Novel Heterocyclic Anions: Benzo[*b*]thiophene Dianion, the First Sulphur Doubly Charged 4*n*π System

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Benzo[*b*]thiophene dianion $(1)^{2-}$, the first sulphur-containing 4*n*π polycyclic dianion, was prepared *via* metal reduction and characterised by ^1H and ^{13}C n.m.r. spectroscopy; the reaction products depend on the reduction conditions.

Extensive theoretical and experimental studies have been performed on charged π-conjugated polybenzenoid systems in the last two decades.[1,2] The scarcity of information on heterocyclic doubly charged species[3] as well as the limited success in the preparation of nitrogen polyheterocyclic dianions[4] prompted us to undertake the investigation of a sulphur-containing polycyclic dianion. In view of the weakness of the carbon–sulphur† bond, the preparation of such an anion represents a challenge to the synthetic chemist as well as to the spectroscopist.

This communication reports the preparation and spectroscopic characterisation of benzo[*b*]thiophene dianion **(1)**$^{2-}$, the first dianion of this novel class of charged species. The products of the metal reduction of **(1)** depend on the experimental conditions (temperature and reducing metal) (Scheme 1). Reduction of **(1)** with sodium metal at −78 °C ([$^2H_8$]tetrahydrofuran, THF) afforded a purple solution of **(1)**$^{2-}$ which undergoes oxidation to **(1)** upon reaction with oxygen. The assignment is confirmed by ^1H, ^{13}C n.m.r. (Table 1), and double resonance experiments including 2D ^1H homonuclear *J*-resolved spectra.[5] The centre of gravity of the ^1H n.m.r. spectrum of **(1)**$^{2-}$/2Na$^+$ appears at δ 5.79 and that of the benzo[*b*]thiophene **(1)** is at δ 7.62. The high-field shifts may correspond to a singly charged species according to chemical shift charge density correlations for carbocyclic systems.[6] This discrepancy is only apparent as it is expected that a significant portion of the negative charge is located on the sulphur atom. A one electron reduction would yield a radical anion and the detection of the n.m.r. spectrum of **(1)**$^{2-}$ would be precluded. Indeed, a transient, very broad line of a yellow species did appear prior to the appearance of the sharp spectrum of the purple solution attributed to dianion **(1)**$^{2-}$. The fact that oxygen affords the starting material as the sole product and the unequivocal n.m.r. spectrum of the dianion proves the structure of **(1)**$^{2-}$/2Na$^+$.

In the ^1H n.m.r. spectrum of **(1)**$^{2-}$/2Na$^+$, bands of a minor product **(2)** (*ca.* 10%) could be observed (*vide infra*). The reduction of **(1)** with lithium metal ([$^2H_8$]THF, −78 °C) afforded an entirely different ^1H n.m.r. spectrum from that of **(1)**$^{2-}$/2Na$^+$. This spectrum is assigned as the *ortho* metallation product of **(1)**, *viz.* **(3)**. As expected from a carbon–lithium species, the eight carbon bands are not shifted to high-field to the same extent as those of **(1)**$^{2-}$/2Na$^+$. Moreover, this spectrum shows a band at δ_C 189.1 which is characteristic of the ^{13}C chemical shift of a carbon–lithium bond.[7] The presence of a carbon–lithium species was verified by an independent preparation of **(3)** *via* the reaction of **(1)** with butyl-lithium ([$^2H_8$]THF, −78 °C).This metallation reaction gave a neat spectrum identical with that of the lithium reduction product of **(1)** (Table 1). The pale yellow solution of this reaction product was quenched with D_2O, to yield **(4)** (Scheme 1). In the proton spectrum the band at δ_H 7.42 has disappeared while the carbon (proton decoupled) band at δ_C 126.9 appears as a triplet (*J* 28 Hz). The deuteriation took place at the α-position according to the literature assignment of the proton spectrum of **(1)**.[8a] However, the band at δ_C 126.9 has been attributed to the β-carbon.[8b] In view of the *ortho* metallation in general[9] and the well documented *ortho* metallation of **(1)** in particular,[10] we believe that the literature assignment of the β-carbon is erroneous. Interestingly, the bands of the minor component in the sodium reduction spectrum of **(1)** are almost identical to those of **(3)**. From the above it is clear that this minor component belongs to an *ortho* metallation process which appears to be a by-product in the sodium reduction. When the experiment was repeated with sodium metal at −20 °C ([$^2H_8$]THF) the *ortho* metallation dominated and afforded **(2)** as a major product. Dianion **(1)**$^{2-}$/2Na$^+$ is the smallest 4*n*π polycyclic dianion which can be

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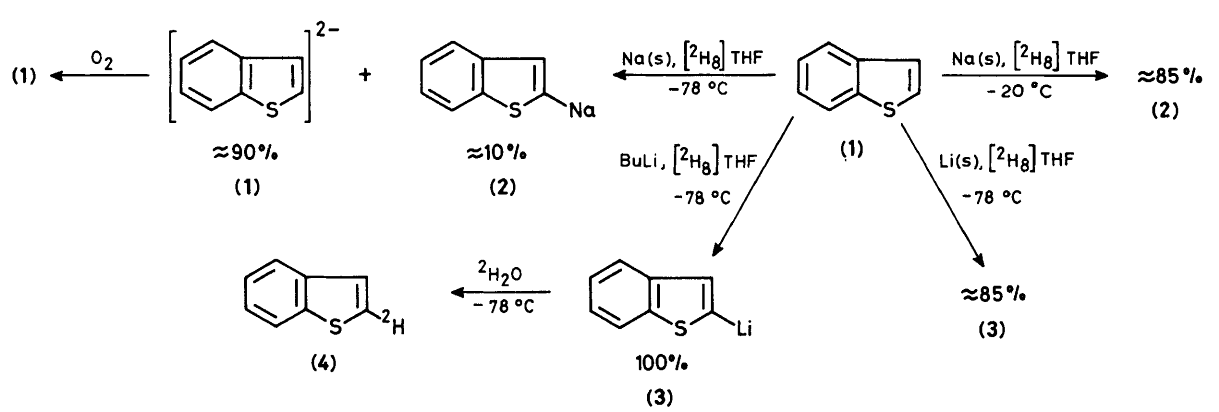
† The average value of the C–S bond energy is only 65 kcal mol^{-1}, 1 cal = 4.18 J.

Table 1. N.m.r. parameters of $(\mathbf{1})^{2-}$, (**2**), and (**3**).[a]

Experiment	Product[b]	N.m.r. parameters δ (*J* in Hz)	Centre of gravity δ	Centre of gravity of (**1**) δ
(**1**)/Na(s) in [^{2}H$_8$]THF at −78 °C	$(\mathbf{1})^{2-}$ [c]	^{1}H: 6.83 (d, *J* 7); 6.32 (t, *J* 7); 6.23 (d, *J* 7); 5.43 (d, *J* 9); 5.25 (t, *J* 7); 4.79 (d, *J* 9)	5.79	7.62
		^{13}C: 144.1, 135.0, 125.2, 124.1, 109.1, 103.0, 101.8, 70.4	111.6	127.5
(**1**)/Li(s) in [^{2}H$_8$]THF at −78 °C	(**3**)[d]	^{1}H: 7.71 (d, *J* 8); 7.55 (d, *J* 8); 7.28 (s); 7.00 (t, *J* 7); 6.84 (t, *J* 7)	7.27	7.62
		^{13}C: 189.1, 149.1, 145.5, 130.2, 121.4, 121.2, 120.1, 118.5	136.9	127.5
(**1**)/BuLi in [^{2}H$_8$]THF at −78 °C	(**3**)[e]	^{1}H: 7.71 (d, *J* 8); 7.56 (d, *J* 8); 7.30 (s); 7.01(t, *J* 7); 6.85 (t, *J* 8)	7.28	7.62
(**1**)/Na(s) in [^{2}H$_8$]THF at −20 °C	(**2**)[d]	^{1}H: 7.76 (d, *J* 8); 7.64 (d, *J* 8); 7.45 (s); 7.05 (t, *J* 7); 6.88 (t, *J* 7)	7.35	7.62

[a] N.m.r. spectra were recorded on Bruker WH-300 pulsed FT-spectrometer operating at 300.133 MHz and 75 MHz for ^{1}H and ^{13}C respectively. The field frequency regulations were maintained by ^{2}H locking. The free-induction decay signals were digitalised and accumulated on an Aspect-2000 computer (32K). The *J*-resolved 2D-^{1}H n.m.r. spectrum was recorded on Bruker WP-200 SY pulse programmable pulsed-FT spectrometer equipped with a ^{2}H lock system and an Aspect-2000 computer (32K). [b] See Scheme 1. [c] Spectrum of $(\mathbf{1})^{2-}$ accompanied by 10% of (**2**). [d] Major product. [e] Only product.



Scheme 1

characterised by n.m.r. spectroscopy found so far. Its moderate stability (even at room temperature) encourages the exploration of new charged sulphur conjugated 4*n*π systems. Efforts to expand this family of anions are under way with the aim of understanding their nature as well as their structure–stability relationships.

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