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

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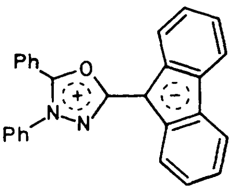
A simple derivative of the meso-ionic analogue of sesquifulvalene has been synthesized and it is suggested that a polarized structure makes a significant contribution to its ground state.

Meso-ionic compounds[1] 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



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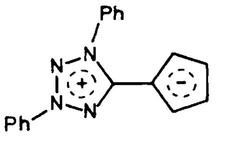

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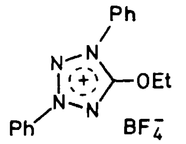

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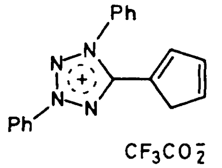

(4)

(3)[4] 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 ^{1}H 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, the fulvalene (**2**) is basic enough to be protonated in CF_3CO_2H 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 ϵ 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 ($Me_2C{=}O$), 548 (Et_2O), and 565 nm (CCl_4). This solvent effect[7] together with the ^{1}H and ^{13}C n.m.r. data indicate considerable electron delocalization and charge separation resulting from the significant contribution of the dipolar (tetrazolium–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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† A satisfactory elemental analysis was obtained.

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