

Synthesis and X-Ray Structure of a Novel 9-Imino Derivative of Anthracene

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The X-ray structure of the novel title compound **1** and a possible mechanism for its formation, which involves a tandem addition–rearrangement as key steps in the reaction of 2-chloro-1,4-dimethylbenzene with 4-methoxyphenylacetonitrile and lithium diisopropylamide.

We reported recently the stereocontrolled synthesis of *cis*-3,4-diaryl-8-methoxy-5-methylisochroman-1-ones (isocoumarins), which involves electrophilic trapping of α -lithio-2-cyanodiarylmethanes obtained from the reaction of 2-bromo-4-methylanisole and arylacetonitriles with lithium diisopropyl-

amide (LDA) in tetrahydrofuran (THF) with various benzaldehydes.¹ The resulting lithiated *anti*-1,1,2-triarylethanol can be smoothly converted diastereospecifically into the *cis* isocoumarins *in situ*, or by redissolving the isolated alcohols in neat LDA–THF solution. We report herein that the similar

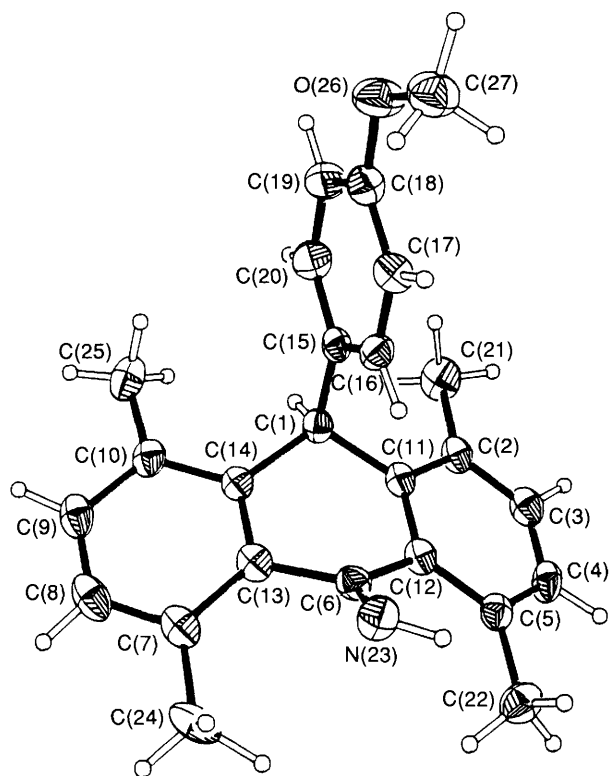
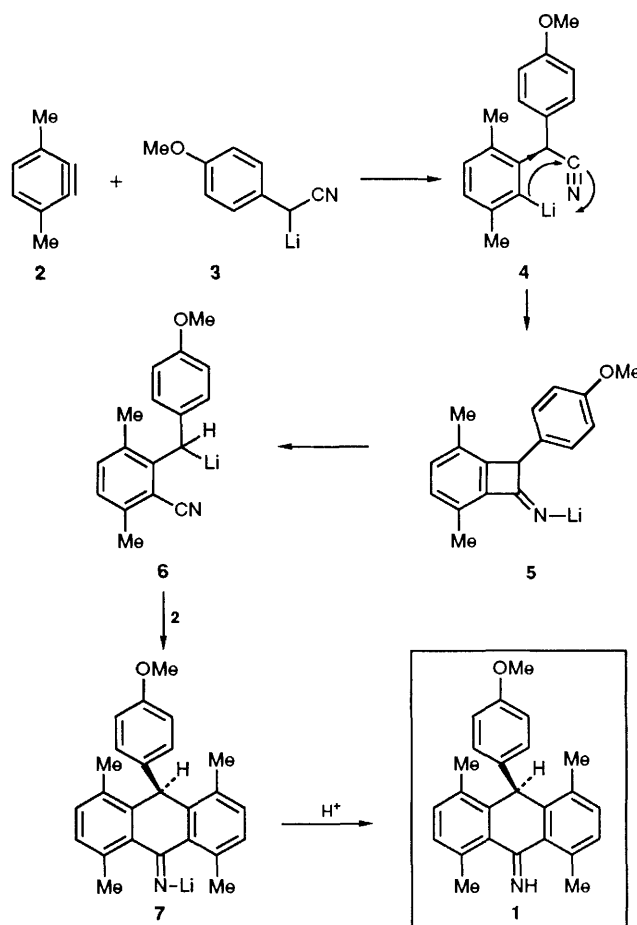


Fig. 1 ORTEP diagram of 1

reaction of 2-chloro-1,4-dimethylbenzene with 4-methoxyphenylacetonitrile and LDA supplies none of the corresponding isocoumarin upon benzaldehyde quench, but rather an unexpected product (*ca.* 13% yield) is obtained the structure of which has been identified as the 9-imino derivative of 9,10-dihydro-10-methoxyphenyl-1,4,5,8-tetramethylanthracene **1** by X-ray crystallography.[†] The ORTEP² drawing of **1** shown in Fig. 1 reveals that the middle ring exists in the boat conformation and that the 10-methoxyphenyl group is projected perpendicular to the plane bisecting the central ring. The 1- and 8-methyl groups constrain the tricyclic molecule from adopting the usual planar conformation, thus preventing the imino group from tautomerizing to the more common 9-aminoanthracene structure. To our knowledge, this is the first example of an isolation of the imino form of a 9-aminoanthracene.

By using 2 equiv. of 2-chloro-1,4-dimethylbenzene, 1 equiv. of 4-methoxyphenylacetonitrile, and 3 equiv. of LDA and working up the reaction mixture in the usual way (*i.e.*, quenching with methanol followed by aqueous acidic work-up), the yield of **1** was increased to 65%. Surprisingly, imine **1**



Scheme 1 Possible pathway for the formation of 1

not only survived the acidic aqueous workup, but also resisted hydrolysis to the corresponding 9-aminoanthracene even when subjected to 2 h refluxing in 10% HCl in methanol-water.

Scheme 1 shows a possible pathway, involving a tandem addition-rearrangement³ as key steps, for the formation of compound **1**. Accordingly, the anion of 4-methoxyphenylacetonitrile **3** adds to 3,6-dimethylbenzyne **2** to give adduct **4**, which undergoes cyclization to the benzocyclobutanium intermediate **5**. This ring then opens to the rearranged ion **6**, which undergoes cycloaddition with another molecule of 3,6-dimethylbenzyne to yield **1** after proton quench of the resulting *N*-lithiated anthracene derivative **7**. We are currently exploring the scope of this novel aryne reaction and will report the results in due course.

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References

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[†] Crystal data for **3**: C₂₅H₂₅NO, *M* = 355.5, triclinic, space group *P* $\bar{1}$, *a* = 7.796(4), *b* = 11.235(6), *c* = 12.001(6) Å, α = 102.36(4), β = 104.00(4), γ = 106.27(4)°, *V* = 933.5(11) Å³, *Z* = 2, *D*_c = 1.265 g cm⁻³, *R* = 0.065, *R*_w = 0.070 for 2104 observed reflections [*I* ≤ 3σ(*I*)]. Intensity data were collected on a Nicolet R3m/v diffractometer with graphite-monochromated Mo-Kα radiation, 3.5 ≤ 2θ ≤ 44.0, θ/2θ scan. The structure was solved by direct methods using SHELXTL-PLUS program package (G. M. Sheldrick, *Structure Determination Software Packages*, Siemens Analytical X-Ray Instruments, Inc, USA, 1990) and anisotropically refined for all non-H atoms by full-matrix least-squares analysis. H-atoms were isotropically refined. Maximum and minimum residuals on final difference Fourier Maps: 0.33 and -0.31 e Å⁻³, respectively. 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.