Inert Carbon Free Radicals. 14. Synthesis, Isolation, and Properties of Two Strongly $\pi-\pi$ Interacting Mixed-Valence Compounds: The Perchloro-4,4′-ethynylenebis(triphenylmethyl) Anion Radical Potassium (18-Crown-6) Salt and the Perchloro-α,α,α′,α′-tetraphenyl-*p*-xylylene Anion Radical Tetrabutylammonium Salt

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The perchloro-4,4′-ethynylenebis(triphenylmethyl) anion radical (**11**) potassium 18-crown-6 salt and perchloro-α,α,α′,α′-tetraphenyl-*p*-xylylene anion radical (**15**) tetrabutylammonium salt have been isolated in pure form as solids perfectly stable in the air and moisture, withstanding temperatures up to 200 °C. Their physical and chemical properties have been studied using UV−vis, NIR, IR, ESR, cyclic voltammetry, magnetic susceptibility, and electrical conductivity and compared with other already reported and structurally related perchlorotriphenylmethyl systems in which an intramolecular "*spin-charge exchange*" takes place. In contrast with those compounds, the acetylene anion radical **11** shows an unusual band in the vis−NIR region (754 nm, 37.7 kcal/mol), not present in its corresponding biradical **10** and dianion **9**, and the Thiele anion radical **15** shows a typical, but bathochromically shifted ca. 10 kcal/mol, radical band and an unusual NIR band at 1342 nm (21.2 kcal/mol) of high intensity. Application of Hush's theory of mixed-valence class III compounds to these unusual bands for PTM compounds, gives the values of ca. 18 and 10 kcal/mol for the resonance energy of **11** and **15** respectively. The close coincidence of these theoretical values with those obtained by comparing the UV−vis spectra of **11** and **15** with the PTM anion radical systems without *resonance interaction* can be regarded as a preliminary test of the validity of Hush's theory of organic mixed-valence class III compounds. The cyclic voltammograms of anion radicals **11** and **15** indicate that their precursors, the biradical **10** and perchloro-Thiele hydrocarbon **16** have suitable redox potentials as acceptor components of electrically conducting charge-transfer complexes. **11** and **15** present magnetic properties similar to those of PTM radicals, but as a consequence of the "spin charge resonance" they show a halving of the hyperfine coupling constants. More spectacular differences are shown in the electrical conductivity of **11** and **15** with values of 10^{-4} and 10^{-6} S cm^{-1}, respectively, which can be a consequence of their molecular design as suggested the $\Delta E_{1/2}$ differences (6.4 vs 12 kcal/mol). These conductivity values are in the range of the corresponding TCNQ salts.

Introduction

The design of new organic ion radicals is a subject of current interest since these structural units are responsible for the unusual optical (NIR),[1] magnetic,[2] and electrical properties of the mixed-valence compounds[3] and some conducting polymers.[4] However, very few organic mixed-valence compounds are known,[5] most of them being formed from an electrically neutral, nonradical species by a single-electron addition or removal (*nondistonic*).[6] One major problem in taking advantage of their interesting properties in technological applications[8] is their lack of stability.

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The intrinsic high chemical and thermal stability of the compounds of the perchlorotriphenylmethyl (**PTM**) series[9] (radicals and ions) have allowed the synthesis of di-,[9,10a,b] tri-,[10a,c] tetra-,[11] and polyradicals,[12] as well as dianions.[7] All these compounds have been isolated as solids, stable in air and heat-resistant up to ≈200 °C. Another attractive feature of the PTM system is its donor or acceptor character derived from the fact that a PTM radical can be converted into either its carbenium ion (PTM^+) or carbanion (PTM^-), both being solids stable in air.[9a] For example, the simplest dimer structure (PTM−PTM) can exist in five oxidation states (++, +·, ··, ·−, − −)[7] and thus having a relatively "broad window" of redox potentials. Despite the high stability and new properties expected for the corresponding mixed-valence compounds, these have never been isolated.

Recently, the generation of stable (*distonic*)[6] **PTM** radical ions (PTM−Sp−PTM, Sp = none, CH_2CH_2) in solution, in equilibrium with the corresponding diradicals and diions has been described.[7] Although the severe steric hindrance of perchloro compounds is well-known,[9] an operative intramolecular "spin-charge exchange" mechanism takes place in the ion radicals.[7] Following the Robin and Day criterion[13] these electroactive species can be classified as "mixed-valence class II" compounds. However, there is a close structurally related system (Sp = C≡C), the perchloro-4,4′-ethynylenebis(triphenylmethyl) anion radical (**11**) recently detected in solution, which has a striking and unusual UV−vis band at 754 nm, accounting for a strong $\pi-\pi$ interacting compound.[14] The principal problem is how to ascertain whether this band corresponds to a partial or a full resonant interaction of the main system. For this purpose, the synthesis of the perchloro-α,α,α′,α′-tetraphenyl-*p*-xylylene anion radical **15**, a smaller sized analogue of **11**, was undertaken. Since its chemical precursor, the perchloro-α,α,α′,α′-tetraphenyl-*p*-xylylene (**16**)[15] ("perchloro-Thiele")[16] has a quinonoid structure (neutral and nonradical species),[15] the anion radical **15** is expected to be a fully resonant system with a *nondistonic* structure[6] and two transitions in its UV−vis spectrum.[9b]

In view of the above considerations, a decision was made to isolate the already detected anion radical **11**,[14] to synthesize and isolate the perchloro-Thiele anion radical **15** and subsequently to study their chemical and physical properties as models of perchloromaterials.

Results and Discussion[17]

Perchloro-4,4′-ethynylenebis(triphenylmethyl) diradical (10).[9c,18] This diradical was synthesized using the new route outlined in Scheme 1: The dimerization of 4*H*-heptachlorotoluene (**3**)[19] with $Fe(CO)_5$[21] or FeC_2O_4[22] gives mixtures of *trans*- and *cis*-4H,4′H-decachlorostilbene (**4** and **5**) which, after separation, were submitted to a Friedel−Crafts reaction with $CHCl_3-AlCl_3$ to afford *trans*- and *cis*-4,4′-bis(dichloromethyl)decachlorostilbene (**6** and **7**). A new Friedel−Crafts condensation of **6** or **7** with pentachlorobenzene−$AlCl_3$ yielded, in both cases, *trans*-α*H*,α′*H*-triacontachloro-4,4′-vinylenebis(triphenylmethane) (**8**).[9c,18] *Cis-trans* isomerization takes place at high temperature in the presence of $AlCl_3$ (Scheme 1). Compound **8**, along with its *cis* isomer, has already been obtained by another route,[9c,18a] the dimerization of αH-heptadecachloro-4-methyltriphenylmethane;[23] however, this synthesis presents the disadvantage of the cumbersome preparation of the starting product, with an unwieldy purification process and low yields. The reaction of **8** (or its *cis* isomer) with an excess of tetrabutylammonium hydrox-

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(6) The *distonic* term, introduced by Radom and now widely accepted, is reserved for radical ions with separated charge and radical sites that formally arise from the ionization of a zwiterion or a diradical. *Nondistonic* are the radical ions that arise by loss or addition of an electron from a stable neutral molecule.[7] Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 5805. Yates, B. F.; Bouma, W. J.; Radom, L. *Tetrahedron*, **1986**, *42*, 6225. The importance of the spin-charge separation in organic conducting materials has been previously reported: Wudl, F. *J. Am. Chem. Soc.* **1981**, *103*, 7064.

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(17) All the new compounds (**6, 7, 9, 11, 12**, and **15**) of this paper have been characterized by elemental analyses, mp or TGA, UV−vis, ^1H NMR, ^{13}C NMR, and IR spectra. In the case of the radicals, the ESR spectrum has also been recorded and its purity checked by TLC and magnetic susceptibility measurements.

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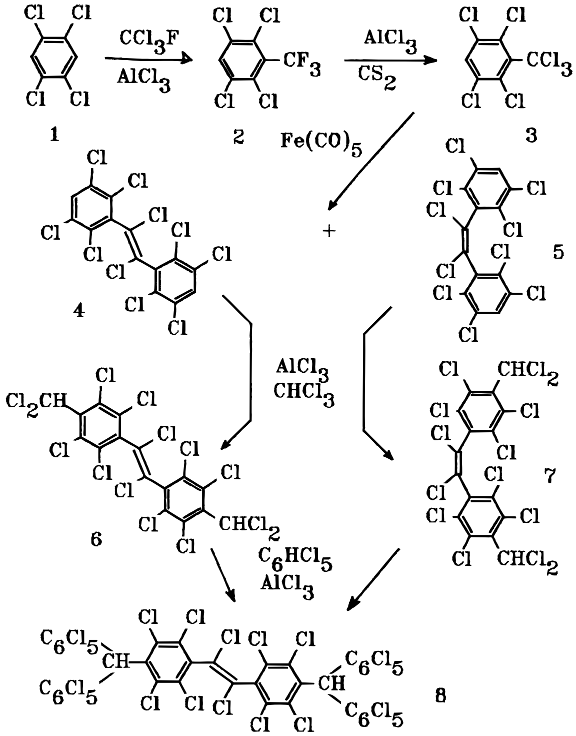
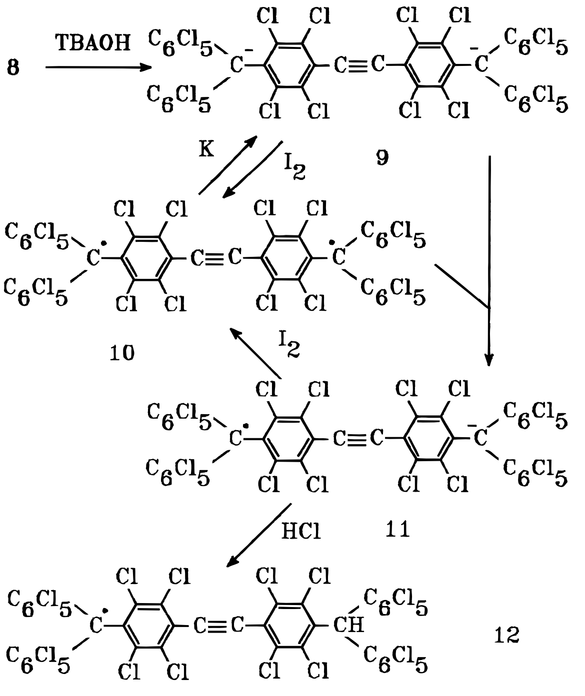
Scheme 1



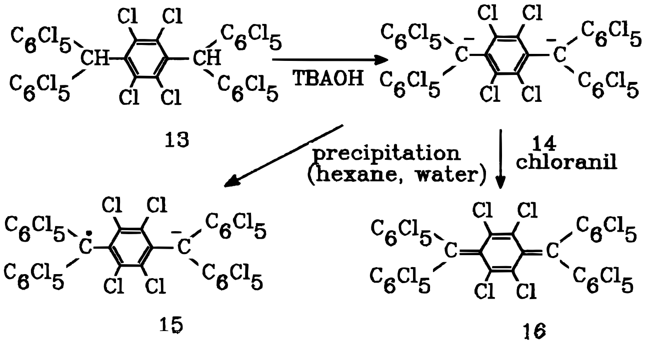
Scheme 2



ide (TBAOH) in THF yields the acetylenic dicarbanion **9** as expected,[18a,24] a simultaneous reductive dechlorination has taken place. The final oxidation of dianion **9** with I_2 affords diradical **10**, as a dark-green powder (Scheme 2).

Perchloro-4,4′-ethynylenebis(triphenylmethide) Bis(potassium-18-crown-6) (9). Salt **9** was obtained by the reaction of diradical **10** with potassium metal in THF in the presence of 18-crown-6 as already carried out for the perchlorotriphenylmethide anion (Scheme 2).[25] It was isolated as a dark blue powder stable to oxygen and moisture.

Scheme 3



Perchloro-4,4′-ethynylenebis(triphenylmethyl) Anion Radical Potassium 18-Crown-6 Salt (11). In view of the already reported detection of anion radical **11**,[14] its isolation was attempted. The admixture of equimolar THF solutions of dianion **9** and diradical **10**, followed by precipitation with ethyl ether afforded anion-radical **11** as a dark gray (almost black) powder, stable to oxygen, moisture, and temperatures up to 280 °C (TGA). Beyond this temperature 18-crown-6 is evolved and the product decomposes. Anion radical **11** is completely stable in THF and CH_2Cl_2 showing no variation of its UV–vis spectrum in both solvents over time. However, in low-polarity solvents (e.g., CCl_4) it oxidizes slowly to diradical **10**.

Octacosachloro-4-(α*H*-triphenylmethan-4-ylethynyl)triphenylmethyl Radical (12). To confirm the structure of anion radical **11**, its protonation yielding monoradical **12** was performed with 0.1 N HCl in THF–water. **12** was isolated as a green powder stable to oxygen as are other radicals of the PTM series.[9]

Perchloro-α,α,α′,α′-tetraphenyl-*p*-xylylene (Perchloro-Thiele) Anion Radical Tetrabutylammonium Salt (15). The isolation of the anion radical **15**, starting from the α*H*,α′*H*-tetraicosachloro-α,α,α′,α′-tetraphenyl-*p*-xylene[15] (**13**), was attempted by a similar two-step route already described for other PTM–anion radicals:[7] (a) The formation of the corresponding dianion **14** using TBAOH and subsequent isolation by precipitation with hexane/water, and (b) The admixture of equimolar solutions of the isolated dianion and perchloro-α,α,α′,α′-tetraphenyl-*p*-xylylene (**16**, Scheme 3).[15] However, the reaction sequence did not work as expected: The reaction of the α*H*,α′*H* compound **13**[15] with a great excess of TBAOH in THF was monitored by UV–vis. The corresponding dark violet dianion **14** shows an UV–vis spectrum with a broad band at 567 nm (ϵ 58 000). However, when the THF solution was treated with hexane/water in order to isolate the dianion, the precipitate formed was not dianion **14**, but anion radical **15**, as ascertained by elemental analyses, IR, UV–vis, magnetic susceptibility, and ESR spectra. This anion radical is also stable to oxygen, moisture, and temperatures up to 340 °C. The greater instability (easier oxidability) of dianion **14**, with respect to the other PTM dianions, can be explained by the short distance between the two negative charges in this dianion that gives rise to a strong Coulombic repulsion. This instability is also reflected in its redox potentials (−0.61 and −1.13 V for **15** versus −0.45 and −0.68 V

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Table 1. UV−Vis Spectral Data

system	neutral (λ, ϵ)	anion (λ, ϵ)	anion-radical (λ, ϵ)
PTM[9]	383, 37 000[9] 562, 1200	520, 31 000[7]	
PTM−PTM[7]	383, 76 500[7] 560, 2700	520, 59 500[7]	383, 40 750[7] 520, 29 750
PTM−CHCH2−PTM[7]	385, 73 800[7] 562, 2430	517, 56 700[7]	385, ∼37 000[7] 517, ∼28 000
PTM−C≡C−PTM	10 385, 52 400[18] 435, 22 700 460, 27 900 637, 41 300	**9**[a] 517, 41 400 665, 103 200	11 369, 17 590 450, 20 500 754, 83 900
PTM−C≡C-αHPTM	12 385, 20 500 439, 18 300 634, 13 800		
perchloro-Thiele	16 508, 23 150[15]	**14** 567, 58 000	**15** 437, 16 000 635, 45 800

[a] The corresponding tetrabutylammonium salt has been previously published[7] with λ values (515, 665) similar to those of **9**.

for acetylenic anion radical **11**; see the Cyclic Voltammetry section).

UV−Vis−NIR Spectra of the PTM Anion Radical Systems. The UV−vis spectra of PTM radicals and anions display the characteristic radical (385, 500−560 nm) or anionic (520 nm) bands of the PTM system,[9] as shown in Table 1. In selected cases, when there are p−π or π−π interactions in the PTM system, as in NH_2−PTM and acetylene diradical **10**, their absorption bands are significantly shifted bathochromically by electron delocalization.[9c,d]

The PTM anion radical systems, stable candidates for organic mixed-valence compounds must show, in some cases, new absorption bands (usually located in the near-infrared region or NIR) which are due to intervalence transfer (IT). Following Robin and Day criterion,[13] they can be classified as follows: (a) Class I: compounds without interactions which exhibit the same properties as the isolated units. (b) Class II: reserved for compounds with *exchange* interactions between the centers. They show the properties of the isolated units and those resulting from IT. In the inorganic field, Hush[26,27] provided a useful criterion for the classification of these type of compounds based on the analysis of the IT spectra:

(1) The position or energy of the IT absorption band "E_{op}" (which is the same as the Marcus λ value for these systems)[5e] is related to the thermal ET barrier "$\Delta H^{\ddagger}$" (Eyring rate theory is often not employed, but E_{op} is an enthalpy, not a free energy)[5e] between the two sites:

$$E_{op} = \lambda = h\nu = 4\Delta H^{\ddagger et} \qquad (1)$$

(2) The bandwidth at half-intensity should be equal to, or exceed, that obtained from the following equation:

$$\Delta\nu_{1/2} \geq 48.06\nu_{max}^{1/2}\ \mathrm{cm}^{-1} \qquad (2)$$

(3) The position of the band maximum is a function of the solvent through eq 3, resulting in E_{op} as the sum of two reorganizational term. The E_{out} term takes into account the influence of the solvent:

$$E_{op} = E_{in} + E_{out} \qquad (3)$$

(4) The degree of electronic coupling (H_{AB}) is related to the band intensity (ϵ_{max})

$$H_{AB}^{2} = [4.2 \times 10^{-4}\epsilon_{max}\Delta\nu_{1/2}\nu_{max}]/r^{2}\ \mathrm{cm}^{-1} \qquad (4)$$

where "r" is the distance between the two units.

(c) Class III: This accounts for systems with *resonance interactions* between centers. They do not show the properties of their isolated units and only they show the new properties of the system. According to Hush and Creutz:[27] (1) The position of the IT band is related to the magnitude of the electronic coupling (H_{AB}). Note that the class III ion also undergoes light absorption by virtue of its mixed-valence nature, but at[27b,c]

$$h\nu = 2H_{AB} \qquad (5)$$

(2) The bandwidth at half-intensity should be narrower than in the case of class II (eq 2).

(3) There is no dependence of the IT band on the solvent.

On the basis of the correlations between UV−vis electron delocalization and classical Hush analyses we shall discuss anion radicals **11** and **15** in comparison with the previously described PTM anion radicals in which a "*spin-charge exchange*" takes place (class II systems).

Distonic Mixed-Valence Class II Systems:[6,7,13] The Perchloro-α,α,α′,α′-tetraphenylbi-*p*-tolyl-α,α′-diyl System (PTM−PTM). The UV−vis spectra of dimeric PTM compounds without resonance interactions between radical or/and ion centers such as those formed by two PTM units connected either directly (PTM−Sp−PTM) (Sp = none) or joined by a saturated spacer (Sp = CH_2CH_2), are virtually identical both in wavelengths (λ) and molar absorptivities (ϵ) to the corresponding monomeric PTM constituents as it has been already shown.[7] Table 1 and Figure 1 present the UV−vis spectra of the perchloro-α,α,α′,α′-tetraphenylbi-*p*-tolyl-α,α′-diyl (PTM−PTM) system, in which, due to *steric inhibition of the π*-electron resonance (perpendicularity of both moieties of the biphenyl ring), the diradical (curve A_2) and the dianion (curve A_1) are identical (per PTM unit) to the PTM radical and anion units, respectively (Table 1), and thus the anion radical (curve A_3) is the sum of those of its isolated PTM units (curve $A_2/2$ + curve $A_1/2$).[7]

The absence of resonance interactions in the UV−vis spectrum of the ion radicals and the presence of a fast exchange in the ESR time scale (through a σ mechanism)[7] are compelling evidence that they can be classified as class II compounds:

$$\mathrm{PTM}^{-}{-}\mathrm{Sp}{-}\mathrm{PTM}^{\bullet} \rightleftharpoons \mathrm{PTM}^{\bullet}{-}\mathrm{Sp}{-}\mathrm{PTM}^{-}$$

Mixed-Valence Class III Systems: The Perchloro-4,4′-ethynylenebis(triphenylmethyl) System (PTM−C≡C−PTM) (9, 10, 11). The comparison of the UV−vis spectra (Figure 1, Table 1) of the acetylenic diradical (**10**, curve B_2), the corresponding dianion (**9**, curve B_1) and anion radical (**11**, curve B_3) with those of the above systems (curves A_2, A_1, and A_3) gives rise to the following statements:

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(27) (a) Hush, N. S. *Prog. Inorg. Chem.* **1967,** *8*, 391. (b) Creutz, C. *Prog. Inorg. Chem.* **1983,** *30*, 1. (c) The energy of stabilization by electron delocalization in the mixed-valence class III systems, equivalent to H_{AB}, has been routinely evaluated from the IT band maximum. See ref 27b, p 31.

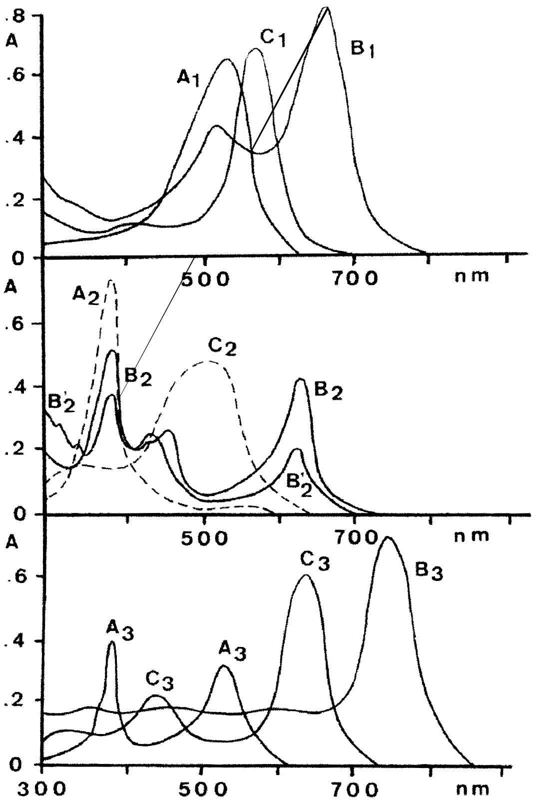

Figure 1. UV−vis spectra: curve A_1, PTM−PTM dianion; curve B_1, acetylene dianion **9**; curve C_1, perchloro-Thiele dianion **14**; curve A_2, PTM−PTM diradical; curve B_2, acetylene diradical **10**; curve C_2, perchloro-Thiele hydrocarbon **16**; curve A_3, PTM−PTM anion radical; curve B_3, acetylene anion radical **11**; curve C_3, perchloro-Thiele anion radical **15**.

(1) The diradical **10** and the dianion **9** present the typical absorptions of the monomeric PTM system (385 nm for the radicals and 520 nm for the anions).[9] However, they display additional bands at 435−460 and 637 nm for diradical **10** and 665 nm for dianion **9**, indicating a strong resonant system[9c,d] with a resonance energy of about 9 or 12 kcal/mol, respectively.

(2) It is worthy to note that diradical **10** and monoradical **12** show very similar UV−vis spectra (Figure 1, curves B_2 and B_2', respectively). The near coincidence of λ (637 and 634 nm) permits us to ascertain that both radicals present the same chromophore, i.e., a PTM−C≡C− unit; consequently it must be stated that although diradical **10** does not present significant steric repulsions, the $\pi-\pi$ electronic interactions of each PTM radical unit with the triple bond occur independently with only "one" of the π-orbitals of the acetylene bridge, and the relevant extended π-MOs of each molecular moiety are most probably orthogonal.[7]

(3) The UV−vis spectrum of the isolated anion radical **11** (Figure 1 curve B_3, $C = 10^{-5}$ M) in THF differs completely from those of its precursors, the diradical **10** and the dianion **9**, displaying an unusual strong band at 754 nm (ϵ 83 900, $\Delta\nu_{1/2}$ 1313 cm^{-1}) in the vis−NIR borderline. This band is quite different from those reported (520 nm) in solution for structurally related, nonresonant, anion radicals (e.g., 4,4′-(1,2-ethylene)bis(tetradecachlorotriphenylmethyl) (PTM−CH_2CH_2−PTM) or perchloro-α,α,α′,α′-tetraphenylbi-*p*-tolyl-α,α′-diyl) (PTM−PTM) anion radicals (Figure 1, curve A_3). Since anion radical **11** absorbs at 754 nm, the bathochromic shift observed (754−520 = 234 nm) is an experimental measurement of the resonance interaction ($H_{AB} \approx 17.5$ kcal/mol). Accordingly, the application of Hush's theory[27] of mixed-valence class III compounds to the band at 754 nm qualifies **11** unambiguosly as a class III compound: (a) The bandwidth at half-intensity ($\Delta\nu_{1/2} = 1313$ cm^{-1}) of the band at 754 nm ($\nu_{max} = 13\,262$ cm^{-1}) is four times narrower than in the case of class II (eq 2). (b) There is no shift of the band maximum in the solvents in which the compound is soluble and stable (THF and CH_2Cl_2). (c) Equation 5 gives a value of $H_{AB} = 18.8$ kcal/mol,[27b,c] in sound accordance with our previous UV−vis calculations.[14] These results indicate a time-independent delocalization (resonance) rather than a fast exchange interaction.

(4) A similar comparison of the wavelengths of acetylene diradical **10** (637 nm) and its anion radical **11** (754 nm) shows a bathochromic shift of 117 nm (≈7 kcal/mol), which can be attributed to an increased resonance stabilization, due to the presence of a more extended chromophore. The chromophore of the diradical **10** is only a PTM−C≡C group as stated before, due probably to the fact that the two limiting structures of a hypothetical resonance are not degenerate. On the contrary, the chromophore of anion radical **11** comprises all the molecule since the limiting structures in this case are fully degenerate, and no steric inhibition problems are here present as the −C≡C− spacer is linear and of small size:

$$\mathrm{PTM}^{-}-\mathrm{C}\equiv\mathrm{C}-\mathrm{PTM}^{\bullet} \leftrightarrow \mathrm{PTM}^{\bullet}-\mathrm{C}\equiv\mathrm{C}-\mathrm{PTM}^{-}$$

Nondistonic Mixed-Valence Class III Systems: The Perchloro-Thiele (16, 15, 14) System. The UV−vis spectrum of the perchloro-α,α,α′,α′-tetraphenyl-*p*-xylylene (**16**,[15] perchloro-Thiele hydrocarbon; Table 1 and Figure 1, curve C_2) with a band at 508 nm (ϵ 23 150) corresponds not to a diradical structure but to a quinonoid one,[15] similar to that of the perchloro-*p*-xylylene (λ 319 nm, ϵ 19 900),[28] since both compounds are diamagnetic.

Perchloro-Thiele anion radical **15** displays an UV−vis spectrum (Table 1 and Figure 1, curve C_3, $c = 10^{-5}$ M) in THF with two absorptions at 437 and 635 nm attributed, according to simple MO considerations,[9b] to the transitions expected for the addition of one more electron to the above-mentioned quinonoid structure. In this case, anion radical **15** (with an aromatic structure) presents the two transitions involving singly occupied MO's as PTM radicals (385 and 510−560 nm; Table 1), but bathochromically shifted about 9 kcal/mol. Therefore, the UV−vis spectrum of anion radical **15** (Figure 1, curve C_3) shows neither the individual absorptions of its PTM constituents (radical and anion), nor the corresponding average spectrum of the perchloro-Thiele dianion **14** (Figure 1, curve C_1) and the quinonoid structure of perchloro-Thiele hydrocarbon **16** (Figure 1, curve C_2).

The NIR spectrum of anion radical **15** was carried out (Figure 2, $c = 10^{-5}$ M), showing a band at 1342 nm (7450 cm^{-1}, 21.2 kcal/mol) with a bandwidth at half-intensity of 2870 cm^{-1}. Application of Hush's analyses (eq 2) shows that **15** is a mixed-valence III compound with a resonance energy (eq 6) of 10.6 kcal/mol.[27c] An estimate of the resonance energy of the anion radical **15** (λ, 635 nm) when compared with the noninteracting anion

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(28) Ballester, M.; Castañer, J. *Anal. Real Soc. Españ. Fis. Quim.* **1960**, *51B*, 207.

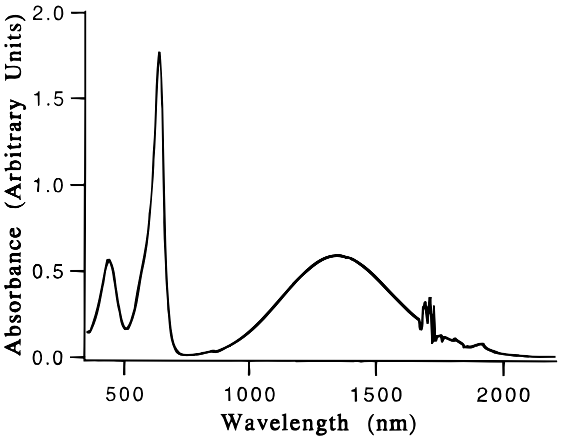

Figure 2. Vis−NIR of Perchloro-Thiele anion radical **15** in THF.

Table 2. ESR Spectral Data (G)

radical/solv	temp	g	ΔH_{pp}[d]	α ^{13}C	arom ^{13}C
PTM CCl_4[33]	rt	2.0026	1.4	29.5	10.7 12.7
PTM MeTHF[34]	rt	2.0026	2.6	*a*	*a*
PTM•−C≡CαHPTM (**12**)	rt	2.0023	1.2	30.3	10.2 12.7
CCl_4	−20 °C		0.8	*b*	10.4 12.9
PTM•−C≡C−PTM$^-$					
(**11**) MeTHF[34]	rt	2.0027	2.30	*a*	*a*
	−80 °C	2.0027	0.64	*b*	5.6
THF	rt	2.0027	1.4	13.9	5.4
	−80 °C	2.0027	1.0	*b*	5.4
	rt[c,7]	2.0027	1.2	14.0	5.2
perchloro-Thiele anion radical **15** THF	rt	2.0026	1.4	12.5	4.8

[a] Not observable because of the increased bandwidth.[34] [b] It has already been reported an abnormal line broadening of the α-^{13}C satellites on lowering the temperature and increasing the viscosity of the solvent, giving rise to very broad, sometimes unobservable lines.[35] [c] Generated in solution by Ballester et al.[7] [d] Line width.

radicals (λ, 520 nm) gives a value of ≈10 kcal/mol. This value is close to our NIR calculations.

The smaller value of the resonance energy of anion radical **15** (10 kcal/mol) with respect to anion radical **11** (17.5 kcal/mol) is accounted for by the smaller size of the resonant system:

$$(C_6Cl_5)_2C^{-}{-}C_6Cl_4{-}C{\equiv}C{-}C_6Cl_4{-}C^{\bullet}(C_6Cl_5)_2 \quad (\mathbf{11})$$

$$(C_6Cl_5)_2C^{-}{-}C_6Cl_4{-}C^{\bullet}(C_6Cl_5)_2 \quad (\mathbf{15})$$

The UV−vis spectrum of the perchloro-Thiele dianion **14** (Table 1, Figure 1, curve C_1; addition of two electrons to the perchloro-Thiele hydrocarbon) exhibits a band at 567 nm, and from the bathochromic shift with respect to PTM anion (520 nm) a resonance energy of ≈4 kcal/mol is calculated. This low resonance energy plus the strong Coulombic repulsion between the two negative charges accounts for the high instability of dianion **14** observed in the isolation attempts. Dianion **14** is stable only in solution, probably due to solvation by the solvent (THF).

NMR Spectra. The ^{1}H NMR spectra of compounds **4**−**8** agree with the data of other highly chlorinated compounds: The aromatic H flanked by two chlorines is here found for **4** at 7.71 ppm, very near the values of 7.81 and 7.74 ppm for 4*H*-heptachlorotoluene[29a] and α*H*,4*H*-hexachlorotoluene,[29a] respectively. The $CHCl_2$ group in **6** and **7** presents a singlet at 7.61 and 7.64 ppm, respectively (reported data for α*H*-heptachlorotoluene and α*H*,4*H*-hexachlorotoluene,[29a] 7.60 and 7.63 ppm, respectively).

Remarkably, *trans*-**8** has two broad signals at 7.04 and 7.08 ppm in the expected 7.0−7.4 ppm region of the αHPTM group. These two signals show the presence of diastereoisomeric forms due to restricted rotation of the pentachlorophenyl groups, as has already shown in related highly chlorinated compounds.[10b]

The ^{13}C NMR spectra of compounds **4** and **6** appear in the range 128−137 ppm and agree with their structure and the reported data of other highly chlorinated compounds.[29b,c] However, compound **6** shows seven resonances in the aromatic/olefinic region; four of them at 134.95, 134.41, 132.48, and 130.51 ppm with low intensity, broad width, and showing line-shape temperature dependence. Consequently, these four signals should be assigned to the aromatic C−Cl carbons as a result of restricted rotation caused by the $CHCl_2$ groups.[29b]

IR Spectra. The IR spectra of dianion **9** and anion radicals **11** and **15** are similar and quite different from its diradical **10** or quinonoid perchloro-Thiele **16** precursors, respectively. Their similarity with PTM anion salts[7] confirm their anionic nature. However, the principal difference with PTM anions is a strong broad absorption (from ≈1600 up to more than 4000 cm^{-1}, reaching the NIR); this is attributed to a very broad charge-transfer band, called band "A" in the mixed-valence conducting organic compounds, due to the intermolecular electronic charge-transfer excitations.[1a,30]

A special feature of the IR spectrum of anion radical **11** is a noticeable shift to lower energy of its aromatic C=C stretching bands[31] (a tridentate band centered at 1240 cm^{-1}) with regards to those of biradical **10** and dianion **9** (1330 and 1340 cm^{-1}, respectively). This bathochromic shift (about 100 cm^{-1}) is an indication that in the fast IR time scale (10^{-13} s) there is delocalization between the anionic and radical moieties,[32] attributable to π−π interactions between the two PTM units and the acetylenic bridge.

The IR spectra of the other highly chlorinated compounds here reported are normal in the perchloroorganic field, however compounds **4** and **5** present a medium−weak band at 1745 cm^{-1} that could be misinterpreted as a carbonyl impurity. These bands are assigned as combination bands present in highly substituted benzenes[31b] (2,3,5,6-tetrachlorobenzene: 1748; 1,2,3,5-tetrachlorobenzene: 1721; pentachlorobenzene: 1724 cm^{-1}).[31c]

Isotropic ESR Spectra. The ESR spectra of the radicals here isolated (**11, 12,** and **15**) are set out in Table 2. The *g* values and the general features of the ESR spectra are close to those of PTM radicals. The spectra of radicals **11**, **12**, and **15** consist of an unre-

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(29) (a) Ballester, M.; Castañer, J.; Riera, J. *An. Quim.* **1977**, 73, 546. (b) Garcia, R.; Riera, J.; Carilla, J.; Julià, L.; Sánchez-Baeza, F. J.; Molins, E. *Tetrahedron* **1995**, *51* (12), 3627. (c) Nery, H.; Canet, D.; Azoui, B.; Lallcz, L.; Caubère, P. *Org. Magn. Reson.* **1977**, *10*, 240.

(30) Torrance, J. B.; Scott, B. A. *Solid. State Commun.* **1975**, 17, 1369.

(31) (a) The normal location of the aromatic C=C stretching bands in perchloroaromatic compounds is around 1350 cm^{-1}: Ballester, M.; Castañer, J.; Riera, J. *Afinidad* **1978**, *35*, 97. (b) Colthup, N. B.; Daly, L. H.; Wiberley, S. E. *Introduction to Infrared and Raman Spectroscopy*; Academic Press: New York, 1964; p 228−30. (c) Fouchert, C. J. *The Aldrich Library of Infrared Spectra*, 2nd ed., 1975.

(32) A similar effect has been postulated by Miller in the diquinone anion radical field.[5a]

Table 3. Electrochemical Data

system	$E^1_{1/2}$ (V)	$E^2_{1/2}$ (V)	ΔE (kcal/mol[c])
PTM	0.12[a]		
PTM−PTM	−0.58[b]	−0.69[b]	2.4
PTM−C≡C−PTM **11**	0.27[a]	−0.01[a]	6.4
	−0.45[b]	−0.68[b]	5.3
perchloro-Thiele **15**	−0.61[b]	−1.13[b]	12

[a] In THF vs SSCE. [b] In DCB vs ferrocene. [c] Calculated from electrochemical data.

solved single main line due to spin coupling with ^{35}Cl and ^{37}Cl nuclei. Like the perchlorotriphenylmethyl (PTM) monoradicals, these radicals display weak hyperfine lines which arise from spin coupling with the ^{13}C nuclei. They usually consist of three nested line pairs due to the α, the bridgehead, and the *ortho* carbons (aromatic ^{13}C).[9,33]

The ESR spectrum of acetylenic monoradical **12** (Table 2) is very similar to that of PTM radicals, as expected. The most remarkable features of the ESR spectra of acetylenic anion radical **11** and Thiele anion radical **15**, are the values of the ^{13}C hyperfine spin coupling (hsc) which are half of those of monoradical PTM (Table 2). These constants show that on the relevant ESR time scale the odd electron is delocalized over both PTM units.

The ESR spectra at low temperatures do not show any significant changes in the electronic distribution of the anion radicals **11** and **15**, as expected (Table 2). The values of hsc's constants of these *resonant* systems through a π mechanism are very similar to the anion radical systems with *exchange* interaction through a σ path. Therefore, it can be concluded that in **11** and **15** the relevant PTM geometry structure is preserved. This fact recalls the importance of the connecting group in the resulting interactions.

Cyclic Voltammetry. This technique was used to study the redox behavior of the biradical **10**, which were further compared with that of radical PTM.

Cyclic voltammograms for the reduction of biradical **10** in 0.1 M TBAP−THF[36] display two consecutive redox couples, O_1/R_1 and O_2/R_2 (Table 3). These two pairs can be observed in

Figure 3, where a cyclic voltammogram of a 0.5 mM solution of biradical **10** at 0.050 V s^{-1} within the potential interval between 0.5 and −0.4 V is presented. In all scan rates investigated, the peak currents for peaks R_1, R_2, O_1, and O_2 are identical, indicating that the O_1/R_1 and O_2/R_2 couples involve the same number of electrons. All of these processes are diffusion-controlled, since their respective peak currents increase linearly with the square root of the scan rate.[37] For each redox pair, the difference between the anodic and cathodic peak potentials ($E_{p,a} - E_{p,c}$), increases gradually from 90 to 190 mV when the scan rate is increased from 0.01 to 0.2 V s^{-1}, as expected for a one-electron system with a quasireversible behavior.[37] This permits the calculation of its half-cell potential, $E_{1/2} = (E_{p,a} + E_{p,c})/2$, its value being independent of the scan rate tested. All these findings allow us to consider that the O_1/R_1 couple corresponds to the following equilibrium reaction between the biradical **10** and its radical anion **11**:

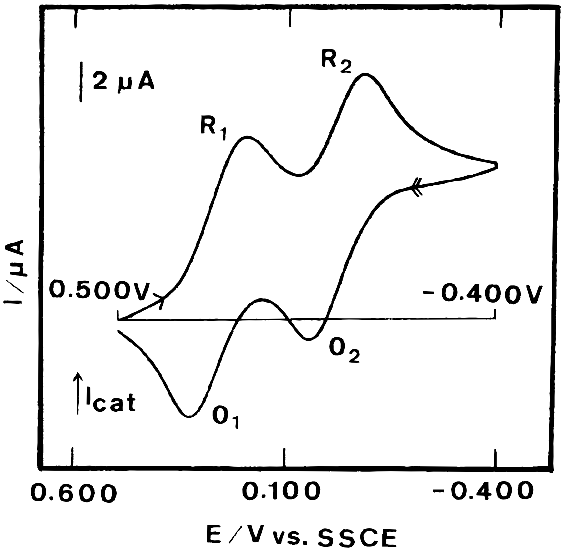

Figure 3. Cyclic voltammogram of a 0.5 mM solution of acetylene diradical **10** at 0.050 V s^{-1} within the potential interval 0.5 and −0.4 V.

$$\underset{\mathbf{10}}{\mathrm{PTM^{\bullet}{-}C{\equiv}C{-}PTM^{\bullet}}} + e^- \rightleftharpoons \underset{\mathbf{11}}{\mathrm{PTM^{\bullet}{-}C{\equiv}C{-}PTM^{-}}}$$

whereas the O_2/R_2 couple is ascribed to the equilibrium reaction between the radical anion **11** and its dianion **9**:

$$\underset{\mathbf{11}}{\mathrm{PTM^{\bullet}{-}C{\equiv}C{-}PTM^{-}}} + e^- \rightleftharpoons \underset{\mathbf{9}}{\mathrm{PTM^{-}{-}C{\equiv}C{-}PTM^{-}}}$$

The presence of the two consecutive O_1/R_1 and O_2/R_2 redox pairs of an equal height is indicative of the strong stability of the biradical **10**, its radical anion **11**, and its dianion **9** in solution. In fact, all these isolated species present identical cyclic voltammograms and do not show any degradation process under our experimental conditions.

The comparison of the half cell potential of PTM radical with that of the first reduction couple of biradical **10** shows that, as expected, biradical **10** with $E_{1/2}(O_1/R_1) = 0.27$ V vs SSCE[38] is more easily reducible than radical PTM with $E_{1/2}(O/R) = 0.12$ V vs SSCE. This can be accounted for by the already postulated higher conjugation of the anion-radical **11**.

The study of the electrochemical data of the PTM−C≡C−PTM (**9**−**11**) system as compared with the PTM−PTM and the perchloro-Thiele (**14**−**16**) systems has been performed with 1 mM of analyte in 0.1 M TBATB−DCB[39] vs ferrocene[40] and is summarized in Table 3.

The first reduction potentials show that the diradical **10** is the easiest to reduce, this being due to the high resonance stabilization of anion radical **11**. The fact

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(33) Ballester, M.; Riera, J.; Castañer, J.; Badía, C.; Monsó, J. M. *J. Am. Chem. Soc.* **1971**, *93*, 2215.

(34) It has been observed that when Me−THF is used as solvent, abnormal ΔH_{pp} values are obtained at room temperature.

(35) Armet, O.; Veciana, J.; Rovira, C.; Riera, J.; Castañer, J.; Molins, E.; Rius, J.; Miravitlles, C.; Olivella, S.; Brichfeus, J. *J. Phys. Chem.* **1987**, *91*, 5608.

(36) Tetrahydrofuran (THF) and tetra-*n*-butylammonium perchlorate (TBAP) analitical grade were used.

(37) Galus, Z. *Fundamentals of Electrochemical Analysis*; Horwood: Chichester, 1976; Chapter 7.

(38) SSCE: A saturated calomelanos electrode with NaCl-saturated aqueous solution.

(39) Tetrabutylammonium tetrafluoroborate (TBATB, Aldrich) was recrystallized three times from water/methanol and dried in vacuo at 70 °C; anhydrous 1,2-dichlorobenzene (DCB, Aldrich) was used as received.

(40) Ferrocene (Aldrich) was sublimed prior use.

that perchloro-Thiele hydrocarbon **16** is even more difficult to reduce than PTM radical or PTM−PTM diradical can be accounted for by the stability of the quinonoid structure, where the addition of a single electron means a reduction of the bond order, although the aromatization of the central ring in **15** partially compensates for this energy difference. Since these redox potentials are close to that of tetracyanoquinodimethane (**TCNQ**, −0.59 vs ferrocene, +0.13 vs SCE[41]), it is concluded that diradical **10** and perchlorotetraphenyl-*p*-xylylene (**16**)[15] can be new acceptors for charge-transfer complexes with tetrathiafulvalene (TTF)-type donors.[42]

The second reduction potentials imply the addition of a second electron into each system, with the anion radical **11** being the easiest to reduce, and the perchloro-Thiele **16** the more difficult. From the difference $E^1_{1/2} - E^2_{1/2}$, the interaction energy can be calculated (Table 3).[43] In the PTM−PTM system, this difference is near to the 100 mV limit,[44] when only a single wave can be detected (localized species, spin-charge exchange);[7] its interaction energy (2.4 kcal/mol) is not zero, since its separation is greater than the limit of 35.7 mV (0.82 kcal/mol) at 20 °C for identical redox centers with purely statistical conditions.[44]

The perchloro-Thiele system (**14**−**16**) shows a high interaction energy (12 kcal/mol) as a result of the strong Coulombic repulsions in the dianion. Consequently, dianion **14**, in contrast with the overwhelmingly majority of the PTM anions and dianions, is highly unstable and during its isolation process, it oxidizes to the more stable perchloro-Thiele anion radical **15**.

Magnetic Susceptibility. The molar magnetic susceptibility data (from 77 K to room temperature) of anion radical **11** and anion radical **15** show that they are magnetically pure; their specific diamagnetic susceptibilities have been calculated with the revised Pascal systematics.[45] They follow the Curie−Weiss law with a thermal behavior corresponding to one radical center ($S = {}^1/_2$) per molecule, and negative Weiss constants (−10 and −4 for **11** and **15**, respectively), accounting for small antiferromagnetic interactions between the radical centers of neighboring molecules.

Conductivity. Conductivity measurements on compressed pellets[46] of acetylene biradical **10**, acetylene dianion **9** and anion radicals **11** and **15** have been performed at 25° C, Ohm's law being obeyed (Table 4). It must pointed out that while the conductivity of biradical **10** falls below the detection limit of the apparatus ($10^{-7}\ \Omega^{-1}\ \mathrm{cm}^{-1}$), those of anion radicals **11** and **15**, as well as dianion **9** are in the semiconductor range. As expected, the conductivity of anion radical **11** is higher (2 powers of 10) than that of dianion **9**; this is due to the mobility (resonance) of the nonbonding electrons in the molecule, and the reduction of the Coulombic forces for the intermolecular charge exchange (see electrochemical and UV−vis data). A related effect has been detected in the conductivity behavior of perchlorotriphenylmethide 18-crown-6 salt;[25] the conductivity of mixtures of this PTM anion and PTM radical shows increasing values, up to a maximum for the 1:1 mixture (Table 4).[25] Anion radical **11** can be considered as an intramolecular 1:1 mixture of PTM radical and PTM anion and must present a conductivity maximum; accordingly, 1:1 mixtures of anion-radical **11** with either diradical **10** or dianion **9** present not increased but decreased conductivities.

Table 4. Conductivities of Compressed Pellets ($\Omega^{-1}\ \mathrm{cm}^{-1}$)

	PTM[a]	PTM−C≡C−PTM		perchloro-Thiele	
radical or diradical	1×10^{-12}	**10**	$< 10^{-7}$ [b]		
anion or dianion	6×10^{-8}	**9**	3×10^{-6}		
anion-radical		**11**	3×10^{-4}	**15**	9×10^{-6}
anion + radical (1:1)	1×10^{-5}				
anion-radical + dianion (1:1)		(**11** + **9**)	4×10^{-5}		
anion-radical + diradical (1:1)		(**11** + **10**)	7×10^{-5}		

[a] See ref 25. [b] The lower detection limit of the apparatus was $10^{-7}\ \Omega^{-1}\ \mathrm{cm}^{-1}$.

The conductivity of perchloro-Thiele anion radical **15** is 2 powers of 10 lower than that of acetylene anion radical **11**, as can be expected from the higher strong repulsions in Thiele dianion **14** when compared with acetylene dianion **9** (see electrochemical and UV−vis data). Surprisingly, the conductivity of the potassium salt of acetylene anion radical **11** is similar to the corresponding TCNQ salt ($\mathrm{TCNQ}^- \mathrm{K}^+$, $\sigma = 10^{-4}\ \Omega^{-1}\ \mathrm{cm}^{-1}$).[47,42]

Conclusions

Traditionally, the high stability of the radical and anionic PTM species, due to steric hindrance, is associated with the steric inhibition of resonance. Consequently, as we have shown, small changes in the architecture of a molecule can convert a localized structure into a delocalized one, while preserving its inherent stability. Since there is a great interest in the design of electronic materials based on molecular properties,[48] this is an important concept for new perchloromaterials. Thus, the acetylene bridge, in contrast with other spacers, can modulate the degree of resonance interaction depending on the redox state of the substituents ("resonant switch").

The isolated, very stable (up to 280 °C), acetylene anion radical **11**, is not a compound with a "*spin charge exchange*" but one with a significative resonance interaction (≈18 kcal/mol), in contrast with the previously reported parent systems. We attribute this fact to the spin-charge delocalization detected on both ESR, IR, cyclic voltammetry, and UV−vis time scales and also by Hush's analysis of its intervalence absorption. Consequently, it is concluded that anion radical salt **11**, can be classified as a class III mixed-valence compound.[13]

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(41) Acker, D. S.; Hertler, W. R. *J. Am. Chem. Soc.* **1962**, *84*, 3370.

(42) (a) Saito, G.; Ferraris, J. P. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2141. (b) Torrance, J. B. *Acc. Chem. Res.* **1979**, *12*, 79.

(43) The difference in potentials does not show a good correlation with the differences in energy from the more bathochromic bands of the UV−vis spectrum of the charged species. However, when the difference between the diradical or neutral species and the anion radical ones is considered, a good correlation is found.

(44) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley: New York, 1980; p 234.

(45) (a) Hellwege, K.; Hellwege, A. *Landolt-Bornstein II. Diamagnetic Susceptibility*; Springer-Verlag: Berlin, 1977; Vol. 16, p 1. (b) Foex, G.; Gorter, C. J.; Smith, L. J. *Constants Selectioneés. Diamagnetisme et Paramagnetisme, Relaxation Paramagnetique*; Masson et Cie., Paris, 1957; p 222. (c) Chlorine specific diamagnetic susceptibility contribution adjusted for perchlorocompounds:[9c] 18.14×10^{-6}.

(46) Wieder, H. H. *Laboratory Notes on Electrical Galvanometric Measurements, Materials Science Monographs*; Elsevier: Amsterdam, 1979; Vol. 2.

(47) Perlstein, J. H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 519.

(48) Carter, F. L. *Molecular Electronic Devices*; Marcel-Dekker: New York, 1982.

While Hush's theory gives good results in the inorganic field, many discrepant results have been found when this is applied to the organic mixed-valence class II compounds.[5e,f] In the case of the stable organic mixed-valence class III compounds **11** and **15**, one of the most exciting results has been the good correlation between the direct experimental UV−vis determination of the resonance energy ($H_{AB} \approx 17.5$ and ≈ 10 kcal/mol, respectively) with the theoretical values calculated from Hush's theory applied to the unusual NIR bands (764 nm, $H_{AB} = 18.8$ kcal/mol and 1342 nm, 10.6 kcal/mol, respectively).

With the synthesis and the physical study of the two first examples of mixed-valence class III perchlorotriphenylmethyl anion radicals with high thermal stability, we have shown their uses as models for polymers with novel optical,[8,50] electrical,[49] and magnetic[12,49] properties. Although the severe steric hindrance of these compounds is known, an intermolecular "spin-charge exchange" mechanism takes place, being the electrochemical and electrical properties of these anion radicals very similar to TCNQ. The differences between the properties of the two anion radicals suggest the importance of synthesizing a new family of ion radicals from their stable diradical precursors instead of neutral and diamagnetic molecules. Diradical **10** and perchloro-Thiele hydrocarbon **16** can be new acceptors for charge-transfer complexes. At the moment, some of the possible applications for anion radicals, that can be envisaged, include "smart windows" [8] and NIR absorbers.[50]

Experimental Section

General Methods. Perkin-Elmer 682, Perkin-Elmer Lambda Array 3840, Perkin-Elmer Lambda 9, Varian E11E, and Varian Unity 300 (working at 300 MHz for ^1H, 75 MHz for ^{13}C), spectrometers were used for IR, UV−vis, UV−vis-NIR, ESR, and NMR spectroscopy, respectively. The magnetic susceptibilities were measured with a Varian 4 in magnet with constant-force caps operating at 8 kOe, and a Cahn RG electrobalance. The osmometric measurements were performed with a V. P. Knauer Model 7311 osmometer using benzyl in $CHCl_3$ (45 °C) as calibrating standard. The thermogravimetric analyses were carried out with a Perkin-Elmer TG-2 system, under N_2 (40 cm^3 min^{-1}). The conductivity measurements were performed by the Van der Pauw method[46] with a 0−900 V electrical source (sensitivity 10^{-7} Ω^{-1} cm^{-1}); the measurements were carried out on powdered samples, compressed into pellets under pressures exceeding 4×10^7 Pa. The workup of the radicals was performed in the dark. Since the location of the IR peaks of the highly chlorinated compounds differs markedly from their nonchlorinated counterparts, they are included in this section for identification purposes, although weak peaks in the 1300−400 cm^{-1} region are not given.

***4H*-Heptachlorotoluene (3).** It was prepared in two steps using the new trifluoromethylating method of Castañer et al.,[20] starting from 1,2,4,5-tetrachlorobenzene **(1)**. **3** was identified by its mp and IR and ^1H NMR spectra.[20]

***trans*- (4) and *cis*-Decachlorostilbene (5).** *(a) With Fe(CO)₅.* $Fe(CO)_5$ (8 mL) was added slowly over a refluxing solution of 4*H*-heptachlorotoluene (**3**; 10.05 g) in anhydrous benzene (200 mL), and the refluxing was continued (1 h) under argon. The cooled reaction mixture was treated with I_2 (to destroy the $Fe(CO)_5$ in excess) and filtered.

The collected solid was extracted with refluxing $CHCl_3$ and, after crystallization (hexane), yielded trans isomer **4** (5.057 g). The benzene filtrate was evaporated to dryness, and the residue was chromatographed over silica gel and recrystallized (hexane) to give cis isomer **5** (1.694 g) and trans isomer **4** (0.279 g). Both compounds were identified by its mp[51] and IR and NMR spectra.[52] **Isomer 4**: IR (KBr) 3100 (w), 3060 (w), 1745 (w), 1550 (m), 1415 (w), 1392 (s), 1225 (s), 1165 (s), 1112 (s), 960 (m), 865 (m), 825 (m), 702 (s), 580 (m), 555 (m), 480 (s) cm^{-1}. ^1H NMR ($CDCl_3$) δ, 7.71 (s, Ar−H). ^{13}C NMR ($CDCl_3$) δ, 136.1, 132.6, 132.1, 132.0, 128.6.

Isomer 5: IR (KBr) 3100 (w), 3060 (w), 1745 (w), 1616 (m), 1545 (m), 1390 (s), 1380 (s), 1350 (w), 1320 (w), 1235 (m), 1217 (m), 1182 (m), 1165 (s), 1155 (m), 1110 (s), 940 (m) 865 (s), 695 (s), 635 (s), 580 (m), 560 (m), 537 (m), 525 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ, 7.72 (s,m Ar−H). The overall yields were trans isomer **4**, 67.5%; cis isomer **5**, 21.4%.

(b) With Ferrous Oxalate. A stirred mixture of 4*H*-heptachlorotoluene (**3**; 7.020 g), ferrous oxalate (7.35 g) and DMF (110 mL) was refluxed for 1 h. The reaction mixture became dark (15 min) and slowly changed to orange.

After cooling the mixture was poured over diluted H_2SO_4. The resulting solid was filtered, washed with water, dried, and submitted to the same purification−separation process as before yielding trans isomer **4** (3.126 g; 56.6%) and cis isomer **5** (1.716 g; 31.5%). Both compounds were identified by their mp[51] and IR and ^1H NMR spectra.[52]

***trans*-Decachloro-4,4′-bis(dichloromethyl)stilbene (6).** A mixture of *trans*-4*H*,4′*H*-decachlorostilbene (**4**; 4.350 g), anhydrous $AlCl_3$ (8.0 g) and $CHCl_3$ (200 mL) was refluxed for 48 h; the reaction mixture darkens very slowly.

After cooling, the reaction mixture was treated with water (until decolorization) to eliminate the $AlCl_3$, dried, and evaporated. The resulting solid was purified through silica gel (hexane) and crystallized (same solvent) to give trans isomer **6** (3.245 g; 56.7%), colorless crystals mp 283−5 °C; IR (KBr) 3030 (w), 1355 (s), 1275 (s), 1225 (m), 1150 (s), 880 (m), 818 (m), 770 (s), 716 (s), 697 (s), 650 (m), 620 (m), 492 (m) cm^{-1}. ^1H NMR ($CDCl_3$, 60 °C) δ 7.64 (s, $CHCl_2$). ^{13}C NMR ($CDCl_3$, 60 °C) δ, 66.26, 128.32, 130.51 (b),[53] 132.48 (b), 134.41 (b), 134.95 (b), 136.31, 137.39. Anal. Calcd for $C_{16}H_2Cl_{14}$: C, 27.8; H, 0.3; Cl, 71.9. Found; C, 27.7; H, 0.3; Cl, 72.2%.

***cis*-Decachloro-4,4′-bis(dichloromethyl)stilbene (7).** The preceding reaction was repeated with *cis*-4*H*,4′*H*-decachlorostibene (**5**; 5.740 g), $AlCl_3$ (13.5 g) and $CHCl_3$ (350 mL) yielding cis isomer **7** (6.212 g; 82.2%); colorless crystals mp 181−3 °C; IR (KBr) 3040 (w), 1618 (w), 1350 (s), 1270 (s), 1250 (m), 1230 (m), 1160 (m), 1146 (s), 1055 (m), 878 (m), 830 (m), 770 (s), 760 (m), 728 (m), 716 (s), 693 (s), 650 (m), 633 (m), 602 (m), 568 (m), 540 (m), 502 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ, 7.61 ($CHCl_2$). Anal. Calcd for $C_{16}H_2Cl_{14}$: C, 27.8; H, 0.3; Cl, 71.9. Found: C, 28.0; H, 0.3; Cl, 71.8%.

***trans*-α*H*,α′*H*-Triacontachloro-4,4′-vinylenebis(triphenylmethane) (8).** *(a) From trans-Decachloro-4,4′-bis(dichloromethyl)stilbene (**6**).* A mixture of **6** (3.000 g; 4.34 mmol), pentachlorobenzene (5.22 g; 20.8 mmol), and anhydrous $AlCl_3$ (2.78 g; 20.8 mmol) was heated at 170 °C for 24 h in a pressure vessel.

The resulting dark-violet solid was treated with water−CCl_4 until decolorization. The solid formed was filtered, washed with water, dried, and purified through silica gel (CCl_4) in a Soxhlet extracting apparatus to give trans isomer **8** (6.352 g; 94.5%), white powder mp 450−5 °C (dec) (DSC);[18a] IR (KBr) 2920 (w), 1530 (w), 1370 (s), 1330 (s), 1310 (m), 1297 (s), 1150 (s), 820 (m), 803 (s), 706 (s), 680 (m), 647 (m), 530 (m), 490

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(53) The ^{13}C NMR spectra recorded from room temperature to 60 °C show a dynamic effect in the 134.95, 134.41, 132.48, and 130.51 ppm resonance bands. Taking into account their shift, number, low intensity (due to the chlorine quadrupolar moment, the relaxation mechanism of the carbon atoms attached to chlorine is less effective than in the case of the quaternary carbons attached to carbons), broad width, and temperature dependence, the assignment to aromatic C−Cl can be made.

(m) cm^{-1}. UV (cyclohexane) λ, 223, 238, 296, 307 nm (ϵ, 179 000, 137 900, 3770, 4050). ^{1}H NMR ($CDCl_3$, 60 °C) δ, 7.08, 7.04. ^{13}C NMR, not recorded due to its extremely poor solubility. Anal. Calcd for $C_{40}H_2Cl_{30}$: C, 31.1; H, 0.1; Cl, 68.8. Found: C, 31.3; H, 0.3; Cl, 68.7%.

*(b) From cis-Decachloro-4,4′-bis(dichloromethyl)stilbene (**7**).* The preceding reaction was repeated with **7** (8.60 g); pentachlorobenzene (16.0 g) and anhydrous $AlCl_3$ (8.5 g), yielding trans isomer **8** (18.455 g; 95.8%), identified by mp and IR and ^{1}H NMR spectra.

Perchloro-4,4′-ethynylenebis(triphenylmethyl) diradical (10). TBAOH (40% in water, 150 mL) was added to a suspension of *trans*-α*H*,α′*H*-triacontachloro-4,4′-vinylenebis(triphenylmethane) (**8**, 15.00 g) in THF (500 mL), and the resulting mixture was stirred in the dark at room temperature and under argon. The reaction was monitored by UV−vis spectroscopy until disappearance of the intermediate tetrabutylammonium perchloro-4,4′-vinylenebis(triphenylmethide) salt was observed (2 weeks).[54] The resulting dark blue solution was poured into hexane/water (1:1, 1 L), and the precipitate formed was filtered and dried. The isolated dark blue solid, without purification, was dissolved in THF (500 mL) and I_2 (2.5 g) was added with stirring (4 h).

The resulting brown suspension was poured into water (500 mL) and the precipitate formed was filtered, washed with water and with acetone, and dried, yielding a dark green solid (12.3 g). This was purified through silicagel (CCl_4) and digested with refluxing ethyl ether to give acetylene diradical **10** (10.50 g, 70%)[55] identified by mp and IR, ESR, and UV−vis spectra.[18] Osmometry ($CHCl_3$, 45 °C), M_n found 1423, calcd for $C_{40}Cl_{28}$ 1472.

Perchloro-4,4′-ethynylenebis(triphenylmethide) Potassium 18-Crown-6 Salt (9). An excess of potassium metal was added to a solution of acetylene biradical **10** (0.109 g, 0.074 mmol) and 18-crown-6 (0.043 g, 0.16 mmol) in THF (50 mL), and the mixture was stirred for 5 h. The excess of potassium was removed, and the solution was filtered. Ethyl ether was added to the filtrate and the resulting precipitate was centrifuged. The bluish-black precipitate was washed with ether and dried affording a microcrystalline solid[55] characterized as the potassium 18-crown-6 salt **9** (0.130 g, 84%), mp >250 °C (dec); IR (KBr) >4000−1600 (b, m), 2880 (m), 2120 (m), 1535 (m), 1500 (s), 1460 (m), 1415 (s), 1340 (s), 1090 (s), 945 (s), 820 (m), 710 (m), 685 (s), 640 (m), 630 (m), 600 (s) cm^{-1}; UV−vis (THF) λ, 305 (sh), 339 (sh), 517, 665 nm (ϵ 19 500, 11 600, 41 400, 103 200); conductivity, $\sigma_{rt} = 3 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$. Anal. Calcd for $C_{64}H_{18}O_{12}K_2Cl_{28}$: C, 36.9; H, 2.3; Cl, 47.7. Found: C, 36.8; H, 2.3; Cl, 47.5%.

Perchloro-4,4′-ethynylenebis(triphenylmethyl) Anion Radical Potassium 18-Crown-6 Salt (11). Equimolecular amounts of biradical **10** (0.291 g, 0.19 mmol) and dianion **9** (0.432 g, 0.2 mmol) were dissolved in THF (50 mL) with stirring (4 h). The resulting greenish-gray solution was poured into ethyl ether (50 mL) and the resulting precipitate formed was centrifuged. The collected precipitate was dried affording a microcrystalline dark gray (almost black) powder[55] characterized as anion radical **11** (0.702 g, 93%), mp >250 °C (dec), 280 °C (dec) (TGA); IR (KBr) 4000−1600 (b, s), 2120 (m), 1520 (m), 1500 (m), 1470 (s), 1420 (s), 1290 (s), 1240 (s), 1200 (m), 1095 (s), 1035 (m), 949 (s), 845 (s), 730 (m), 690 (s), 640 (m) cm^{-1}; UV−vis (THF) λ 222, 369, 450, 754 nm (ϵ, 137 200, 17 590, 20 500, 83 900). ESR (see Table 2) magnetic susceptibility, (77−300 K, 11 kOe), the diamagnetic contribution of the sample was estimated using the Pascal systematics;[45] Weiss constant, −10 K; μ_{eff}, 1.73; spins/mol, 6.24×10^{23}; purity, 100%. Conductivity, σ_{rt}, $3.25 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$. Anal. Calcd for $C_{52}H_{24}KO_6Cl_{28}$: C, 35.1; H, 1.3; Cl, 55,9. Found: C, 35.1; H, 1.3; Cl, 55.7%.

Octacosachloro-4-(α*H*-triphenylmethan-4-ylethynyl)-triphenylmethyl Radical (12). A THF (50 mL) solution of anion radical **11** (0.250 g) was acidified with diluted aqueous HCl. The resulting green solution was evaporated and the product obtained was purified through silica gel ($CHCl_3$) yielding a solid, which after digestion with refluxing ethyl ether gave a green product characterized as monoradical **13** (0.186 g, 90%), mp >250 °C (dec); IR (KBr) 1500 (w), 1420 (w), 1330 (s), 1320 (s), 1290 (s), 1250 (m), 800 (m), 700 (s), 670 (m), 650 (m), 640 (m) cm^{-1}; UV−vis (THF) λ, 307, 320, 347, 385, 439, 634 nm (ϵ 22 900, 27 100, 23 000, 20 500, 18 300, 13 800). ESR: see Table 2. Magnetic susceptibility (300 K, 11 kOe), the diamagnetic contribution of the sample was estimated using the Pascal systematics;[45] μ_{eff}, 1.66; spins/mol, 5.6×10^{23}; purity, 92%. Conductivity, $\sigma_{rt} < 10^{-7}\ \Omega^{-1}\ cm^{-1}$. Anal. Calcd for $C_{40}HCl_{28}$: C, 32.6; H, 0.1; Cl, 67.4. Found: C, 32.7; H, 0.1; Cl, 67.3%

Perchloro-α,α,α′,α′-tetraphenyl-*p*-xylylene Anion Radical Tetrabutylammonium Salt (15). A mixture of α*H*,α′*H*-tetraicosachloro-α,α,α′,α′-tetraphenyl-*p*-xylene[15] (**13**, 0.500 g), 40% aqueous TBAOH (15 mL), and THF (500 mL) was stirred for 30 h.

The resulting violet solution of the dianion **14** (UV−vis monitoring, λ 567 nm, ϵ 58 000) was treated with hexane/water (1:1, 400 mL), and the resulting suspension was centrifuged. The dark compound collected was dried affording a microcrystalline solid[55] which was characterized as anion radical **15** (0.430 g; 73%), mp 340 °C (dec); IR (KBr) >4000−1600 (b, m), 2960 (m), 2880 (m), 1505 (s), 1330 (s), 1210 (m), 1100 (s), 985 (s), 850 (s), 805 (s), 730 (s), 710 (m), 660 (s), 620 (m), 610 (m), 530 (m), 500 (m) cm^{-1}; UV−vis (THF) λ 326, 437, 635 nm (ϵ 7170, 16 000, 45 800); ESR, see Table 2; magnetic susceptibility, (77−300 K, 11 kOe), the diamagnetic contribution of the sample was estimated using the Pascal systematics;[45] Weiss constant, −2.0 K; μ_{eff}, 1.72; spins/mol, 5.92×10^{23}; purity, 98.2%. Conductivity, σ_{rt}, $9.0 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$. Anal. Calcd for $C_{48}H_{36}Cl_{24}N$: C, 39.0; H, 2.4; N, 0.9; Cl, 57.6. Found: C, 39.2; H, 2.5; N, 1.0; Cl, 57.4%.

Cyclic Voltammetry. The cyclic voltammetry experiments were carried out in a three-electrode cell under an Ar atmosphere. A Pt sphere with an area of 0.093 cm^2 was used as the working electrode and a Pt wire as the counter electrode. The reference electrode was a SSCE[38] connected to the cell through a salt bridge containing a 0.1 M TBAP−THF solution.[36] The temperature of the test solutions and the SSCE was maintained at 25 ± 0.1 °C. Cyclic voltammetry measurements were performed with standard equipment consisting of a PAR 175 universal programmer, an Amel 551 potentiostat, and a Phillips 8043 *X*−*Y* recorder. 0.5 mM solutions of diradical **10**, dianion **9** an anion-radical **11** and 1.0 mM of radical PTM in THF with 0.1 M TBAP as background electrolyte were studied. All the voltammograms were recorded in the scan rate range 0.01−0.2 V s^{-1}.

The comparative studies using ferrocene as standard were performed in a single-compartment cell with a Pt disk working electrode and a Pt wire counter electrode using a Bioanalitical Systems 100A electrochemical workstation in an inert atmosphere drybox. An Ag wire in a solution of 0.01 M $AgNO_3$ and 0.09 M tetrabutylammonium hexafluorophosphate served as reference electrode. Solutions consisted of approximately 1 mmol of analyte in 1,2-dichlorobenzene with 0.1 M TBATB;[39] the experiments were performed in the presence of 0.5 mmol of ferrocene[40] added as internal standard.

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(54) Until completion of the dechlorination process.

(55) Unfortunately, no crystals suitable for X-ray studies could be obtained.