

Meso-ionic Fulvalene; Synthesis and Properties of Anhydro-5-cyclopentadienyl-1,3-diphenyl-1,2,3,4-tetrazolium Hydroxide

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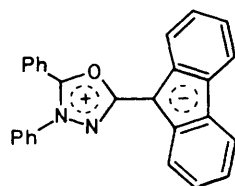
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A simple derivative of the meso-ionic analogue of sesquifulvalene has been synthesized and it is suggested that a polarized structure makes a significant contribution to its ground state.

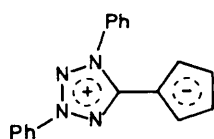
Meso-ionic compounds¹ in which the negative charge is associated with carbanionic and cyclopentadienide groups are isoelectronic with heptafulvene and sesquifulvalene, respectively. Although several examples containing carbanionic groups are known,² the synthesis of cyclopentadienide types has received little attention. The only example so far reported is the 1,3,4-oxadiazole derivative (**1**)³ in which the cyclopentadienyl ring is annelated by two benzene rings. In order to investigate the electronic structure of the meso-

ionic analogues of sesquifulvalene, simple derivatives which have an unsubstituted cyclopentadienyl group are required. In this communication we describe the first synthesis and the physico-chemical properties of a simple derivative (**2**) of meso-ionic sesquifulvalene which has no substituents on the cyclopentadienyl ring.

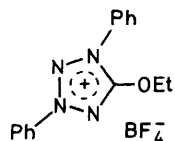
Anhydro-5-cyclopentadienyl-1,3-diphenyl-1,2,3,4-tetrazolium hydroxide (**2**) was synthesised by the reaction of 1,3-diphenyl-5-ethoxy-1,2,3,4-tetrazolium tetrafluoroborate



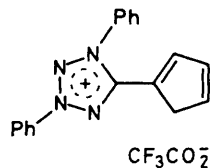
(1)



(2)



(3)



(4)

(3)[†] with sodium cyclopentadienide in tetrahydrofuran. The meso-ionic compound (2) was obtained as brown crystals with a purple lustre in 69% yield after recrystallization from ethanol.[†] The fulvalene (2) is stable in air at room temperature, m.p. 215 °C (decomp.). The mass spectrum of (2) revealed an intense molecular ion peak at m/z 286, and the i.r. spectrum showed characteristic absorptions at 1561, 1354, 1056, 984, 880, 762, 735, and 714 cm^{-1} . In the ¹H n.m.r. spectrum in CDCl_3 , the cyclopentadienyl ring protons appeared as a complex multiplet centred at δ 6.20 and the phenyl signals at δ 7.71 (8H) and δ 8.23 (2H). The chemical shifts of the cyclopentadienyl carbons (96.9, 113.1, and 116.5 p.p.m.) are comparable with that of the cyclopentadienide anion (102.1 p.p.m.⁵) but are more shielded than those of the olefinic carbons of cyclopentadiene (132.2 and 132.8 p.p.m.⁶). These spectral properties indicate the high electron density on the cyclopentadienyl ring of (2). Indeed,

[†] A satisfactory elemental analysis was obtained.

the fulvalene (2) is basic enough to be protonated in $\text{CF}_3\text{CO}_2\text{H}$ to give the corresponding conjugate acid (4), which reversibly regenerates the base (2) on the treatment with aqueous sodium hydrogencarbonate. In acetonitrile, the fulvalene (2) shows electronic absorption maxima at 258 ($\log \epsilon$ 4.26), 335 (4.49), and 475 nm (3.08). The longest wavelength transition shows a large red shift on going from polar to less polar solvents: 464 (MeOH), 476 (EtOH), 493 ($\text{Me}_2\text{C}=\text{O}$), 548 (Et_2O), and 565 nm (CCl_4). This solvent effect⁷ together with the ¹H and ¹³C n.m.r. data indicate considerable electron delocalization and charge separation resulting from the significant contribution of the dipolar (tetrzolium–cyclopentadienide) structure to the ground state of (2). These findings are in contrast with the fact that sesquifulvalene itself is a reactive polyolefin rather than an aromatic compound.⁸

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