UV–VIS and ESR Spectroscopic Evidence for a Strongly π–π Interacting (Resonant) Allodial Mixed-valence Compound: the Perchloro-4,4′-ethynylenebis(triphenylmethyl) Anion Radical

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Compelling UV–VIS and ESR spectroscopic evidence for the formation of the first stable allodial anion radical with strong π–π electron interaction (resonance) in perchloroorganic chemistry, the potassium(18-crown-6) salt of the perchloroethynylenebis(4-triphenylmethyl) anion radical, is presented and discussed.

The intramolecular single-electron transfer (SET) in allodial† radical ions with two perchlorotriphenylmethyl (PTM) units linked by different bridges has been recently investigated.[1] In that study a 'fast spin-charge exchange' through a σ-path mechanism was postulated, since while UV–VIS spectroscopy (time scale 10^{13} s^{-1}) shows inhibition of resonance due to steric interactions[2] (Sp = none) or to a saturated spacer (Sp = CH_2CH_2), ESR spectroscopy (time scale 10^8 s^{-1}) shows spin-charge delocalization (halving of the hyperfine ^{13}C coupling constants).

Perchloro-4,4′-ethynylenebis(triphenylmethyl) anion radical **2**, with Sp = C≡C, has also been studied. Its ESR spectrum shows delocalization (halving of the ^{13}C coupling constants); however, in that paper it was stated that 'the $^-$PTM–C≡C–PTM$^-$ salt decomposes in THF solution yielding a compound with a very intense band at 750 nm, suggesting a cyclization reaction leading to an increased π–π conjugation'.[1]

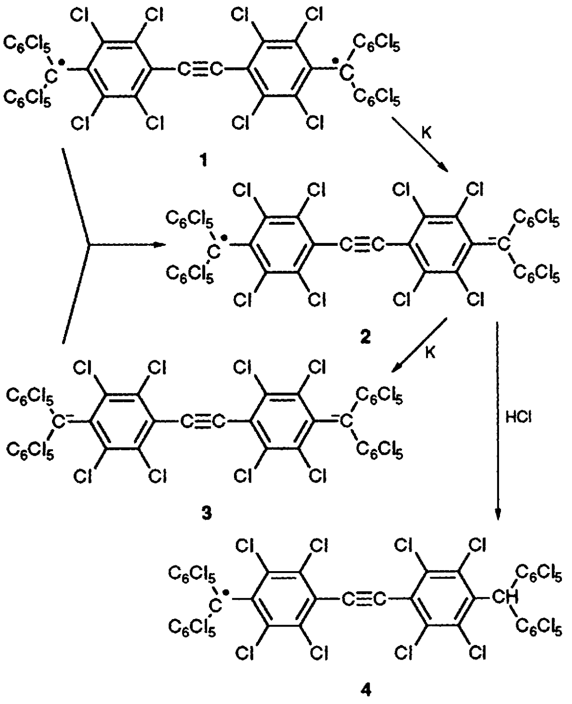
Here we present strong evidence showing that the band at 750 nm belongs to the stable, resonant, potassium(18-crown-6) perchloro-4,4′-ethynylenebis(triphenylmethyl) anion radical **2**.

(*a*) The reaction of perchloro-4,4′-ethynylenebis(triphenylmethyl) biradical **1**,[3] with potassium(18-crown-6) in THF was monitored by UV–VIS spectroscopy. The evolution of the UV–VIS spectrum shows two main steps: (i) [Fig. 1(*a*)] a slow decrease of the bands of radical **1** and the rise of a new one at 753 nm that reaches a maximum (ε *ca*. 72700) when the radical bands have disappeared; (ii) [Fig. 1(*b*)] a slow decrease of the band at 753 nm and the rise of new ones at 664 and 520 nm reaching their maxima (ε *ca*. 96600 and 50000, respectively), when the band at 753 nm has disappeared completely. These final absorptions agree with those found (665, 515 nm; ε 82800, 40000) for the bis(tetrabutylammonium)perchloro-4,4′-ethynylenebis(triphenylmethide).[1]

(*b*) The admixture of equimolar THF solutions of diradical **1** and potassium(18-crown-6) dianion **3** yields a stable solution with a UV–VIS spectrum identical to that of the intermediate step of the preceding reaction [Fig. 1(*a*), curve *d*], and quite different from the simple average of the spectra of diradical **1** (Fig. 1, curve *a*) and dianion **3** (Fig. 1, curve *h*), which would be the result for a non-resonant system.[1]

(*c*) The treatment of the final solution obtained in (*b*) with a drop of aq. HCl (hydrolysis of the anion) yields a green solution with a UV–VIS spectrum characteristic of a PTM radical with a conjugated acetylenic group (but different from the initial biradical **1**); this is in agreement with the proposed structure of octacosachloro-4-[(αH-triphenylmethan-4-yl)ethynyl]triphenylmethyl radical **4**.

(*d*) The ESR spectrum of anion radical **2** (the final solution of paragraph (*b*) shows delocalization (halving of the normal aromatic ^{13}C hyperfine couplings).



Scheme 1

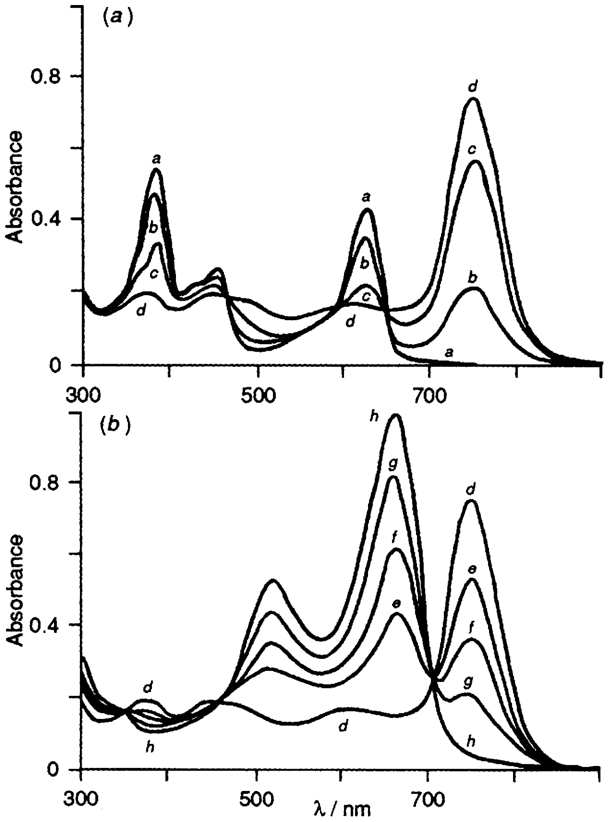


Fig. 1 Monitoring (UV–VIS spectroscopy) of the reaction of biradical **1** with potassium. (*a*) 1st step, *a* → *d*, formation of anion radical **2**. (*b*) 2nd step, *d* → *h*, formation of dianion **3**.

The above evidence can be rationalized as follows: the slow reaction of biradical **1** with potassium yields, in the first step, the anion radical **2** (band at 753 nm), and subsequently dianion **3**. Moreover, the equilibration of equimolar solutions of diradical **1** and dianion **3** also yields **2**. The existence of this anion radical is sustained by the fact that the protonation of **2** with aq. HCl yields a green radical different from **1**; its acetylenic radical band at 632 nm, with an intensity (ε 20 370) approximately half that of diradical **1** (637 nm; ε 41 300), suggests that it is monoradical **4**.

Once the formation of **2** has been established, the existence of a strong π–π electronic interaction (resonance) with a symmetrical spin-charge distribution through the π-system is evident, taking into account the fact that such a structure must have a UV–VIS spectrum (band at 753 nm) quite different from those allodial anion radicals with no π–π interaction (their spectra are the average of those of the corresponding diradical and dianion).[1] The bathochromic shift observed (116 nm for **1** → **2**, 88 nm for **3** → **2**), equivalent to 5–7 kcal mol^{-1} (1 cal = 4.184 J), is a measurement of its resonance stabilization. When the resonance stabilization is calculated starting from a non-resonant anion radical such as 4,4′-(1,2-ethylene)bis(tetradecachlorotriphenylmethyl) anion radical[1] (λ = 517 nm) the resulting value is *ca.* 17 kcal mol^{-1}, reaching the adiabatic limit of the electron transfer reactions.[4] Accordingly, application of Hush's theory[4d] for mixed valence class III compounds[5] to the band at 753 nm of **2** gives ($\lambda = 2H_{AB}$) a value of H_{AB} = 18.8 kcal mol^{-1} close to our experimental estimations. These results show a time-independent delocalization (resonance), rather than a fast exchange interaction.

Anion radical **2** is the first example of a strong π–π interacting allodial anion radical in chlorocarbon chemistry. This is probably due to the fact that the acetylenic bridge does not present the steric hindrance problems caused by the presence of bulky chlorine atoms in the connecting bridge.

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Footnote

† Allodial radical ion denotes that the electric charge and the odd electron have an independent existence.[1]

$$\text{PTM}^\bullet\text{–Sp–PTM}^* \rightleftarrows \text{PTM}^*\text{–Sp–PTM}^\bullet \quad (\text{Sp = spacer})$$

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