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Syntheses and Spectra of Some Inert Triphenylmethyl Diradicals. A Concurrent Diradical Form

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Abstract: The synthesis and characterization of 11 inert diradicals of the perchlorotriphenylmethyl class, (p)R-$C_6Cl_4(C_6Cl_5)\dot{C}$-C_6Cl_4-Sp-C_6Cl_4-$\dot{C}(C_6Cl_5)$-C_6Cl_4-R(p), where R is Cl, OH, or O^- and Sp is a spacer chain from zero to nine atom links, are described. The ESR spectra of these species in solution from room temperature to −140 °C (glassy matrix) point to the concurrence of two isomeric diradical forms: the conventional species, displaying spin–spin dipolar interaction, and a form *apparently devoid* of it. The ESR ^{13}C hyperfine couplings, the magnetic susceptibility, and the IR and UV–vis spectra of these diradicals are described. Some related monoradicals and a triradical are also reported.

Introduction

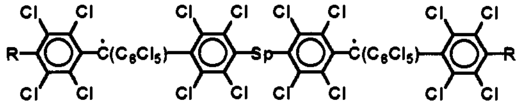
It is known[1] that some radicals and diradicals that are short-lived and very reactive become *stable* and *even chemically inert* when perchlorinated, *i.e.*, when all their hydrogens are substituted by chlorines. For example, while the half-lives of the triphenylmethyl radicals in aerated solution may be as low as a fraction of a second, those of their perchlorinated counterparts, the so-called *inert free radicals*,[1b,e,2,3] are of *the order of 100 years*. Therefore, perchlorination often allows (1) easy handling, (2) excellent yields and high purity because of blocking and/or shielding of the potential reaction sites by the chlorine atoms, (3) new phenomena that could be observed with difficulty in conventional organic chemistry,[1e] and (4) simplified ESR spectra. For example, perchlorotriphenylmethyl radical (PTM$^\bullet$) displays just one line compared with about 100 for its unsubstituted counterpart.

The study of relatively stable diradicals have so far been hampered by the presence of substantial proportions of byproducts and contaminants (monoradicals, oligomers, quinonoid compounds, and hydrogen abstraction, oxidation, disproportionation, and degradation products). Consequently, in spite of the theoretical advances in this field, rather meager and ambiguous experimental data, accompanied by risky, unconvincing conclusions, often painfully achieved, abound in the chemical literature.

Therefore, it was regarded as both promising and significant to undertake the synthesis and study of the perchlorinated versions of some symmetrical perchlorobistriphenylmethyl diradicals related to bis(diphenylmethyl)-4,4′-biphenyl, the Chichibabin hydrocarbon,[4] varying the nature of the link between their two moieties by inserting different spacer chains (Sp) in their central position.

Results and Discussion

Perchloro Diradicals. The diradicals studied are shown below.



(1; R-$\dot{\rm P}$TM-Sp-PT$\dot{\rm M}$-R)

R = Cl, HO, O^-

Sp = none, CH_2-CH_2, C≡C, CCl=CCl(trans), CO-O-CO, CO-O-CH_2-CH_2-O-CO, CO-O-CH_2-CH_2-O-CH_2-CH_2-O-CO, CO-O-CH_2-CH(OH)-CH_2-O-CO, CO-O-CH_2(CH_2OH)-CH_2-O-CO

They have been synthesized according to the six methods (a–f) outlined in Scheme 1. Except for diradical $^-$O-$\dot{\rm P}$TM-PT$\dot{\rm M}$-O$^-$, they have been isolated as highly pure solids and identified or characterized by elemental analyses, UV–vis and IR spectra, and, in some cases, magnetic susceptibility measurements (number of spins per mole). Their purity has also been checked by analytical thin-layer chromatography (TLC).

Except for HO-$\dot{\rm P}$TM-PT$\dot{\rm M}$-OH and $^-$O-$\dot{\rm P}$TM-PT$\dot{\rm M}$-O$^-$, which oxidize readily (as do their monoradical counterparts) $(C_6Cl_5)_2\dot{C}$-C_6Cl_4-OH(p) (HO-PTM$^\bullet$) and $(C_6Cl_5)_2\dot{C}$-C_6Cl_4-O^-(p) ($^\bullet$PTM-O^-),[5] the diradicals described here are extremely unreactive, with unmeasurably large half-lives in solution in air.[1e] Nevertheless, as are the perchlorotriphenylmethyl monoradicals,[6,7] they are active in single electron transfer (SET) processes such as, for example, the reaction between their dianions and their dication counterparts giving the corresponding radical ions.[8]

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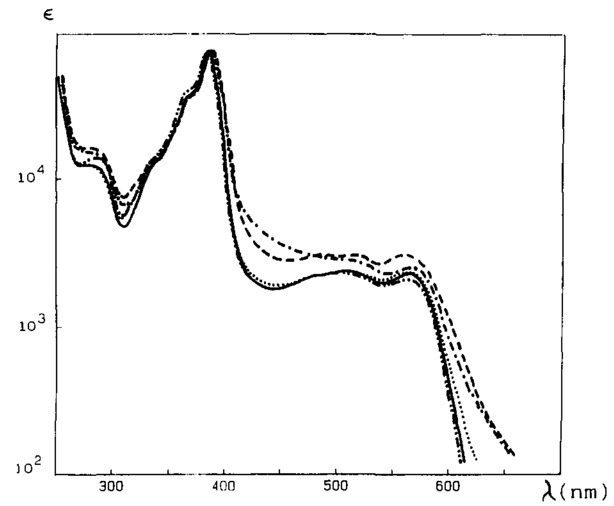
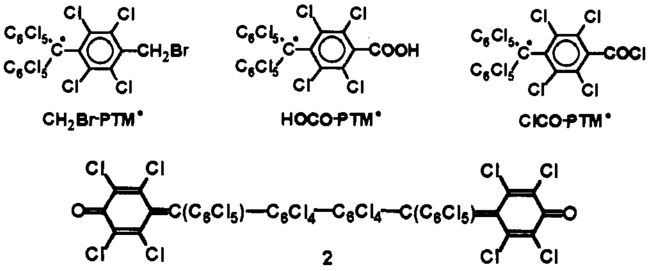


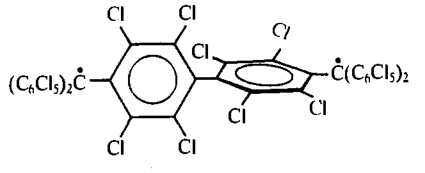
Figure 1. Uv-vis spectra of PTM• (2ε) (—); •PTM-PTM• (- - -); •PTM-CH_2CH_2-PTM• (···); •PTM-CCl=CCl-PTM•(*trans*) (-·-); and •PTM-$COOCH_2CH_2OCO$-PTM• (-···-).

Scheme 1. (a) Oxidation of the corresponding dicarbanion with I_2: **1** (R = Cl). (b) Chlorine addition to an alkyne diradical with Cl_2/I_2: **1** (R = Cl, Sp = CCl=CCl). (c) Reductive self-condensation of a *p*-(bromomethyl)-substituted monoradical (CH_2Br–PTM) with Sn^{2+}: **1** (R = Cl, Sp = CH_2CH_2). (d) Formation of an anhydride linkage between two *p*-acyl-substituted monoradicals (ClCO–PTM• and HOCO–PTM•): **1** (R = Cl, Sp = CO(O)CO). (e) Bis-acylation of ethylene glycol, diethylene glycol, or glycerol with ClCO–PTM•: **1** (R = Cl, Sp = CO(O)R′(O)CO). (f) One-electron reduction of *p*-quinodimethane **2** with HO^- or with HI/I_2: **1** (R = HO, O^-, Sp = none)



UV-Vis Spectra of the Diradicals. The UV-vis spectra of these *red* perchloro diradicals are virtually identical, both in wavelengths (λ) and absorptivities (ε/2), to those of perchlorotriphenylmethyl monoradicals, as shown in Figure 1, which includes the UV-vis spectra of PTM• (($(C_6Cl_5)_3C^•$), •PTM-PTM•, •PTM-CH_2CH_2-PTM•, •PTM-CCl=CCl-PTM•(*trans*), and (•PTM-$COOCH_2CH_2)_2O$ (Scheme 1). This means that the absorptive monoradical centers are nearly noninteractive electronically.[2,8,9] Bands at 380 and 510–560 nm, the so-called "radical bands", absent in structurally related nonradical species, originate from electronic transitions involving singly-occupied molecular orbitals.[2,9] The similarity between spectra of the various diradicals is due to the two π-systems corresponding to their two molecular moieties being electronically noninteracting. This, in turn, originates from two main causes.

(1) Steric inhibition of π-electron resonance between the two triphenylmethyl moieties. Although the two biphenyl benzene rings of Chichibabin hydrocarbon are coplanar,[4] in perchlorobiphenyl, C_6Cl_5-C_6Cl_5 (Figure 2), the four bulky chlorines in the ortho positions directed together about the central bond would cause a colossal strain in the all-planar conformation and therefore force the rings to become nearly perpendicular. This has been shown by X-ray analysis.[10] Therefore, the pertinent π-electron systems are orthogonal, and hence noninteracting, the ultraviolet spectrum being indistinguishable from that of an unconjugated perchlorobenzene.[1e] The virtually total steric inhibition of resonance, observed in other perchlorinated biphenyl derivatives as well, accounts therefore for the spectral similarity in biphenyl diradicals •PTM-PTM• and HO-$\dot{P}$TM-PT$\dot{M}$-OH.



•PTM-PTM•

Figure 2. "Perpendicular" •PTM-PTM•.

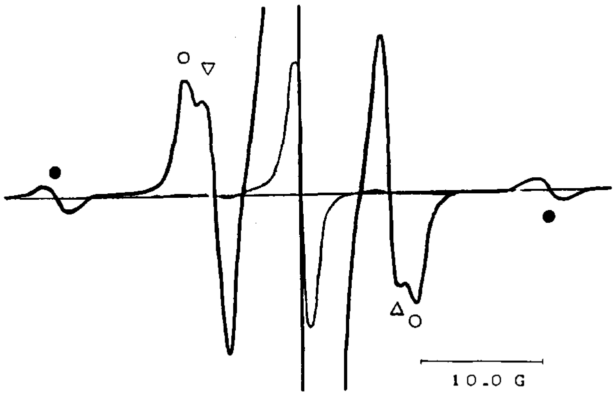


Figure 3. ESR spectrum of the monoradical $(C_6Cl_5)_2\dot{C}$-C_6Cl_4-$COOCH_2$-CH_2OH in CCl_4 at room temperature. ^{13}C line pairs: α, ●; bridgehead, ○; ortho, ▽.

Perchloro-*trans*-stilbene does not display in the ultraviolet any significant conjugation, either, because of steric repulsions among the two ethylene chlorines and the four ortho chlorines.[11] By the same token, the two monoradical centers of stilbene diradical •PTM-CCl=CCl-PTM• (*trans*) absorb independently.

In this connection, diradical •PTM-C≡C-PTM• behaves differently. Because the physical separation between its two pairs of ortho chlorines is significantly larger than that in •PTM-PTM•, there are no significant steric repulsions and consequently no appreciable steric inhibition of resonance. Consequently, this is a *green* radical, its two radical absorption bands being much shifted bathochromically by electron delocalization (λ 435–460 and 637 nm).

(2) Electronic isolation of the two triphenylmethyl π-systems because of the σ-bonds of spacer Sp. That molar absorptivities for each absorption band, ϵ_{max}(380 nm) and ϵ_{max}(510–560 nm), for each of the diradicals described here have nearly the same value (Figure 1) indicates that no significant proportion of monoradical (ε/2) or other impurities is present.

In a synthesis parallel to that leading to the diradicals •PTM-$COOCH_2CH$(OCO-PTM•)CH_2OH and (•PTM-$COOCH_2)_2$-CHOH, triradical (•PTM-$COOCH_2)_2$CHOCO-PTM• is formed. Its UV-vis absorptivities also correspond to three perchlorotriphenylmethyl structural units (ϵ_{max}(380 nm) = 97 000 ≈ 3 × ϵ_{max}(PTM•)).

ESR Spectra of PTM Diradicals.[2,7,12-14] In solution at room temperature, the ESR spectra of the diradicals are nearly coincident with those of closely related perchlorotriphenylmethyl

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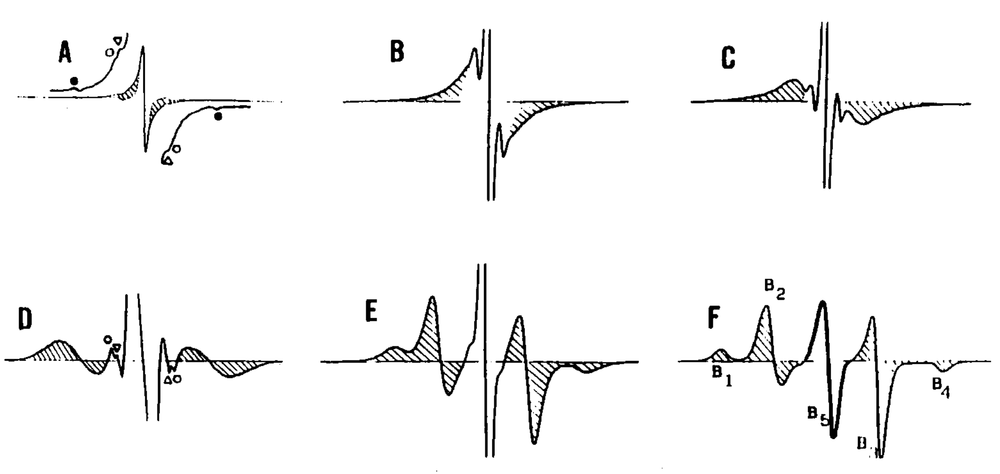

Figure 4. ESR spectra in 2MeTHF. Diradical •PTM-PTM•: (A) 25 °C; (B) -50 °C; (C) -70 °C; (D) -90 °C; (E) -110 °C; and (F) -140 °C. ^{13}C line pairs: α, ●; bridgehead, ○; ortho, ▽.

(PTM) monoradicals, consisting of a moderately broad line ($\approx$0.13 mT) (Figure 4A). Unresolved lines, due to spin couplings (Fermi interaction[15a]) with ^{35}Cl and ^{37}Cl nuclei, are significant contributors to line width. In addition, particularly in CCl_4, dioxane, THF, or 2MeTHF, the broad line displays abnormally intense tails ("*thick wings*") (Figure 4A), not observed for the perchlorotriphenylmethyl monoradicals. The tails are significantly narrower in C_2Cl_4, thus permitting precise ^{13}C hyperfine coupling (hc) measurements (see point b, below).

The "triplet" half-field transition ($\Delta M = 2$) has been detected in the (•PTM-$COOCH_2CH_2$)$_2$O diradical. This "forbidden" transition was not observed in the rest of the diradicals, although the measurements were performed under the same conditions and settings.

(a) **Dipole–Dipole Interaction.** The ESR spectra of the seven diradicals in 2-methyltetrahydrofuran (2MeTHF) were measured at temperatures ranging from 25 °C to -140 °C (glassy matrix). The sequence in Figure 4A–F shows the dramatic effect of temperature on the spectrum of the •PTM-PTM• diradical: as the temperature diminishes, extensive expansion and reshaping of the line tails take place, while two intense, nested line pairs (hatched areas) emerge. The final spectrum (Figure 4F) is reached when the solvent becomes a glass. The other diradicals display similar behavior.

This effect is due to diradical anisotropy. The latter is averaged and vanishes when the rate of diradical tumbling in the solvent is high. Consequently, at moderate (room) and higher temperatures just one line is observed. The anisotropy is the direct result of the magnetic dipolar interaction between the two unpaired electrons. This interaction, which splits the spin energy levels and their observed spin transitions, is given by the zero-field splitting energy parameters *D* and *E*.

In a glassy matrix, the diradicals are randomly oriented. A detailed analysis of such systems has been made by Wasserman *et al.*,[16,17] who have shown that the ESR spectrum consists then of *three* line pairs.[15b] However, as already mentioned, the diradicals reported here display *two* line pairs instead (Figure 4F), indicating that $E = 0$, *i.e.*, they behave as axially symmetric species.

The magnetic field difference (line pair separation), $\mathbf{B}_4 - \mathbf{B}_1$, is twice $\mathbf{B}_3 - \mathbf{B}_2$ (Figure 5, Table 2), as predicted by theory. From $\mathbf{B}_4 - \mathbf{B}_1$ or $\mathbf{B}_3 - \mathbf{B}_2$, the parameter *D* has been calculated, and, from it, the distance R_0 between the two centers of spin density is obtained.[16,17] Table 2 reports the pertinent data, including the values of R_0 and the mathematical expression employed. For •PTM-PTM• (Figure 4F), R_0, calculated from *D*,[16] is 8.3 Å, close to the distance calculated from angles and bond lengths between its two α trivalent carbons (10 Å), where most of the spin density resides. Accordingly, for •PTM-C≡C-PTM•, •PTM-CH_2CH_2-PTM•, (•PTM-CO)$_2$O (Figure 5), •PTM-CCl=CCl-PTM•(*trans*), and (•PTM-$COOCH_2$)$_2$, R_0 is somewhat longer (Table 2). It is remarkable that R_0 for diradical (•PTM-$COOCH_2CH_2$)$_2$O (8.1 Å) is nearly equal to that for •PTM-PTM• (8.3 Å), in spite of the spacer Sp being a 10-σ-bond chain. This suggests that Sp adopts here a coiled structure (if uncoiled, the distance would be about 18 Å). The $g_\parallel$ and $g_\perp$ (Landé factors) have also been calculated as usual (Table 2).[16,17] Note that for the diradicals (•PTM-$COOCH_2$)$_2$ and (•PTM-$COOCH_2CH_2$)$_2$O, those *g*-values are virtually coincident. No samples of the diradical diphenol and the diradical diphenoxide were available for glassy matrix measurements.

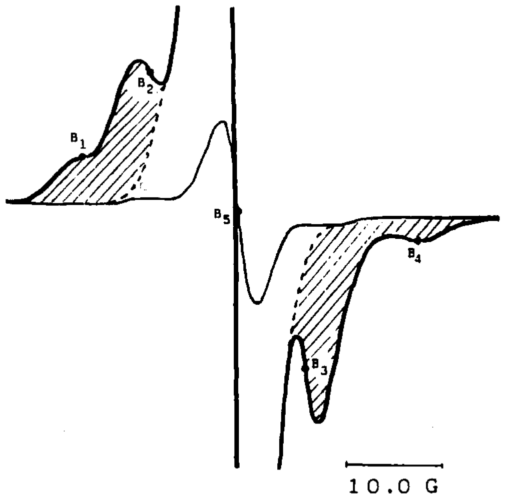

Figure 5. ESR spectrum of diradical ($(C_6Cl_5)_2\dot{C}\text{-}C_6Cl_4\text{-}CO)_2O$ ((•PTM-CO)$_2$O) in 2MeTHF at -140 °C.

(b) **^{13}C Hyperfine Couplings.** Like the perchlorotriphenyl (PTM) monoradicals (Figure 3, Table 1),[1e,2,7,12-14] the majority of diradicals described here display in solution at room temperature weak hyperfine lines which arise from spin coupling with the ^{13}C nuclei. They consist of three nested line pairs due to the α, the bridgehead (bh), and the ortho carbons. They may be observed by increasing the signal gain about 100-fold (^{13}C natural abundance, 1.1%) (Table 1, Figures 3 and 4A–D). On the basis of the ^{13}C hyperfine couplings, the diradicals described here are sorted into three classes. Class A includes the diradicals in which the ^{13}C hyperfine couplings are virtually coincident with those of related monoradicals, such as PTM• (Table 1): •PTM-PTM•, •PTM-C≡C-PTM•, HO-ṖTM-PTṀ-OH, and $^-$O-ṖTM-PTṀ-O$^-$, Class B comprises the diradicals where the ^{13}C hcs are half

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Table 1. Diradicals and Monoradical Analogues: ESR Data

radical species	g	^{13}C couplings (mT) α	bridgehead[a]	ortho[a]	solvent[c]
PTM$\cdot$	2.0026	2.95	1.27	1.07	CCl_4
$\cdot$PTM-PTM$\cdot$	2.0028	2.91	1.32	0.95	CCl_4
$\cdot$PTM-C$\equiv$C-PTM$\cdot$	2.0027	2.83	1.22	1.02	CCl_4
$\cdot$PTM-CCl=CCl-PTM$\cdot$ (*trans*)	2.0028	1.39	0.50		$CHCl_3$
$\cdot$PTM-CH_2CH_2-PTM$\cdot$	2.0026	*b*	*b*	*b*	C_2Cl_4
$\cdot$PTM-OH	2.0026	2.95	1.27	1.07	C_2Cl_4
HO-PTM$\cdot$-$\cdot$PTM-OH	2.0028	2.89	1.21	0.97	CCl_4
$\cdot$PTM-O$^-$		2.18	0.95	0.79	THF
$^-$O-PTM$\cdot$-$\cdot$PTM-O$^-$		2.24	0.94	0.80	THF
($\cdot$PTM-CO)$_2$O	2.0027	1.50	0.53		C_2Cl_4
$\cdot$PTM-$COOCH_2CH_2OH$	2.0026	3.00	1.28	1.07	CCl_4
($\cdot$PTM-$COOCH_2$)$_2$	2.0027	*b*	0.57		C_2Cl_4
$\cdot$PTM-$COOCH_2CH_2OCH_2CH_2OH$	2.0026	3.04	1.13	1.00	CCl_4
($\cdot$PTM-$COOCH_2CH_2$)$_2$O	2.0027	*b*	*b*	*b*	C_2Cl_4
$\cdot$PTM-$COOCH_2CH$(OCO-PTM$\cdot$)CH_2OH	2.0024	1.43	0.53		C_2Cl_4
($\cdot$PTM-$COOCH_2$)$_2$CHOH	2.0026	1.45	0.52		C_2Cl_4
($\cdot$PTM-$COOCH_2$)$_2$CHOCO-PTM$\cdot$	2.0020	*b*	*b*	*b*	C_2Cl_4

[a] By computer simulation. [b] Swamped by the line wings. [c] At room temperature.

Table 2. ESR Data in Glassy Matrix (2MeTHF; −130 °C to −140 °C): Dipolar Interaction Parameters[a]

radical species	$B_3 - B_2$ (mT)	$B_4 - B_1$ (mT)	D[a] (cm^{-1})	$g_\parallel$	$g_\perp$	R_0[e] (Å)
$\cdot$PTM-PTM$\cdot$ [c]	4.80	9.65	0.0045	2.0015	2.0035	8.3
$\cdot$PTM-C$\equiv$C-PTM$\cdot$ [c]	1.87	3.94	0.0018	2.0003	2.0035	11.3
$\cdot$PTM-CCl=CCl-PTM$\cdot$ [c]	1.89	3.81	0.0018	2.0010	2.0033	11.3
$\cdot$PTM-CH_2CH_2-PTM$\cdot$ [d]	1.95	4.05	0.0019	2.0004	2.0029	11.1
($\cdot$PTM-CO)$_2$O	1.40	3.45	0.0016	2.0018	2.0031	11.7
($\cdot$PTM-$COOCH_2$)$_2$	1.28	2.55	0.0012	2.0022	2.0024	12.9
($\cdot$PTM-$COOCH_2CH_2$)$_2$O[d]	5.20	10.40	0.0048	2.0023	2.0023	8.1

[a] See Figures 1 and 2. [b] 1 cm^{-1} ∝ 1070.5 mT. [c] Chiefly, the diradical displaying dipolar interaction. [d] Predominantly, the species apparently *devoid* of dipole interaction (supernumerary ESR line). [e] Calculated distance between the two spin centers: $R_0 = (0.65g_\parallel^2/D)^{1/3}$.[17,18]

those for Class A: $\cdot$PTM-CCl=CCl-PTM$\cdot$(*trans*), ($\cdot$PTM-CO)$_2$O, ($\cdot$PTM-$COOCH_2$)$_2$CHOH, and $\cdot$PTM-$COOCH_2CH$(OCO-PTM$\cdot$)CH_2OH. Class C includes those diradicals for which no ^{13}C lines are observed, being apparently swamped by the main line wings: ($\cdot$PTM-$COOCH_2$)$_2$ and ($\cdot$PTM-COO-CH_2CH_2)$_2$O.

The halving of the ^{13}C hcs in class B is caused by the so-called "spin–spin exchange", a phenomenon that has been analyzed, both theoretically and experimentally, by Reitz and Weissman for non-perchlorinated diradicals.[18] Those authors envisaged this effect as a rapid oscillation of each unshared electron between the two equivalent diradical moieties, although it is properly and strictly accounted for in terms of quantum mechanics. Consequently, the relevant spin densities on the atoms and the pertinent hyperfine couplings would be halved. In diradicals of class A, the spin–spin exchange is virtually absent. Diradicals of class C might be regarded as belonging to the "twilight zone" between class A and class **B**.

The fact that the diradicals of class A behave as if they were monoradicals indicates that the spin–spin exchange is hindered. The authors attribute it, in the biphenyl diradicals (Figure 2), to steric inhibition of resonance between the two molecular moieties caused by the repulsions among chlorines and, in the tolane diradical, to orthogonality between the two triple-bond π-orbitals.

The ESR spectrum of diradical diphenoxide, $^-$O-$\dot{\text{P}}$TM-PT$\dot{\text{M}}$-O$^-$, displays a significant feature. It belongs to class A, since it displays ^{13}C hcs equal to those of the monoradical anion counterpart $\cdot$PTM-O$^-$.[5] Yet, those couplings are 25% lower than those exhibited by $\cdot$PTM-PTM$\cdot$ or the perchlorotriphenylmethyl monoradicals, *i.e.*, 2.20 (α), 0.95 (bh), and 0.80 mT (o) vs 2.90, 1.30, and 0.95 mT, respectively (Table 1). Therefore, 25% of the normal spin density on the carbons is transferred to the para oxygens, as it occurs in $\cdot$PTM-O$^-$.[5]

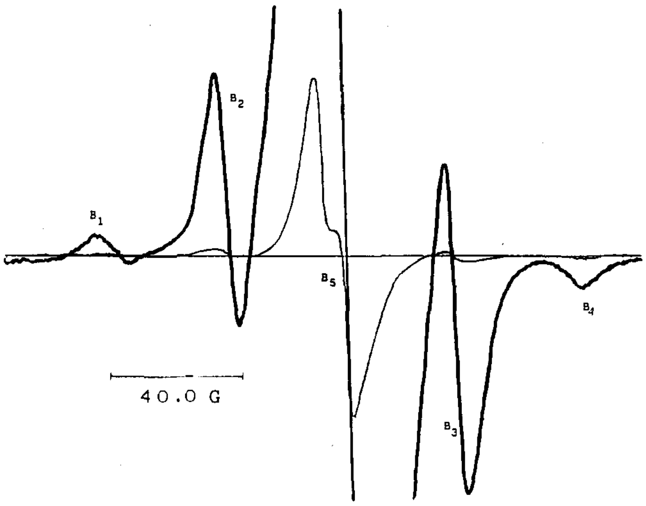

Figure 6. ESR spectrum of diradical ((C_6Cl_5)$_2\dot{C}$-C_6Cl_4-$COOCH_2CH_2$)$_2$O (($\cdot$PTM-$COOCH_2CH_2$)$_2$O) in 2MeTHF at −130 °C.

It is remarkable that the spin–spin exchange is present even in diradicals (class B) where the spacer Sp is a chain involving σ-bonds exclusively. However, the σ-bond chain may be an appropriate path for spin–spin exchange.[19] The latter is also significant in diradical $\cdot$PTM-CCl=CCl-PTM$\cdot$(*trans*),[1e] in spite of the considerable steric inhibition of resonance between the two diradical moieties caused by repulsion among its ethylene and ortho chlorines, as in the perchlorostyrenes.[11]

Triradical ($\cdot$PTM-$COOCH_2$)$_2$CHOCO-PTM$\cdot$ in solution at room temperature shows a very wide ESR line (0.21 mT, CCl_4; 0.19 mT, C_2Cl_4) with very thick line wings. Therefore, no ^{13}C hyperfine coupling is observed.

Supernumerary ESR Line at $g \approx 2$. In a glassy matrix, at the center of the spectrum ($g \approx 2$), all the diradicals reported here display an additional, abnormal ESR line of variable intensity (Figures 4F, 5, and 6). Actually, the presence of a spurious line about $g = 2$ has frequently been reported in the spectra of non-perchlorinated diradicals such as the triplet naphthalene-d_8[17] and bisgalvinoxyl,[20] to mention two quite unrelated diradicals. This line has *invariably* been attributed to a monoradical impurity,[16,17,20] formed presumably in the preparation of the diradical and/or by attack of the latter on the solvent or other chemical species present. This cannot be the case here because, for example, in diradical $\cdot$PTM-PTM$\cdot$ (Figure 4), double integration of the supernumerary ESR line allows estimation of its proportion (up

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to 30%). Most remarkably, in •PTM-CH$_2$CH$_2$-PTM•, (•PTM-COOCH$_2$CH$_2$)$_2$O, and •PTM-COOCO-PTM• this line is absolutely predominant (Figure 5). Monoradical impurities cannot account for this intense line for several reasons, as detailed below.

(1) The perchloro diradicals have been exhaustively purified by preparative TLC and flash chromatography, no variation in intensity of absorption among the purified samples obtained being observed. (2) No example of thermal atom abstraction from the environment has ever been observed in inert perchlorotriphenylmethyl mono- and diradicals. With the exception of a very few mono- and diradicals, provided with reactive substituents (HO, O$^-$, COOH), they not only are inert *vs* typical hydrogen donors (boiling toluene, cycloheptatriene, 2MeTHF, hydroquinone) but they also withstand radical reagents and aggressive chemical species (NO, NO$_2$, Cl$_2$, Br$_2$, SOCl$_2$, SO$_2$Cl$_2$, and concentrated H$_2$SO$_4$).

(3) In the pure diradicals, no impurity has been detected by analytical TLC and IR spectroscopy (absence of α-hydrogen, spurious lines, etc.).

(4) In some significant cases, radical purity has eventually been checked by magnetic susceptibility measurements in helium (12×10^{23} spin/mol) (see General Methods in the Experimental Section). The calculated number of spins per mole for the diradical would fall sharply below twice Avogadro's number with the presence of a significant monoradical impurity of comparable molecular weight.

(5) The UV–vis maximum molar absorptivities of the two radical bands ($\epsilon_{\max}$ at 380 and 510–560 nm) in all diradical samples employed are nearly twice those for their monoradical analogues. Therefore, no significant proportion of a monoradical ($\epsilon_{\max}/2$) of similar molecular weight could be present.

(6) In some perchlorodiradicals, the supernumerary line is greatly predominant, so it must derive from a dominant diradical species, not an impurity.

Diradical (•PTM-COOCH$_2$CH$_2$)$_2$O displays a peculiar ESR spectrum. In a glassy matrix, it displays two intense, moderately wide, strongly overlapping lines instead of just one supernumerary line (Figure 6). Such an additional pair cannot be due to loss of the axial symmetry ($E \neq 0$), since its gap value is in full disagreement with $\mathbf{B}_4 - \mathbf{B}_1$ and $\mathbf{B}_3 - \mathbf{B}_2$.[16,17] If the abnormal diradical species ($g \approx 2$) is weakly anisotropic, some line splitting would be apparent,[21] independent of those from the conventional diradical.

Nature of the Supernumerary Line. The ESR spectra in C$_2$Cl$_4$ of diradicals (•PTM-CO)$_2$O (Figure 5) and (•PTM-COOCH$_2$-CH$_2$)$_2$O (Figure 6) belonging to class B are particularly enlightening. The absorption of their supernumerary ESR line is predominant, yet the *only set of ^{13}C line pairs observed* belongs to a diradical (triplet) with intramolecular spin–spin exchange (Table 1). Consequently, that line *must correspond to an isomeric diradical form* devoid of appreciable dipolar interaction. No ^{13}C lines ("normal" hc values) are detected, and hence the presence of a monoradical is again ruled out, at least in a significant proportion. In this connection, it is emphasized that at room temperature the ^{13}C hyperfine lines are easily detected, and their hcs can therefore be calculated. The main single line "wings" (Figure 4A) do not interfere because of the lower proportion of the wing-thickening triplet, particularly when C$_2$Cl$_4$ is the solvent.

Energy splitting due to spin dipolar interaction occurs because the distance between the two spin centers here is moderate ($\approx$10 Å). Paradoxically, the splitting is missing in the supernumerary absorption at $g \approx 2$, assigned here to an additional diradical form. The authors are unable to explain this fact on the basis of the current diradical theory. Concurrent diradical clusters, where the dipolar interactions would cancel, might account for this remarkable phenomenon. The more soluble the diradical, the higher is the proportion of the abnormal form.

The most interesting observation, at least within the domain of the perchlorotrityl diradicals, is the sharp disagreement between the spectra expected from diradical theory and those observed experimentally.

Experimental Section

General Methods and Equipment. The IR, UV–vis, and ESR spectra were recorded with Perkin-Elmer Model 682, Beckman Acta M-VI and Perkin-Elmer Model Lambda array 3840, and Varian Model E109 spectrometers, respectively. The magnetic susceptibilities were measured from 77 K to room temperature in helium with a Varian 4-in. magnet with constant-force caps and a Cahn RG electrobalance; the number of spins per mole was calculated by improved Pascal's systematics.[13,22] The syntheses and handling of radicals, diradicals, and the radical anion were carried out in the dark.

Diradicals •PTM-PTM•,[2] •PTM-CH$_2$CH$_2$-PTM•,[14] and difuchsone **2**[8] were prepared as previously described. Although a preliminary note on the diradicals •PTM-C≡-PTM• and •PTM-CCl=CCl-PTM•(*trans*) has been published,[13] some significant data and experimental procedures, including some improvements, are reported here for the first time.

Perchloro-$\alpha,\alpha,\alpha',\alpha'$-tetraphenylbi-*p*-tolyl-α,α'-ylene Diradical (•PTM-PTM•).[2] Anal. Calcd for C$_{38}$Cl$_{28}$: C, 31.5; Cl, 68.5. Found: C, 31.5; Cl, 68.5. From magnetic susceptibility:[23] 12.0×10^{23} spin/mol. UV–vis (radical character bands): λ 386, 510–560 nm (ϵ = 74 750, $\approx$2500 cm$^{-1}\cdot$M^{-1}).

4,4′-Ethylenebis(tetradecachlorotriphenylmethyl) Diradical (•PTM-CH$_2$CH$_2$-PTM•).[14] Anal. Calcd for C$_{40}$H$_4$Cl$_{28}$: C, 32.5; Cl, 67.2. Found: C, 32.5; Cl, 67.4. From magnetic susceptibility:[23] 12.6 spin/mol. UV–vis (radical character bands): λ 385, 510–562 nm (ϵ = 73 800, $\approx$2500 cm$^{-1}\cdot$M^{-1}).

***cis*-$\alpha H,\alpha' H$-Triacontachloro-4,4′-vinylenebis(triphenylmethane).**[13a] Fe(CO)$_5$ (0.65 g) was added to a solution of αH-heptadecachloro-4-methyltriphenylmethane (1.055 g) in anhydrous benzene (60 mL), and the resulting mixture was refluxed for 45 min under argon. The residue resulting from elimination of the volatile parts under vacuum was digested with warm diluted hydrochloric acid (1 h) and the solid separated, treated with CHCl$_3$ at room temperature until total dissolution. Silica gel (15 g) was added, and finally the solvent was evaporated to a thick slush, which was added to the top of a chromatographic column and then eluted first with hexane to eliminate impurities and next with hexane/CCl$_4$ (7:3), yielding *cis*-$\alpha H,\alpha' H$-triacontachloro-4,4′-vinylenebis(triphenylmethane) (0.70 g, 72.5%): mp 416–418 °C dec; UV–vis (C$_6$H$_{12}$) 284, 304 (sh), 313 (sh) nm (ϵ 10 500, 4250, 1300); IR (KBr) 2920, 1605, 1530, 1370, 1334, 1313, 1298, 1241, 1209, 1190, 1148, 1122, 1060, 1028, 977, 943, 898, 877, 844, 812, 755, 720, 710, 702, 692, 687, 672, 664, 655, 613, 573, 552, 541, 532, 510 cm^{-1}; ^{1}H NMR (CCl$_4$) δ 7.14 (2 H, s, CH). Anal. Calcd for C$_{40}$H$_2$Cl$_{30}$: C, 31.1; H, 0.1; Cl, 68.8. Found: C, 31.0; H, 0.2; Cl, 68.6. This compound had been obtained for the first time by A. Ibáñez, along with its *trans* isomer, using Ph$_3$P as the condensation agent.[12a]

4,4′-Perchloroethynylenebis(triphenylmethyl) diradical (•PTM-C≡C-PTM•).[12] A mixture of *cis*-$\alpha H,\alpha' H$-triacontachloro-4,4′-vinylenebis(triphenylmethane) (0.50 g), ethyl ether (300 mL), DMSO (50 mL), and finely ground NaOH (6 g) was shaken at room temperature (24 h). The excess of NaOH was filtered off with sintered glass. The resulting solution was poured over I$_2$ (1.2 g) and left undisturbed at room temperature (24 h). After treatment of the solution with an aqueous solution of NaHSO$_3$ (removal of I$_2$), the nonaqueous layer was washed with water, and the suspended diradical was separated by filtration, washed with water and ethyl ether, dried under vacuum, and dissolved in CCl$_4$. The solution obtained was passed through silica gel, eluted with CCl$_4$/hexane (3:2), giving, after solvent elimination, green solid diradical •PTM-C≡C-PTM• (0.186 g). The residue from the ethereal layer was submitted to chromatography, eluting with hexane/CCl$_4$ (7:3), giving an additional amount of diradical (0.104 g, total yield, 61%). It was identified by IR, UV–vis, and ESR (Table 1) spectra.[13] Anal. Calcd for C$_{40}$Cl$_{28}$: C, 32.6; Cl, 67.4. Found: C, 32.6; Cl, 67.3. From magnetic susceptibility: 11.8 spin/mol.

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(21) Carrington, A.; McLachlan, A. D. *Introduction to Magnetic Resonance*; Chapman and Hall: London, 1979; p 129.

(22) Foex, G.; Gorter, C. J.; Smith, L. J. *Constants Sêlectionées. Diamagnêtisme et paramagnêtisme, relaxation paramagnetique*; Masson et Cie: Paris, 1957; p 222. Chlorine specific magnetic susceptibility contribution: 18.15×10^{-6}, adjusted for perchloro compounds.

(23) Addition of pentane converts the resinous residue, obtained by evaporation of the solvent, into a microcrystalline powder. In this process, as it is known to occur in other perchloro organic compounds, a molecule of pentane is incorporated. The latter cannot be removed by heating under vacuum.

4,4′-Perchloro-*trans*-vinylenebis(triphenylmethyl) Diradical (•PTM-CCl═CCl-PTM•(*trans*)).[12] Through a solution of diradical •PTM-C≡C-PTM• (0.092 g) and I_2 (0.03 g) in CCl_4 (30 mL) was passed a moderate stream of Cl_2 (60 min). The excess of Cl_2 was swept off with a stream of N_2, the mass was poured into aqueous $NaHSO_3$, and the organic layer was washed with water, dried, and evaporated, giving a residue (0.081 g) which was digested with hexane, yielding red solid diradical •PTM-CCl═CCl-PTM•(*trans*) (0.073 g, 78%), which was identified by IR, UV–vis (Figure 1), and ESR (Table 1) spectra. UV–vis (radical character bands): 388, 510–540 nm (ε 74 500, ≈2400). Anal. Calcd for $C_{40}Cl_{30}$: C, 31.1; Cl, 68.9. Found: C, 31.0; Cl, 69.0. From magnetic susceptibility: 11.8 spin/mol.

Hexacosachloro-α,α′-bis(4-hydroxyphenyl)-α,α′-diphenylbi-*p*-tolyl-α,α′-diylene Diradical (HO-$\dot{\mathrm{P}}$TM-PT$\dot{\mathrm{M}}$-OH). To a solution of difuchsone **2** (0.25 g) in benzene (130 mL) a 57% aqueous solution of HI (3 mL) containing I_2, and then the mixture was stirred at room temperature (24 h) under argon. The benzene layer was washed consecutively with a diluted aqueous solution of H_3PO_2, diluted aqueous HCl, and water, dried over Na_2SO_4, and evaporated to dryness under vacuum. The red residue (0.23 g, 92% yield) was the title diradical: mp 318–323 °C dec; UV–vis ($CHCl_3$) 280, 365 (sh), 385, 515, 565 nm (ε 13 500, 31 500, 66 000, 2900, 3600); IR (KBr) 3500, 1530, 1420, 1365, 1330, 1320, 1270, 1250, 1190, 950, 730, 700, 540, 510 cm^{-1}; ESR data, Table 1. Anal. Calcd for $C_{38}H_2Cl_{26}O_2$: C, 32.3; H, 0.1. Found: C, 32.6; H, 0.4.

Perchloro-α,α′-diphenyl-α,α′-bis(4-oxocyclohexadienylidene)bi-*p*-tolyl Diradical Dianion ($^-$O-$\dot{\mathrm{P}}$TM-PT$\dot{\mathrm{M}}$-O$^-$). This diradical dianion has been obtained from difuchsone **2** as described.[5]

4-Carboxytetradecachlorotriphenylmethyl Anhydride Diradical ((•PTM-CO)$_2$O). A mixture of 4-chlorocarbonyltetradecachlorotriphenylmethyl radical (•PTM-COCl, 0.050 g), 4-carboxytetradecachlorotriphenylmethyl radical (•PTM-COOH, 0.049 g), triethylamine (0.006 g), and $CHCl_3$ was shaken at room temperature (60 h). The resulting mass was filtered, and the filtrate gave a red solid residue (0.140 g) which was submitted to preparative TLC on silica gel (CCl_4), giving only a moving fraction consisting of (•PTM-CO)$_2$O (0.054 g, 56%): mp 182 °C dec; UV–vis (C_6H_{12}) 288, 338 (sh), 368 (sh), 382, 482 (sh), 505, 562 nm (ε 12 000, 11 000, 37 000, 69 000, 2250, 2300, 2120); IR (KBr) 1815, 1775, 1490, 1330, 1315, 1250, 1205, 1155, 1060, 985, 895, 870, 810, 750, 725, 705, 695, 665, 635 cm^{-1}; ESR data, Tables 1 and 2, $\Delta M = 2$ absent; magnetic susceptibility $\chi_{dia} = -0.505 \times 10^{-6}$ emu, Weiss Constant = −5.3 K, μ = 2.48, spin/mol = 12.4×10^{23}. Anal. Calcd for $C_{40}Cl_{28}O_3$: C, 31.6; H, 0.0. Found: C, 31.7; H, 0.1. The stationary layer was extracted with acetone, and by evaporation of the latter, impure radical •PTM-COOH (0.039 g) was recovered. No radical •PTM-COCl was detected.

4-((β-Hydroxyethoxy)carbonyl)tetradecachlorotriphenylmethyl Radical (•PTM-COOCH$_2$CH$_2$OH) and 4,4′-[ethylene-1,2-di(oxycarbonyl)]bis(tetradecachlorotriphenylmethyl) Diradical (•PTM-COOCH$_2$)$_2$. Depending upon whether the preparation was aimed at the monoradical or the diradical, the ratio ClCO-PTM•/HOCH$_2$CH$_2$OH was 1:1 or 2:1, respectively. A mixture of •PTM-COCl (0.150 or 0.199 g), HOCH$_2$CH$_2$OH (0.012 or 0.008 g), 4-(dimethylamino)pyridine (0.035 or 0.066 g), and CH_2Cl_2 (10 mL) was shaken at room temperature (24 h) in a dry atmosphere. The resulting mass was poured into diluted aqueous HCl and extracted with ethyl ether. The ethereal layer was washed with water, dried, and evaporated to dryness, and the residue was submitted to preparative TLC on silica gel ($CHCl_3$). The products are reported in order of decreasing R_f.

Ratio 1:1, two fractions. Fraction 1 (0.039 g) was rechromatographed (CCl_4), giving diradical (•PTM-COOCH$_2$)$_2$ (0.034 g, 23%): mp 224–227 °C; UV–vis (C_6H_{12}, Figure 1) 290, 338 (sh), 368 (sh), 382, 505, 562 (ε 14 000, 16 500, 41 000, 78 000, 2300, 2150); IR (KBr) 2940, 1750, 1530, 1500, 1450, 1335, 1325, 1260, 1220, 1200, 1130, 1110, 1030, 820, 790, 765, 730, 715, 695, 670, 660, 640, 610, 575, 520 cm^{-1}; ESR data, Table 1, $\Delta M = 2$ absent; magnetic susceptibility $\chi_{dia} = -0.509 \times 10^{-6}$ emu, Weiss constant = +3.4 K, μ = 2.39, spin/mol = 11.5×10^{23}. Anal. Calcd for $C_{42}H_4Cl_{28}O_4$: C, 32.2; H, 0.3; Cl, 63.4. Found: C, 32.2; H, 0.3; Cl, 63.4.

Fraction 2 (0.108 g) was rechromatographed twice as fraction 1, yielding radical •PTM-COOCH$_2$CH$_2$OH (0.103 g, 66.5%): mp 203–206 °C; UV–vis (C_6H_{12}) 290, 338 (sh), 368 (sh), 382, 505, 560 nm (ε 6700, 6500, 19 500, 36 500, 1150, 1065); IR (KBr) 3440, 2940, 2840, 1745, 1530, 1500, 1445, 1335, 1320, 1260, 1230, 1135, 1115, 1075, 1035, 1000, 820, 795, 760, 730, 715, 695, 670, 660, 640, 615, 570, 520 cm^{-1}; ESR data, Table 1; magnetic susceptibility $\chi_{dia} = -0.447 \times 10^{-6}$ emu, Weiss constant = +2.7 K, μ = 1.73, spin/mol = 6.05×10^{23}. Anal. Calcd for $C_{22}H_5Cl_{14}O_3$: C, 32.5; H, 0.6; Cl, 61.0. Found: C, 32.4; H, 0.7; Cl, 61.2.

Ratio 2:1, three fractions: diradical (•PTM-CO)$_2$O (0.009 g), diradical (•PTM-COOCH$_2$)$_2$ (0.131 g, 66%), and monoradical •PTM-COOCH$_2$CH$_2$OH (0.033 g, 16%).

4-(((5-Hydroxy-3-oxopentyl)oxy)carbonyl)tetradecachlorotriphenylmethyl Radical (•PTM-COOCH$_2$CH$_2$-O-CH$_2$CH$_2$-OH) and 4,4′-[3-Oxopentylene-1,5-di(oxycarbonyl)]bis(tetradecachlorotriphenylmethyl) Diradical (•PTM-COOCH$_2$CH$_2$)$_2$O. A mixture of •PTM-COCl (0.200 g), diethylene glycol (0.019 g), 4-(dimethylamino)pyridine (0.060 g), and CH_2Cl_2 (10 mL) was shaken at room temperature (24 h) in a dry atmosphere. The resulting mass was worked up as in the preceding reaction, yielding the diradical and the monoradical.

Diradical (•PTM-COOCH$_2$CH$_2$)$_2$O (0.117 g, 57%): mp 226–229 °C; UV–vis (C_6H_{12}) 271, 286, 340 (sh), 368 (sh), 382, 505, 560 nm (ε 14 000, 15 000, 16 000, 37 500, 67 000, 2200, 2040); IR (KBr) 2950, 2860, 1745, 1450, 1335, 1325, 1255, 1225, 1130, 1110, 1030, 870, 815, 730, 710, 665, 635, 610, 575, 520 cm^{-1}; ESR data, Table 1, ΔM = 2, 169.3 mT; magnetic susceptibility $\chi_{dia} = -0.512 \times 10^{-6}$ emu, Weiss constant = −3.5 K, μ = 2.50, spin/mol = 12.7×10^{23}. Anal. Calcd for $C_{44}H_8Cl_{28}O_5$: C, 32.8; H, 0.5; Cl, 61.7. Found: C, 32.8; H, 0.6; Cl, 61.7.

Monoradical •PTM-COOCH$_2$CH$_2$-O-CH$_2$CH$_2$OH (0.087 g, 40%): mp 195–198 °C; UV–vis (C_6H_{12}) 287, 342 (sh), 368 (sh), 382, 505, 560 nm (ε 7200, 7500, 20 000, 37 000, 1180, 1080); IR (KBr) 3400, 2920, 2860, 1745, 1450, 1335, 1325, 1260, 1230, 1130, 1110, 1060, 1030, 875, 815, 730, 715, 690, 635, 610, 575, 520 cm^{-1}; ESR data, Table 1; magnetic susceptibility $\chi_{dia} = -0.452 \times 10^{-6}$ emu, Weiss constant = −2.8 K, μ = 1.78, spin/mol = 6.41×10^{23}. Anal. Calcd for $C_{24}H_9Cl_{14}O_4$: C, 33.6; H, 1.1; Cl, 57.9. Found: C, 33.8; H, 1.1; Cl, 57.9.

Glycerol Spin-Labeling: •PTM-COOCH$_2$CH(OCO-PTM•)CH$_2$OH, (•PTM-COOCH$_2$)$_2$CHOH, and (•PTM-COOCH$_2$)$_2$CHOCO-PTM•. A mixture of ClCO-PTM• (0.308 g), glycerol (0.012 g), 4-(dimethylamino)pyridine (0.095 g), and CH_2Cl_2 (15 mL) was shaken at room temperature (24 h) under argon. The mass was then poured into diluted aqueous HCl, and the resulting mixture was extracted with $CHCl_3$. The organic layer was washed with water and evaporated to dryness, giving a red residue (0.360 g) which was submitted to preparative TLC on silica gel (CCl_4), giving four fractions, reported in order of decreasing R_f: fraction 1, mp 281–284 °C, 0.077 g; fraction 2, mp 225–228 °C, 0.089 g; fraction 3, mp 218–222 °C, 0.016 g; and fraction 4, not eluted by CCl_4, discarded. The first three fractions were triradical (•PTM-COOCH$_2$)$_2$CHOCO-PTM• and diradicals (•PTM-COOCH$_2$)$_2$CHOH and •PTM-COOCH$_2$CH(OCO-PTM•)CH$_2$OH. Fraction 4 was not investigated since it was presumably a mixture of predominantly acid radical •PTM-COOH, resulting from unreacted •PTM-COCl, and monoradicals.

(•PTM-COOCH$_2$)$_2$CHOCO-PTM•: red solid; UV–vis (C_6H_{12}) 286, 340 (sh), 370 (sh), 381, 502, 562 nm (ε 20 850, 22 600, 62 700, 97 200, 3350, 3380); IR (KBr) 1755, 1335, 1255, 1220, 1200 cm^{-1}; ESR data, Table 1. Anal. Calcd for $C_{63}H_5Cl_{42}O_6 \cdot C_5H_{12}$:[23] C, 33.7; H, 0.7. Found: C, 33.6; H, 0.7.

(•PTM-COOCH$_2$)$_2$CHOH: UV–vis (C_6H_{12}) 290, 340, 370, 383, 508, 563 nm (ε 14 000, 13 450, 38 000, 71 600, 2300, 2169); IR (KBr) 1740, 1335, 1320, 1255, 1220, 1200 cm^{-1}; ESR data, Table 1; magnetic susceptibility $\chi_{dia} = -0.240 \times 10^{-6}$ emu, Weiss constant = −4.1 K, μ = 2.52, spin/mol = 12.8×10^{23}. Anal. Calcd for $C_{43}H_6Cl_{28}O_5 \cdot C_5H_{12}$:[23] C, 34,6; H, 1.1. Found: C, 34.2; H, 0.8.

•PTM-COOCH$_2$CH(OCO-PTM•)CH$_2$OH: IR (KBr) 2950, 1745, 1335, 1320, 1255, 1200 cm^{-1}; ESR data, Table 1. Anal. Calcd for $C_{43}H_6Cl_{28}O_5 \cdot C_5H_{12}$:[23] C, 34.6; H, 1.1. Found: C, 34.6; H, 1.1.

Structural Assignments. The structures of the diradicals given here are based on the R_f, which is significantly lower in •PTM-COOCH$_2$CH(OCO-PTM•)CH$_2$OH (more polar, unshielded), and the yield, about 6 times higher in (•PTM-COOCH$_2$)$_2$CHOH, since the two (unhindered) primary carbinol groups must be labeled at a higher rate.

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