

New Heterocyclic Dianions:^{1a} N.M.R. Characterization of 1,3-Diphenylbenzo[*c*]-thiophene Dianion, a Stable $4n\pi$ Charged System Containing Sulphur

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1,3-Diphenylbenzo[*c*]thiophene dianion, (1)²⁻ a member of the novel series of $4n\pi$ polyheterocyclic dianions, has been prepared and characterized by n.m.r.; it shows a high stability and a peculiar charge distribution pattern in which the sulphur atom polarizes the charge towards the α -positions.

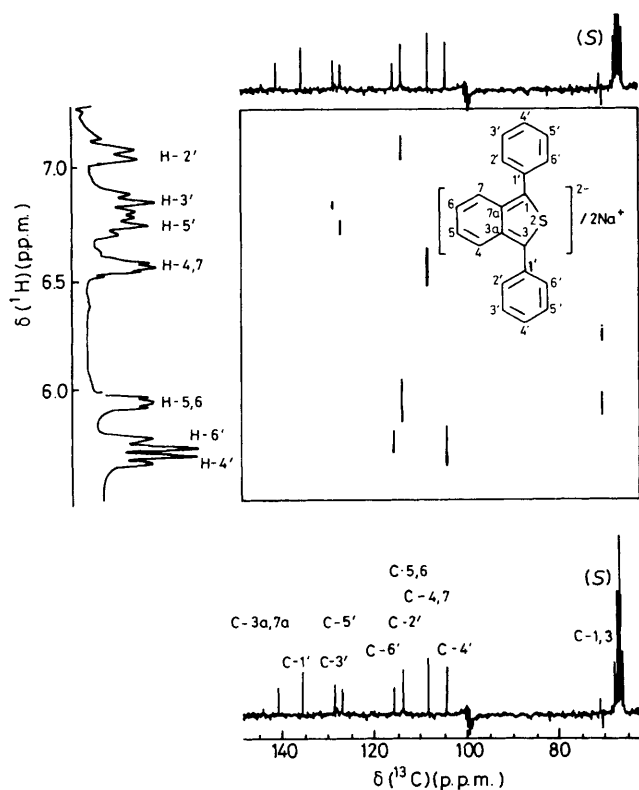
Much effort has been directed towards the preparation and characterization of polycyclic charged systems, and many $4n\pi$ carbocyclic systems have been characterized by n.m.r. spectroscopy.^{1b-c} In contrast, the scarcity of information concerning heterocyclic $4n\pi$ charged systems is striking. Recently, we have been able to prepare and characterize by n.m.r.

spectroscopy a series of nitrogen-containing heterocyclic dianions.² The preparation of $4n\pi$ polyheterocyclic dianions containing sulphur in their path of electron delocalization was a challenge, in view of the relative weakness of the carbon-sulphur bond. Such compounds are of major importance in fuel and coal chemistry,³ yet the only example of a $4n\pi$

Table 1. N.m.r. parameters (^1H and ^{13}C) of 1,3-diphenylbenzo[*c*]thiophene (**1**) and its disodium salt [$^2\text{H}_8$]tetrahydrofuran.

Compound (T/K)	N.m.r. parameters ^{a,b}	Centre of gravity of the spectrum
(1) (293)	^1H : 7.92 and 7.17 (AA'BB', H-4,7; H-5,6), 7.78 (dt, J_1 8.1, J_2 1.1, H-2', H-6'), 7.58 (tt, J_1 7.2, J_2 1.1, H-3', H-5'), 7.45 (tt, J_1 7.3, J_2 1.3, H-4')	7.61
	^{13}C : 135.9 (C-3a,7a), 134.8 (C-1'), 134.5 (C-1,3), 129.5 (C-2',6'), 129.5 (C-3',5'), 127.9 (C-4'), 124.7 (C-5,6), 121.5 (C-4,7)	129.8
(1) ²⁻ (293)	^1H : 6.84 (br t, J 6.7, H-3',5'), 6.57 and 5.97 (AA'BB', H-4,7, H-5,6), 5.75 (t, J 6.8, H-4')	—
	^{13}C : 141.1 (C-3a,7a), 135.9 (C-1'), 127.3 (br s, C-3',5'), 115.1 (br s, C-2',6'), 113.9 (C-5,6), 108.4 (C-4,7), 104.7 (C-4'), 70.7 (C-1,3)	116.0
(253)	^1H : 7.03 (d, J 8.1, H-2'), 6.82 (t, J 8.0, H-3'), 6.72 (t, J 7.9, H-5'), 6.55, 5.96 (AA'BB', H-4,7, H-5,6), 5.74 (d, J 9.3, H-6'), 5.68 (t, J 6.8, H-4')	6.36
	^{13}C : 141.0 (C-3a,7a), 135.4 (C-1'), 128.4 (C-3'), 126.9 (C-5'), 115.7 (C-6'), 113.8 (C-2'), 113.7 (C-5,6), 108.4 (C-4,7), 104.1 (C-4'), 71.3 (C-1,3)	115.9

^a Chemical shifts in p.p.m. downfield from external Me_4Si ; coupling constants in Hz. ^b The n.m.r. spectra were obtained with a Bruker SY-200 pulsed FT spectrometer equipped with a pulse programmer operating at 200.133 and 50.32 MHz for ^1H and ^{13}C n.m.r., respectively. The free induction decay (FID) signals were digitized and accumulated on an Aspect-2000 computer and field/frequency regulations were maintained by ^2H locking. ^c The doublets attributed to H-2' and H-6' are not observed due to proximity to the coalescence temperature.

**Figure 1.** The 2D-C/H correlation spectrum of the anion (**1**)²⁻ as disodium salt in [$^2\text{H}_8$]tetrahydrofuran at 253 K.

polycyclic dianion containing sulphur, characterized by n.m.r., is benzo[*b*]thiophene. However, benzo[*b*]thiophene dianion has only limited stability.⁴

We report here the preparation and n.m.r. characterization (1D- and 2D-n.m.r.) of 1,3-diphenylbenzo[*c*]thiophene dianion (**1**)²⁻. Reduction to the dianion is accomplished by sodium metal in [$^2\text{H}_8$]tetrahydrofuran at -40°C . In 1,3-diphenylbenzo[*c*]thiophene (**1**) there are no α -hydrogen atoms present, thus *ortho*-metallation is excluded. We believe that this is the reason for the enhanced stability of (**1**)²⁻ as compared with benzo[*b*]thiophene dianion. The ^1H and ^{13}C n.m.r. param-

eters of compound (**1**)[†] and the dianion (**1**)²⁻ are summarized in Table 1. The dianionic nature of (**1**)²⁻ was deduced from the high-field shifts and the spectral patterns, as well as by quenching experiments. Relaxation measurements (T_1) (by inversion recovery^{7a}) were used to distinguish between the two non-equivalent *ortho*-hydrogen atoms (H-2' and H-6'); see structure in Figure 1) and the different types of hydrogen atom to which the AA'BB' pattern of the ^1H n.m.r. spectrum of (**1**)²⁻ is attributed. Owing to the proximity of the corresponding protons, one doublet (at δ 7.03) and one part of the AA'BB' structure (at δ 6.55) have the shortest T_1 . We therefore assign the doublet at δ 7.03 to H-2' and the absorption at δ 6.55 to H-4 and -7. A full assignment of the ^1H n.m.r. spectrum of (**1**)²⁻ is then easily achieved from double resonance experiments. The carbon spectrum is assigned from results of two different $^{13}\text{C}/^1\text{H}$ correlation experiments optimized for 1J $^{13}\text{C}/^1\text{H}$ and 3J $^{13}\text{C}/^1\text{H}$ (Figure 1). The difference in ^1H and ^{13}C chemical shifts between (**1**) and (**1**)²⁻ is shown in Figure 2. The variations of the proton chemical shifts are small and the centre of gravity of the ^1H n.m.r. spectrum of (**1**)²⁻ appears at low field (δ 6.36). On this basis the dianion cannot be classified as a paratropic system. Such a paratropic system would be expected to exhibit an enhanced high-field ^1H n.m.r. shift beyond the contribution of the charge effect.⁸

The carbon spectrum of (**1**)²⁻ reveals two interesting phenomena. (a) There are specific carbon atoms (C-1 and -3) for which the chemical shift difference between (**1**) and (**1**)²⁻ [$\Delta\delta(^{13}\text{C})$] is much larger than for the other carbon atoms. (b) The total high-field shift of the carbon spectrum [$\Sigma\Delta\delta(^{13}\text{C})$] is 278 p.p.m.

In the 1,3-diphenylbenzo[*c*]furan dianion (**2**)²⁻,^{1a} the oxo analogue of (**1**)²⁻, the peak at highest field attributed to C-4 and -7 appears at δ ca. 99, whereas in (**1**)²⁻ the peak attributed to C-1 and -3 appears at higher field, *i.e.* δ 71. The $\Delta\delta(^{13}\text{C})$ value for C-1 and -3 of (**2**)²⁻ is ca. 28 p.p.m., whereas in (**1**)²⁻ the corresponding chemical shift difference is ca. 64 p.p.m. This observation can be interpreted in terms of a significant polarization of charge in (**1**)²⁻ towards the position α to sulphur, much more pronounced in this case than in the

[†] 1,3-Diphenylbenzo[*c*]thiophene (**1**), m.p. 118°C (lit.,⁵ 120°C) was prepared by the reaction of *o*-dibenzoylbenzene with P_2S_5 in dry pyridine (reflux 4 h, inert atmosphere).⁶

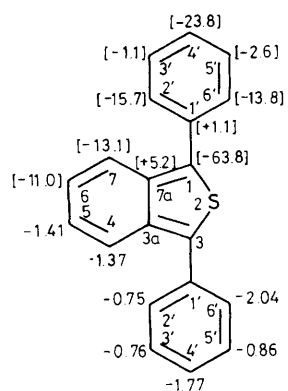


Figure 2. The differences between the chemical shifts of the dianion (**1**)²⁻ and the neutral compound (**1**) in [²H₈]tetrahydrofuran [$\Delta\delta(^1\text{H})$] and (in square brackets) $\Delta\delta(^{13}\text{C})$].

analogue (**2**)²⁻. However, a change in hybridization of C-1 and -3 from *sp*² to *sp*³-like may also contribute to this high-field shift.

It is accepted that a sulphur atom stabilizes a negative charge, although the mechanism of this stabilization is controversial.⁹ It is therefore surprising that the total high-field shift of the carbon spectrum of (**1**)²⁻ is so large [$\Sigma\Delta\delta(^{13}\text{C})$ 278 p.p.m.]. For comparison, in the dianion (**2**)²⁻ $\Sigma\Delta\delta(^{13}\text{C})$ is only 238 p.p.m.⁸ These large values seem to corroborate the quenched paratropicity of these dianions^{8c,1a}

The reduction of (**1**) induces an increase in the order of the C(3)–C(1') and C(1)–C(1') bonds, thus increasing the energy barrier to free rotation of the phenyl groups about these bonds. This fact is manifested in the ¹H and ¹³C n.m.r. spectra (Figure 1). The free energy of activation (ΔG^\ddagger 295) for rotation about these bonds is *ca.* 13 ± 1 kcal mol⁻¹,^{7b} comparable with the energy barrier for *o*-terphenyl dianion.¹⁰

It should be noted that temperature variations have some effect on the ion-pairing equilibrium of the charged system, which may in turn influence the chemical shifts of the interchanging sites.^{2d} This implies that only a rough estimate of the energy barrier for the rotation can be made.

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References

- (a) Part 4, Y. Cohen, J. Klein, and M. Rabinovitz, *J. Chem. Soc., Perkin Trans. 2*, in the press. For general reviews, see (b) R. N. Young, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1978, **12**, 261; (c) M. Rabinovitz, I. Willner, and A. Minsky, *Acc. Chem. Res.*, 1983, **16**, 296; (d) K. Müllen, *Chem. Rev.*, 1984, **84**, 603; (e) K. Müllen and W. Huber, *Acc. Chem. Res.*, 1986, **19**, 300.
- (a) A. Minsky, Y. Cohen, and M. Rabinovitz, *J. Am. Chem. Soc.*, 1985, **107**, 1501; (b) Y. Cohen, A. Y. Meyer, and M. Rabinovitz, *ibid.*, 1986, **108**, 7039.
- M. Nishioka, M. L. Lee, and R. N. Castle. Preprints, ACS Division of Petroleum Chemistry, 1986, **31**(4), 827.
- Y. Cohen, J. Klein, and M. Rabinovitz, *J. Chem. Soc., Chem. Commun.*, 1985, 1033.
- L. Lepage and Y. Lepage, *J. Heterocycl. Chem.*, 1978, **15**, 1185.
- M. J. Haddadin, B. J. Agha, and R. F. Tabri, *J. Org. Chem.*, 1979, **44**, 494.
- (a) See for example H. Günther, 'NMR Spectroscopy,' Wiley, Chichester, 1980, p. 225; (b) for calculation of the barrier see pp. 242–243.
- (a) A. Minsky, A. Y. Meyer, and M. Rabinovitz, *Tetrahedron*, 1985, **41**, 785; (b) M. Rabinovitz and Y. Cohen, Preprints ACS Division of Petroleum Chemistry, 1986, **31**(4), 777; (c) B. Eliasson, U. Edlund, and K. Müllen, *J. Chem. Soc., Perkin Trans. 2*, 1986, 937.
- See for example (a) J. M. Lehn and G. Wipff, *J. Chem. Soc., Chem. Commun.*, 1975, 800; *J. Am. Chem. Soc.*, 1976, **98**, 7498, and references cited therein.
- W. Huber, A. May, and K. Müllen, *Chem. Ber.*, 1981, **114**, 1318.