Evidence for the Aromatic Character of Sulphonium Cyclopentadienylide from Nuclear Magnetic Resonance Measurements

By Z. YOSHIDA,* S. YONEDA, and M. HAZAMA

(*Department of Synthetic Chemistry, Kyoto University, Yoshida, Kyoto* 606, *Japan*)

Summary By analysis of the n.m.r. spectrum of dimethylsulphonium cyclopentadienylide (I) the π-bond orders ($p_{r,s}$) were estimated and found to be within the aromatic range.

FROM the behaviour of dimethylsulphonium cyclopentadienylide (I) towards electrophiles and dienophiles, it has been suggested that (I) is aromatic.[1] Here, we discuss the aromaticity of (I) from its n.m.r. parameters. (I) was prepared according to Behringer and Scheidl[2] and purified by sublimation at 80°/0·002 mmHg, m.p. 129·5—130°. The n.m.r. spectrum of (I) ($CDCl_3$; Varian HA-100) showed a multiplet centred at τ 3·80 (4H, cyclopentadienyl) and a singlet at 7·40 (Me). The multiplet for the ring protons appears as an AA′BB′ type (see Figure 1). The spectrum in Figure 1 was satisfactorily reproduced with a Jeolco JRA-1 computer with the parameters listed in Table 1. The simulated spectrum is given in Figure 2.

According to the proposed relationship between π-bond order ($p_{r,s}$) and the vicinal coupling constant,[3] $p_{2,3}$ and $p_{3,4}$ were calculated from the equation $J_{vic} = 7{\cdot}12p_{r,s} - 1{\cdot}18$. The π-bond orders were also calculated by the HMO and the SCF-MO method (see Table 2).

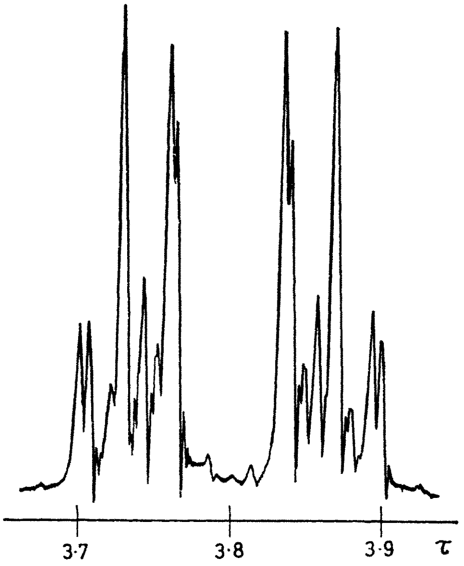
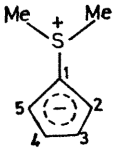


FIGURE 1. *N.m.r. spectrum of the ring protons in* (I).

The three sets of results all show that although $p_{2,3}$ is somewhat larger than $p_{3,4}$, both values are not very different from each other.

TABLE 1

N.m.r. parameters for (I) (Hz)



γ^{a}	Δ_{AB}	$J_{2,3}$	$J_{3,4}$	$J_{2,4}$	$J_{2,5}$
3·8	12·7	3·9	2·8	1·9	2·1

[a] Centre of the ring-protons' signal.

Streitwieser[4] has suggested that in π-systems single bonds have $p_{r,s} < 0{\cdot}4$, aromatic bonds have $p_{r,s} = 0{\cdot}5$—$0{\cdot}7$, and double bonds are characterized by $p_{r,s} > 0{\cdot}8$. The π-bond orders in our study are clearly in the "aromatic" range. The ^{13}C–H coupling constant of the ring protons of (I) was found to be 162 ± 1 Hz indicating that the cyclopentadienyl carbon atoms of (I) are typical sp^2 carbons. Thus, we conclude that (I) is aromatic.

TABLE 2

π-Bond orders of (I)

	$p_{2,3}$	$p_{3,4}$
Smith's method[3]	0·71	0·56
HMO method	0·678	0·626
SCF method	0·704	0·617

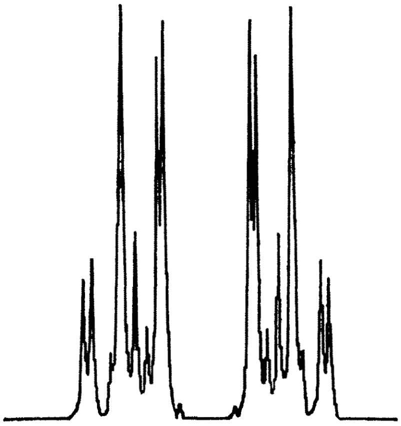


FIGURE 2. *Simulated spectrum for the ring protons of* (I).

(*Received, April 5th,* 1971; *Com.* 496.)

---

[1] Details will be published elsewhere.

[2] H. Behringer and F. Scheidl, *Tetrahedron Letters*, 1965, 1757.

[3] W. B. Smith, W. H. Watson, and S. Chiranjeevi, *J. Amer. Chem. Soc.*, 1967, **89**, 1438.

[4] A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley, New York, 1961, p. 172.