

## An Authentic *ortho*-Quinodimethane Radical Anion

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Photolysis of  $\alpha, \alpha'$ -dilithio- $\alpha, \alpha'$ -bis(trimethylsilyl)-*o*-xylene leads to an ESR spectrum assigned to the  $\alpha, \alpha'$ -bis(trimethylsilyl)-*o*-quinodimethane radical anion, the first representative of this class of radical anions to have been observed in solution.

The  $8\pi$ -electron *o*-quinodimethane system is a well known intermediate in organic chemistry,<sup>1,2</sup> but the  $9\pi$ -electron quinodimethane radical anion and its derivatives have remained elusive. Although resonance-energy calculations<sup>3</sup> suggest that the *o*-quinodimethane radical anion **1** should be well stabilised, it has eluded unequivocal experimental observation.<sup>2,4,5</sup> Michl *et al.*<sup>2</sup> speculated on the possible detection of **1** in a low temperature matrix. Bauld *et al.*<sup>4</sup> have implicated derivatives of **1** in reductive ring-openings of benzocyclobutenes, but a species reported<sup>5</sup> to be **1** was later shown<sup>6,7</sup> to be a benzocyclobutene radical anion in which ion-pairing effects gave rise to the unsymmetrical ESR spectrum. We now report the ESR spectrum of the bis-trimethylsilyl **2** derivative of **1** in solution at low temperature. As far as we are aware,

this is the first direct experimental observation of an *o*-quinodimethane radical anion.

The most promising method for producing radical anions of antiaromatic neutral precursors is one-electron oxidation of the corresponding dianion.<sup>8</sup> We were, for instance, able to observe the ESR spectrum of the pentalene radical anion by photolysing the dilithium salt of the dianion.<sup>8</sup> *o*-Quinodimethane dianions are readily accessible from the double deprotonation of *o*-xylenes,<sup>9</sup> and the X-ray structures of some derivatives are available.<sup>10,11</sup> We chose the bis-trimethylsilyl derivative **3a**<sup>10</sup> as a suitable precursor to **2**. Photolysis of **3a** in 2-methyltetrahydrofuran (2-MTHF) at  $-120^\circ\text{C}$  with a high-pressure mercury lamp (500 W) led to a strong ESR signal ( $g = 2.0029$ ) that showed hyperfine splittings of 0.698 mT (2H) and

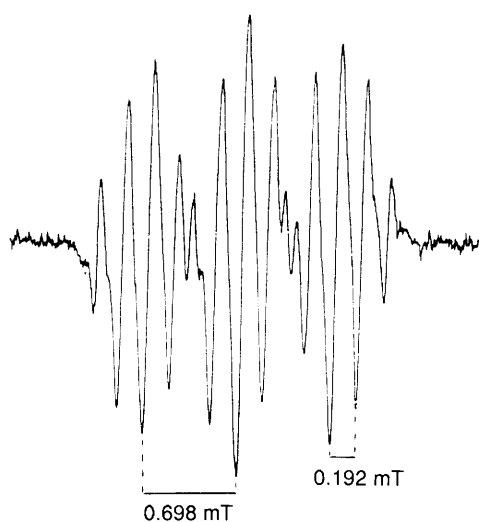
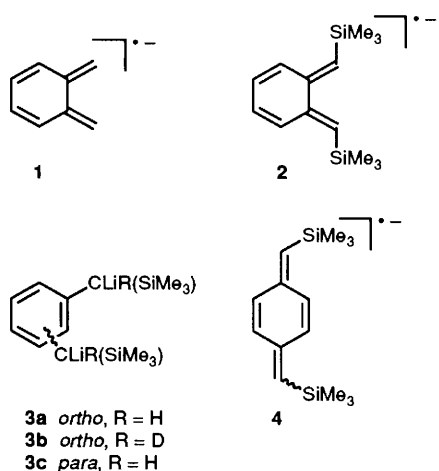


Fig. 1 ESR spectrum obtained by irradiating **3a** in 2-MTHF at  $-120^\circ\text{C}$

0.192 mT (4H) (Fig. 1). The signal could be observed after covering the light source without any apparent loss of intensity. The same spectrum was observable at  $-70^\circ\text{C}$ , but with considerably reduced intensity.

In order to confirm the assignment of the spectrum to the  $\alpha, \alpha'$ -bis(trimethylsilyl)-*o*-quinodimethane radical anion **2**, we irradiated the dideuterio-derivative **3b** under the same conditions. The resulting spectrum showed splittings of 0.193 mT (4H) and 0.101 mT (2D), confirming that the two equivalent protons are those in the  $\alpha$ -positions and that the two sets of ring protons are accidentally equivalent.

AM1<sup>12</sup> semiempirical MO calculations were used to investi-

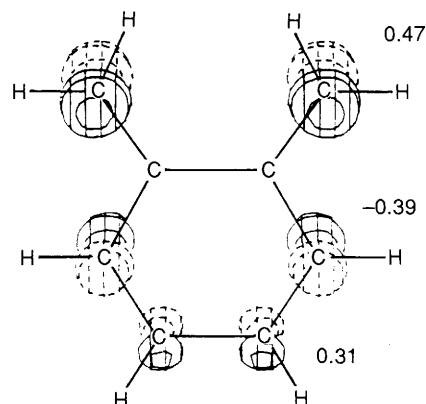


Fig. 2 Coefficients of the SOMO of **1** calculated with AM1-RHF

conrotatory				disrotatory			
$\sigma^*$ — A	$\pi_8$ — S	$\sigma^*$ — A	$\pi_8$ — A				
$\pi_6$ — S	$\pi_7$ — A	$\pi_6$ — A	$\pi_7$ — S				
$\pi_5$ — A	$\pi_6$ $\uparrow$ S	$\pi_5$ — S	$\pi_6$ — A				
$\pi_4$ $\uparrow$ S	$\pi_5$ — A	$\pi_4$ $\uparrow$ A	$\pi_5$ $\uparrow\downarrow$ S				
$\pi_3$ $\uparrow\downarrow$ A	$\pi_4$ $\uparrow\downarrow$ S	$\pi_3$ $\uparrow\downarrow$ S	$\pi_4$ $\uparrow$ A				
$\pi_2$ $\uparrow\downarrow$ S	$\pi_3$ $\uparrow\downarrow$ S	$\pi_2$ $\uparrow\downarrow$ A	$\pi_3$ $\uparrow\downarrow$ A				
$\pi_1$ $\uparrow\downarrow$ A	$\pi_2$ $\uparrow\downarrow$ A	$\pi_1$ $\uparrow\downarrow$ S	$\pi_2$ $\uparrow\downarrow$ S				
$\sigma$ $\uparrow\downarrow$ S	$\pi_1$ $\uparrow\downarrow$ A	$\sigma$ $\uparrow\downarrow$ S	$\pi_1$ $\uparrow\downarrow$ S				

Fig. 3 Correlation diagrams of the MOs calculated for the ring-opening of the benzocyclobutene to the *o*-quinodimethane radical anion

ESR spectra. Since ring-closure cannot occur in **4**, the similarity of the spectra of **2** and **4** supports the interpretation that **2** is an authentic *o*-quinodimethane radical anion.

The reverse reaction, the ring-opening of the benzocyclobutene radical anion to give **1**, was predicted by Bauld *et al.*<sup>4</sup> to be allowed in the conrotatory and forbidden in the disrotatory mode on the basis of orbital correlation diagrams. We have reanalysed this reaction with more modern theoretical methods and come to different conclusions. The benzocyclobutene-*o*-quinodimethane radical anion interconversion was investigated by calculating the enthalpy of formation as a function of the distance  $d$  between the exocyclic carbon atoms with the AM1-UHF method. The conrotatory mode is confirmed<sup>4</sup> to be more favourable energetically. The UHF reaction profile was corroborated using configuration interaction (CI) including all single and double excitations involving eight electrons in seven MOs. Both UHF and CI AM1 computations predict an activation energy of 27 kcal mol<sup>-1</sup> for the ring-opening (1 cal = 4.184 J). Analysis of the CI results shows the typical avoided crossing found for Wood-

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