

1,3,4,5-Tetramethyl-2-methyleneimidazoline—an Ylidic Olefin

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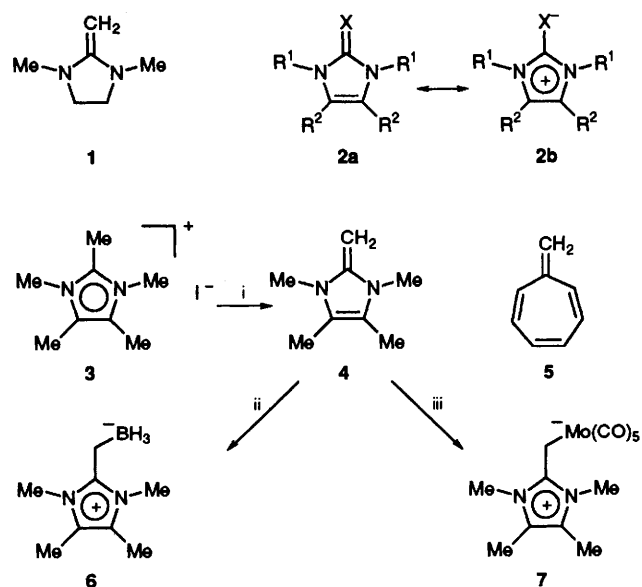
The ylidic properties of 1,3,4,5-tetramethyl-2-methyleneimidazoline **4**, obtained by deprotonation of the pentamethylimidazolium ion **3**, are revealed both by its physical and chemical properties; the X-ray structure of **4** is reported.

The polarisation of the olefinic double bond in enamines¹ depends on the donor ability of the nitrogen atoms. Consequently, strongly basic properties are reported for the 2-methyleneimidazolidine **1**,² in which the π -interaction of the endiamine fragment is optimised by incorporation of the nitrogen atoms into a five-membered ring system. In the imidazoline system **2**, the separation of formal charges (**2b**) is further favoured by aromatisation of the ring, as has recently been demonstrated by the structure of the 2-telluroimidazolines³ (**2**; X = Te).⁴ Thus, an increase in ylidic properties can be expected for 2-methyleneimidazolines (**2**; X = CH₂) relative to their imidazolidine analogues.

Deprotonation of the pentamethylimidazolium ion **3**⁵ with *tert*-butyllithium and subsequent thermolysis of the intermediate LiI adduct gives 1,3,4,5-tetramethyl-2-methylene-

imidazoline **4** as a highly air-sensitive solid.[†] The strong shielding of the methylene carbon in ¹³C NMR (δ 40.23) corresponds with a high electron density (–0.44) obtained from AM1 calculations. On comparison with the data of **1** (δ 51.8, –0.41) and heptafulvene **5** (δ 111.9, –0.26) a near linear correlation of NMR shifts and electron densities is obtained in which compound **4** lies at the negative end of the scale; we therefore suggest this compound to be the most ylidic in this series.

The X-ray structure[‡] of **4** (Figs. 1 and 2) shows a planar five-membered ring. The plane includes all atoms except the methyl hydrogens.⁶ The bond lengths of the imidazole ring [C(1)–N(1) 1.382(3), N(1)–C(3) 1.401(3), C(3)–C(2) 1.347(3), C(2)–N(2) 1.407(2), N(2)–C(1) 1.376(3) Å] are very similar to those found both in the pentamethylimidazolium ion⁵ and in 2-telluro-1,3-diisopropyl-4,5-dimethylimidazoline³ confirming that also in the case of **4** the π -electrons are completely delocalised over the five-membered ring. The distance between C(1) and C(4) [1.357(3) Å] demonstrates the



Scheme 1 Reagents and conditions: i, Bu^tLi in n-pentane at –78 °C (1 h) and room temp. (12 h) followed by vacuum thermolysis of the LiI adduct [b.p. 90 °C/10^{–3} Torr (Torr = 133.3 Pa), 30% yield]; ii, Me₂S·BH₃ in Et₂O (54% yield); iii, Mo(CO)₆ in Et₂O (10 h, 39% yield)

[†] Spectroscopic data for **4**: ¹H NMR. (C₆D₆): δ 2.77 (CH₂), 2.58 (N–CH₃), 1.70 (C–CH₃). ¹³C NMR. (C₆D₆): δ 153.65 (C–2), 114.33 (C–4,5), 40.22 (CH₂), 29.27 (N–CH₃), 8.53 (C–CH₃) MS (70 eV): *m/z* = 138 (21%, M⁺), 123 [100, (M⁺ – Me)], and further fragments.

6: ¹H NMR (CDCl₃): δ 3.50 (N–CH₃), 2.10 (C–CH₃), 1.87 (CH₂). ¹¹B NMR (CDCl₃): δ –31.73 (q, ¹J 86.13 Hz).

7: ¹H NMR. (C₆D₆): δ 2.66 (N–CH₃), 1.37 (CH₂), 1.33 (C–CH₃). ¹³C NMR (C₆D₆): δ 214.60 (CO *trans*), 209.78 (CO *cis*), 163.77 (C–2), 119.47 (C–4,5), 29.63 (N–CH₃), 7.74 (C–CH₃), –6.74 (CH₂). IR(CO) σ /cm^{–1} (KBr): 1955, 1928 and 1924.

[‡] Crystal data for C₈H₁₄N₂ **4**: orthorhombic, space group *Pca*2₁, *a* = 16.427(4), *b* = 7.058(2), *c* = 14.201(4) Å, *U* = 1646.5(6) Å³, *Z* = 8, *D_c* = 1.115 g cm^{–3}, *T* = 125 K, μ = 0.07 mm^{–1}, two independent molecules in the elemental cell, related by a pseudo inversion centre in (0.375, 0.81, 1.05), the existence of a higher symmetry space group has been checked but excluded. Empirical absorption correction. The structure analysis is based on 5717 independent reflections (Mo-K α , 2 θ _{max} 70°), 4475 of which were observed [*F_o* ≥ 4 σ (*F_o*)]. The structure was solved using direct methods and refined using SHELXTL-PLUS to *R* = 0.0583, *R_w* = 0.0604. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

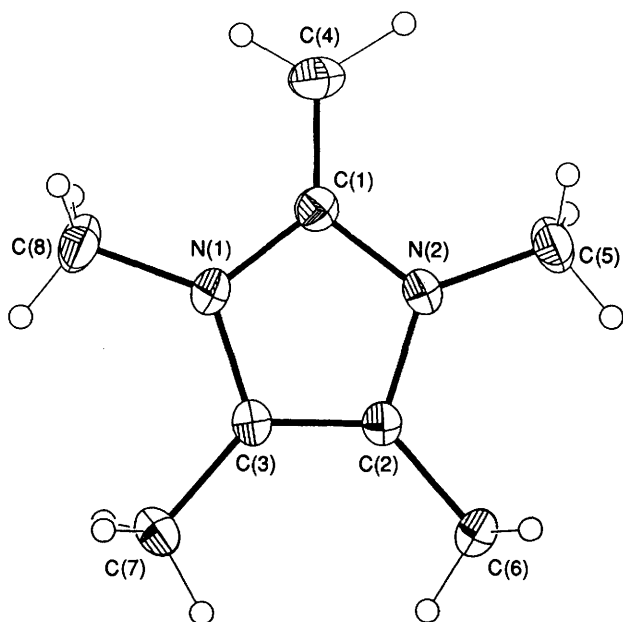


Fig. 1 The structure of $C_8H_{14}N_2$ **4**. Selected bond lengths (Å) and angles ($^\circ$), values of the second independent molecule in parentheses: C(1)–C(4) 1.357(3) [1.369(3)], C(1)–N(1) 1.382(3) [1.373(3)], C(1)–N(2) 1.376(3) [1.373(3)], C(2)–C(3) 1.347(3) [1.353(3)], C(2)–N(2) 1.407(2) [1.405(3)], C(3)–N(1) 1.401(3) [1.402(3)]; N(1)–C(1)–N(2) 105.2(2) [105.5(2)], C(1)–N(2)–C(2) 110.0(1) [110.0(2)], N(2)–C(2)–C(3) 107.3(2) [107.2(2)], C(2)–C(3)–N(1) 107.7(2) [107.3(2)], C(3)–N(1)–C(1) 109.8(2) [110.1(2)], C(4)–C(1)–N(1) 127.3(2) [127.2(2)], C(4)–C(1)–N(2) 127.6(2) [127.3(2)].

characteristic shortening of ylidic single bonds by electrostatic interaction as discussed for methylene phosphoranes.⁷

Further evidence for the ylidic nature of the exocyclic olefinic bond in **4** comes from its chemical properties. In the borane **6** and pentacarbonyl molybdenum **7** adducts, ¹¹B and ¹³C NMR data† indicate the methylene compound to be a strong donor ligand. The end-on coordination of **4** in the molybdenum complex is also confirmed by an X-ray structure analysis.⁸

In summary, the pronounced ability of the 2-imidazoline fragment to accept a formal positive charge causes an ylide-type polarisation of the exocyclic alkene bond in 1,3,4,5-tetramethyl-2-methyleneimidazoline as indicated both by its reactivity and spectroscopy. We are continuing our investigations on 2-methyleneimidazolines and the results will be reported in due course.

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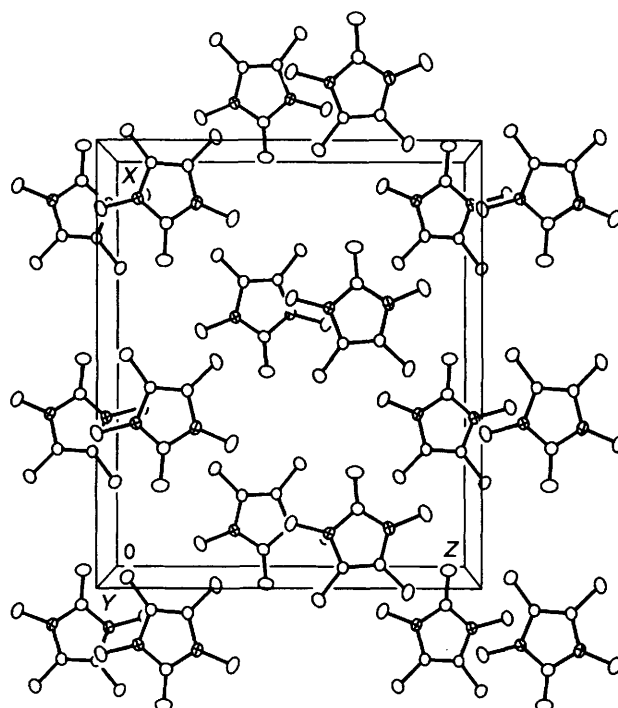


Fig. 2 Packing diagram of **4**, viewing down the y-axis.

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