

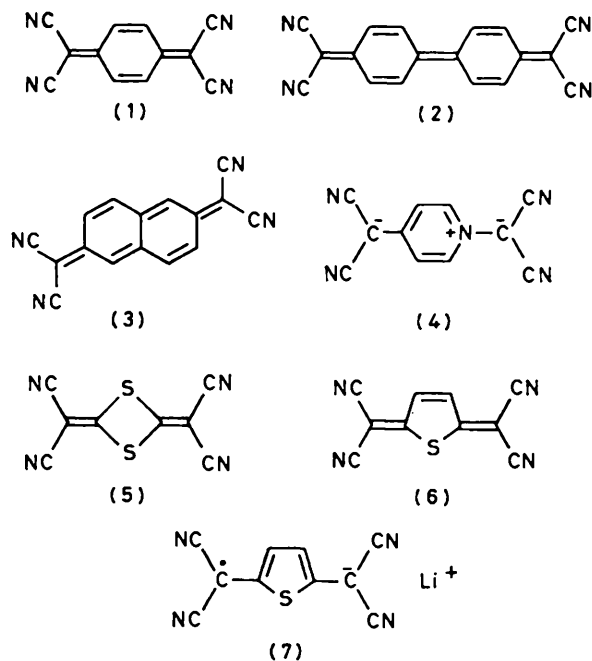
## Preparation and Properties of Lithium 2,5-Bisdicyanomethylene-2,5-dihydrothiophen Radical Anion, a Monosulphur Analogue of Tetracyanoquinodimethane

By NEIL F. HALEY

(Research Laboratories, Eastman Kodak Company, Rochester, New York 14650)

**Summary** The title compound was synthesized, and its electrical and complexing properties are compared with those of its carbon analogue, 7,7,8,8-tetracyanoquinodimethane.

RECENT interest in highly conducting charge-transfer salts derived from the electron acceptor 7,7,8,8-tetracyanoquinodimethane (TCNQ) (1) has prompted the design of new organic acceptors whose structures would enhance their electrical properties when complexed with donor molecules (*e.g.* tetrathiafulvalene, TTF).<sup>1</sup> Besides extending the conjugation of TCNQ, *e.g.* (2) and (3), heteroatom substitution has also been used to prepare new acceptors, *e.g.* (4)<sup>2</sup> and (5). We recently reported the synthesis of (5), the disulphur analogue of (1).<sup>3</sup> However, the monosulphur analogue (6) offers an advantage over (5) since an aromatic sextet is created upon reduction to the radical anion (7). The benefit of gaining aromaticity was recently elucidated by Perlstein.<sup>4</sup> Compound (6) is easily synthesized from 2,5-dibromothiophen and tetracyanoethylene oxide in 70% yield, as reported by Gronowitz and Uppstrom,<sup>5</sup> and was obtained as a yellow-orange crystalline solid ( $\lambda_{\max}$  (MeCN) 413 (log  $\epsilon$  4.49) and 394 (4.45) nm; <sup>13</sup>C n.m.r.  $\delta$  (CDCl<sub>3</sub>; Me<sub>4</sub>Si) 168.8 (=C<), 139.6 (HC=), 110.5 (CN), 109.8 (CN), and 81.7 [C(CN)<sub>2</sub>] p.p.m.}. However, (6) formed only weak complexes with TTF and isobenzofuran, and these did not exhibit any characteristics of a charge-transfer salt. Cyclic voltammetry of (6) at a platinum electrode in MeCN shows two reversible one-electron reductions at +0.05 V (0.1 V s<sup>-1</sup> scan), similar to TCNQ (+0.17 V) but dissimilar to (5) (-0.62 V and



irreversible), and -0.47 V. The reversible nature of the reduction of (6) indicated that radical anion (7) might be isolable. The anion (7) was indeed synthesized by slow addition of (6) in methylene chloride to anhydrous LiI in acetonitrile under argon and was obtained as a blue-black

crystalline solid in 78% yield [ $\lambda_{\max}$  (MeCN) 732 (log  $\epsilon$  4.38), 662 (4.18), 610 (3.59), 481 (4.62), 468 (4.49), 405 (3.63), and 265 (3.72) nm;  $\nu_{\max}$  (KBr) 2193s, 1481s, 1383s, 1274m, 1179m, 1087m, and 760w  $\text{cm}^{-1}$ ; satisfactory elemental analyses were obtained]. Cyclic voltammetry of (7) shows a reversible one-electron oxidation at +0.05 V and a one-electron reversible reduction at -0.47 V, indicating we have isolated the radical anion (7).

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