. The resulting eight-membered ring thus adopts a stair-like conformation shown in Figure 1. In addition, both lithium cations are complexed by TMEDA molecules and have roughly tetrahedral co-ordination. However, as has been observed in other instances, the TMEDA ligands are disordered.

MNDO calculations,[6] which are proving to be so effective in helping to understand organolithium chemistry,[2—4] are in close agreement for the dimer. Compare the experimental (Figure 1) and the MNDO-minimized structures (Figure 2, with ethylenediamine as the model solvent). MNDO is known to give C–Li distances which are too short,[2] but the overall agreement is remarkable.

Four recently reported related crystal structures of trimethylsilyl (**4**) and bis-trimethylsilyl (**5**) derivatives of (**2**) show significant differences from our results.[7,8] While steric effects also may contribute, our interpretation of these variations stresses electronic effects.[3a,4] The unsolvated dimer of (**5**), like our dimer, also has a stepped eight-membered ring structure but with a flattened geometry. This is due to the carbanion-localizing[3a,9] effects of the two trimethylsilyl substituents which greatly stabilize the negative charge through polarization and reduce the need for π delocalization into the pyridine ring.

In the presence of donor ligands, monomers of (**5**) are favoured. The two available structures show η^3-aza-allyl geometries like those calculated for (**3**); the trigonal planes at the α-carbon atoms are skewed relative to the pyridine plane by 39.5 ± 1.5°.[8] The large stabilization due to $SiMe_3$ groups precludes the need for dimerization when donor ligands also are present. The fourth structure of Raston and co-workers[8] is a diethyl ether solvated dimer of (**4**). This is intermediate in showing η^3-aza-allyl bonding [unlike the dimers of (**2**) or (**5**)], dimerization proclivity, and single solvent attachment to each lithium.

These interpretations are supported, *inter alia*, by the calculated C(2)–C(α) distances which indicate the increasing degree of carbanion delocalization into the pyridine ring: 1.42 Å for the (**5**) derivatives, 1.40(1) Å for the structure based on (**4**), and 1.379(1) Å for the dimer of (**2**).

The structure of a Reformatsky reagent, with zinc as the metal, also has an eight-membered ring with an extended chair arrangement.[10]

---

§ *Crystal data*: Monomer = $C_{13}H_{24}N_3Li$, M = 229.295, triclinic, space group $P\bar{1}$, a = 8.625(3), b = 8.923(3), c = 10.103(2) Å, α = 101.30(2), β = 110.06(2), γ = 97.90(2)°, U = 698 Å^3, Z = 2, D_x = 1.090 g/cm^3 (at 119 K) with one monomer in the asymmetric unit. Graphite monochromated Mo-K_α radiation, λ = 0.71069 Å. The crystal, dimensions 0.5 × 0.3 × 0.3 mm^3, was mounted in a capillary under argon but was too long with respect to the monochromated beam. The reflection profiles were unusually broad and many of them showed satellite maxima. A total of 70066 reflection profiles ($2° < \theta < 40°$) were measured at 119 K. Averaging yielded a unique set of 8637 structure factors; 3015 of these were stronger than 4σ. The averaging R value $R_{av.} = \Sigma|F_o^2 - F_{av.}^2|/\Sigma(F_o^2)$ was 0.079 for the 21546 measurements above 2σ and 0.049 for the 11901 measurements above 4σ. The structure was solved by direct methods (MULTAN 76[11]) and refined by full-matrix least-squares methods (X-RAY 76[12]) using weights $1/\sigma^2(F_o^2)$ and including all hydrogen atoms. All carbon atoms of the TMEDA moiety were disordered. Each of them was approximated by two positions with populations 0.58 and 0.42, respectively. The R values, based on the 3015 $F_o^2 > 4\sigma$ (of the average values), converged to $R(F^2)$ = 0.093, $R_w(F^2)$ = 0.095. The largest peaks in the final difference map had the heights 0.32, 0.35, 0.37, and 0.39 e/Å^3, respectively. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

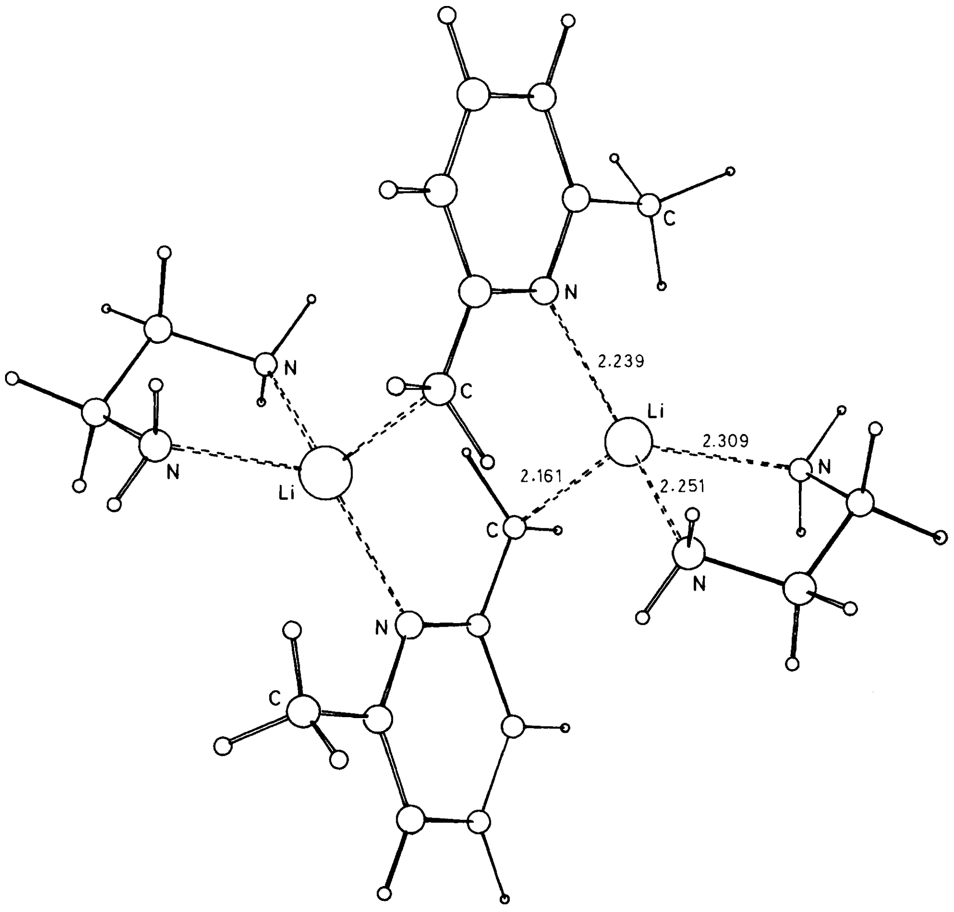


Figure 2. The MNDO optimized structure of the α-lithio-2,6-dimethylpyridine–ethylenediamine dimer, a simplified model for the title compound. Note the close agreement with the general features of the experimental geometry (Figure 1); calculated distances in Å.

This work was supported by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft. We thank T. Clark for his interest and assistance.

Received, 31st December 1984; Com. 1800

References

1 M. Schlosser, 'Polare Organometalle,' Springer-Verlag, New York, 1973.

2 Review of the *X*-ray structures of organolithium compounds: W. Setzer and P. v. R. Schleyer, *Adv. Organomet. Chem.*, 1984, in the press.

3 (a) See, *e.g.*, P. v. R. Schleyer, A. J. Kos, D. Wilhelm, T. Clark, G. Boche, G. Decher, H. Etzrodt, H. Dietrich, and W. Mahdi, *J. Chem. Soc., Chem. Commun.*, 1984, 1495; (b) D. Seebach, Proceedings of the Welch Foundation Conference on Chemical Research, XXVII, November, 1984, in the press.

4 See P. v. R. Schleyer, *Pure Appl. Chem.*, 1984, **56**, 51; 1983, **55**, 355, for references.

5 S. P. Patterman, I. L. Karle, and G. D. Stucky, *J. Am. Chem. Soc.*, 1970, **92**, 1150; G. D. Stucky, *Adv. Chem. Ser., Am. Chem. Soc.*, 1974, **130**, 56.

6 MNDO: M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899, 4907.

7 R. I. Papasergio, C. L. Raston, and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1983, 1419.

8 D. Colgan, R. I. Papasergio, C. L. Raston, and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1984, 1708.

9 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.*, 1984, **106**, 6467.

10 J. Dekker, P. H. M. Budzelaar, J. Boersma, G. J. M. van der Kerk, and A. L. Spek, *Organometallics*, 1984, **3**, 1403; J. Dekker, J. Boesma, and G. J. M. van der Kerk, *J. Chem. Soc., Chem. Commun.*, 1983, 553.

11 P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, MULTAN 76, Universities of York, England, and Louvain, Belgium, 1976.

12 J. M. Stewart, P. A. Machin, C. W. Dickinson, H. L. Ammon, H. Heck, and H. Flack, XRAY 76. Technical Report TR 446, Computer Science Center, University of Maryland, 1976.