Tetra-anion of 9,9′-Bianthryl

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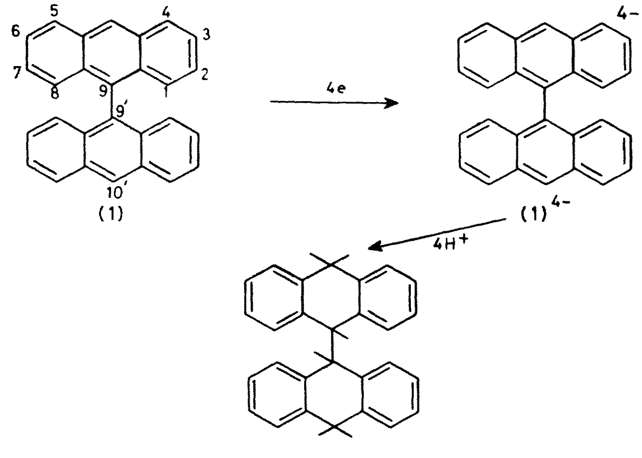
Summary 9,9′-Bianthryl is reduced with lithium to yield a stable tetra-anion which can be characterised by n.m.r. spectroscopy and chemical evidence.

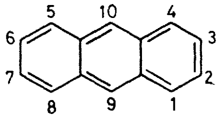
THE well known inter-ring conjugation in biaryl species is expected to have further significance when extended to the corresponding ionic derivatives.[1] Problems have been encountered, however, owing to reductive cleavage of the central C–C bond.[2] A recent paper[2] reporting the formation of anthracene and 9,10-dihydroanthracene on electrochemical 2-, 3-, or 4-electron reduction of 9,9′-bianthryl[3] prompts us to describe a stable lithium salt of the tetra-anion of 9,9′-bianthryl.



(3)

9,9′-Bianthryl (**1**) in a conformation with two orthogonal (*i.e.*, non-interacting) π-units (D_{2d}-symmetry) is predicted to possess two energetically degenerate LUMO's. This structural feature readily explains the existence of a triplet ground-state[4] in the dianion (**1**)^{2} and also suggests that the molecule will accept more than two electrons. We therefore treated (**1**) (0·05 M solution in degassed fully deuteriated tetrahydrofuran, -20 °C) with lithium in a sealed n.m.r. tube. In the course of the reduction the originally colourless solution turned blue, green, and then brown with no n.m.r. signals being observed until, after 3 weeks of metal contact, the blue-violet solution gave rise to a well resolved ^{1}H n.m.r. spectrum.

The splitting patterns (as clarified by decoupling experiments) and relative signal intensities of the signals (see Figure) indicate the existence of an intact bianthryl framework; reoxidation by air to yield the starting compound and protonation with methanol resulting in formation of a tetrahydro derivative of (**1**) (see below) leave no doubt that the final ^{1}H n.m.r. spectrum is due to the lithium salt of the 9,9′-bianthryl tetra-anion (**1**)$^{4-}$. Clearly, the singlet signal at highest field has to be assigned to H-10(10′) while the doublet signals at δ 3·34 and 2·75 are due to absorptions of H-1(8,1′,8′) or H-4(5,4′,5′), respectively. In the Figure the spectra of (**1**) and (**1**)$^{4-}$ are shown together with those of anthracene (**2**) and its corresponding dianion (**2**)$^{2-}$.[5] The sequence of signals in (**2**)$^{2-}$, namely the high-field resonance of H-9, can be explained on the basis of π-charge densities resulting from simple MO-models. The relative order of signals within (**1**)$^{4-}$ is essentially the same, thus supporting the description of the tetra-anion as being two non-interacting anthracene dianion units. As has been pointed out by Musso[6] the term δ(H-1) $-$ δ(H-4) within (**1**) can be taken as a probe of the anisotropic ring current effects of the neighbouring π-fragment. While in the neutral compounds (**1**) and (**2**) a diamagnetic ring current is present, the chemical shifts of (**2**)$^{2-}$ have been explained as indicating the existence of a peripheral paramagnetic ring current.[5] It is, therefore, tempting to ascribe the shift difference of H-1 and H-4 within (**1**)$^{4-}$ as being due to the influence of a paramagnetic ring current in the second ring. Moreover, it follows that the low-field doublet (δ 3·34) has to be assigned to H-1(8,1′,8′), the protons above the neighbouring π-system.



(2)

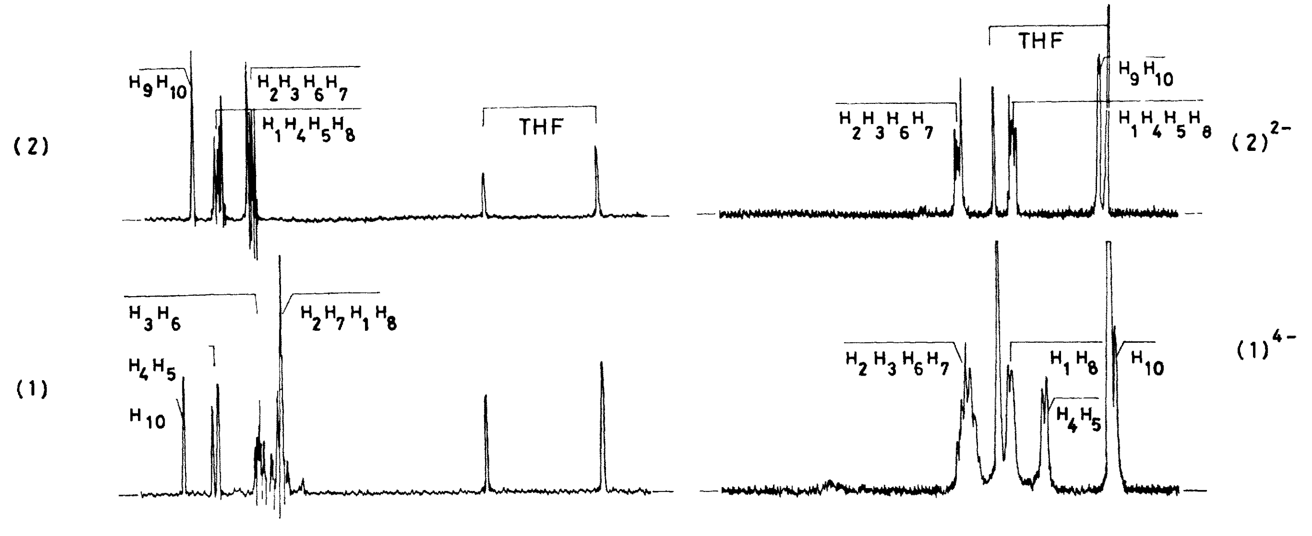


FIGURE. ^{1}H n.m.r. spectra (90 MHz) of anthracene (**2**), 9,9′-bianthryl (**1**), as well as of anthracene dianion (**2**)$^{2-}$ and 9,9′-bianthryl tetra-anion (**1**)$^{4-}$ (ions as lithium salts, fully deuteriated tetrahydrofuran, -20 °C).

Hammerich and Savéant[2] electrolysed (**1**) at a potential (−2·80 V) corresponding to the formation of both the trianion radical and the tetra-anion. Under their experimental conditions they obtained monomeric species, *i.e.*, (**2**) and 9,10-dihydroanthracene. Similarly, when reducing (**1**) with an excess of lithium metal in liquid ammonia (containing ether as co-solvent) we identified 9,10-dihydroanthracene as the only product after quenching with ammonium chloride. However, the lithium salt of (**1**)$^{4-}$, with methanol, affords, besides polymeric material, a 50% yield of a tetrahydro species, m.p. 242 °C, which, from its spectral data, can be identified as 9,10,9′,10′-tetrahydro-9,9′-bianthryl (**3**) [^{13}C n.m.r. δ 136·4, 135·1, 127·3, 125·4, 124·6, 123·8, 53·9, (C-9,9′), and 32·8 p.p.m. (C-10,10′), ^{1}H n.m.r. δ 7·15—6·7 (m, 16H), 4·42 (s, 2H), 3·42 (d, 2H), and 2·92 (d, 2H)]. The non-equivalence of the two protons attached to C-10 (or C-10′) (AB-system with J_{AB} 19·0 Hz) indicates that the cyclohexadiene rings of (**3**) are fixed in a non-planar conformation.[7]

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