Inert Carbon Free Radicals. 8. Polychlorotriphenylmethyl Radicals. Synthesis, Structure, and Spin-Density Distribution[†]

O. Armet,[‡] J. Veciana,^{*‡} C. Rovira,[‡] J. Riera,[‡] J. Castañer,[‡] E. Molins,[§] J. Rius,[§] C. Miravitlles,[§] S. Olivella,¹ and J. Brichfeus¹

Departamento de Materiales Orgánicos Halogenados, Centro de Investigación y Desarrollo (CSIC), 08034 Barcelona, Spain, Instituto de Ciencia de Materiales (CSIC), 08028 Barcelona, Spain, and Departament de Química Orgánica, Facultat de Química, Universitat de Barcelona, 08028 Barcelona, Spain (Received: April 24, 1987)

Some symmetrical $Ar_3\dot{C}$ and unsymmetrical $(C_6Cl_5)_{3-x}Ar_x\dot{C}$ radicals with different chlorine substitution patterns (x = 1, 2; Ar: $2H-C_6HCl_4$, $3H, 5H-C_6H_2Cl_4$, $4H-C_6HCl_4$, C_6H_5) are prepared. X-ray crystal structures for most of them have been obtained at room temperature. The general conformations are conditioned by the great volume of the chlorine atoms in the ortho positions resulting in unsymmetrical, propellerlike conformations. Experimental evidence of the steric shielding of the trivalent carbon atom, as well as the practical nonexistence of the so-called buttressing effect, is given. The steric shielding is in correlation with the observed stabilities. The magnetic susceptibilities of the radicals are discussed and related to molecular packing and spin densities in terms of McConnell's theory, when antiferromagnetism is observed. The g-factors, hyperfine coupling constants (hcc) of ¹H and ¹³C nuclei, and line widths of the radicals are determined at several temperatures by ESR experiments in solid-state and isotropic solutions. Different conformational dynamic behaviors are traced to the number of chlorine atoms in ortho positions. Temperature-dependent line widths are explained by the relative contribution of the modulation of the dipolar hyperfine interaction through molecular tumbling and chlorine nuclear quadrupolar relaxation mechanism. The hcc values have been calculated according to the INDO method with the experimental X-ray geometries and compared with the experimental values; a good agreement is obtained. The assignment of the ¹³C satellites to bridgehead and ortho positions is confirmed.

Introduction

In the course of our studies on derivatives of perchlorotriphenylmethyl radical (PTM; 1), their high stabilities have been traced predominantly to the shielding of the trivalent carbon atom by their phenyl rings with a propellerlike conformation and their six ortho chlorines.¹ However, the effect of the absence of ortho or meta chlorines on the twist angles of the rings, and therefore on their stability, has never been assessed, basically because the suitable compounds were not at all synthetically accessible. Until now the twist angles in triphenylmethyl radicals have been usually estimated by comparison of the experimental hcc values with data from quantum-mechanical calculations, but these angles are not reliable enough, at least when only ¹H hcc values are compared. In addition, while crystal structure determinations of many triphenylmethides and triphenylcarbonium ions have been reported,² as far as the authors known, there is just one example of such studies on triphenylmethyl radicals: that of tris(4-nitrophenyl)methyl radical.³ It seemed therefore of interest to start a systematic study of the influence of substitution on geometries and electronic structures of triphenylmethyl radicals, based on direct methods.

Recently some of the authors have reported a method for the synthesis of both symmetrical and unsymmetrically substituted highly chlorinated triarylmethanes,⁴ usual precursors of the free radicals. This allowed the synthesis of radicals 2-9 (Table I), suitable for the study of the influence of chlorine substitution (both in solid state and in solution) on the stability, magnetic properties, geometry, and spin-density distributions of polychlorinated triphenylmethyl radicals.

This paper reports the synthesis as well as magnetic and spectral data of radicals 1-9 (Table I), together with the X-ray crystal structures of radicals 1-6;⁵ from these, and by using the INDO method, ESR hcc values have been calculated and compared with those obtained in isotropic solution.

Results and Discussion

Synthesis of the Radicals. Radicals 1-9 were prepared from the corresponding triarylmethanes in an "one-pot" reaction by

TABLE I: Numbering of the Polychlorinated Triphenylmethyl Radicals, Ar¹Ar²Ar³C, Studied

	,		
radical	Ar ¹	Ar ²	Ar ³
 1	C ₆ Cl ₅	C ₆ Cl ₅	C ₆ Cl ₅
2	4H-C ₆ HCl ₄	C ₆ Cl ₅	C ₆ Cl ₅
3	$4H-C_6HCl_4$	4H-C ₆ HCl ₄	4H-C ₆ HCl ₄
4	$3H, 5H-C_6H_2Cl_3$	C ₆ Cl ₅	C ₆ Cl ₅
5	$3H, 5H-C_6H_2Cl_3$	$3H_{5}H_{C_{6}}H_{2}Cl_{3}$	$3H, 5H-C_6H_2Cl_3$
6	2H-C6HCl4	C ₆ Cl ₅	C ₆ Cl ₅
7	2H-C6HCl4	2H-C6HCl4	C_6Cl_5
8	$2H-C_6HCl_4$	2 <i>H</i> -C ₆ HCl ₄	2H-C ₆ HCl ₄
9	C ₆ H ₅	C ₆ Cl ₅	C ₆ Cl ₅

treatment with aqueous tetra-n-butylammonium hydroxide in THF, followed by oxidation of the resulting carbanions with *p*-chloranil. This method offers important advantages over the stepwise traditional one,¹ such as shorter reaction times, easier workup, and better yields. Radicals 3-7, which had not been previously reported, can be isolated even in the solid state and present physical properties similar to those of radicals 1 and 2, already reported.^{1,6} On the other hand, radicals 8 and 9 can only

[†] This paper is dedicated to Professor M. Ballester on the occasion of his retirement from the Instituto de Química Orgánica (CSIC).

^tCentro de Investigación y Desarrollo. § Instituto de Ciencia de Materiales.

Universitat de Barcelona

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Figure 1. Perspective view of radical 3 with atom numbering. A similar numbering is respected for radicals $1 \cdot C_6 H_6$, 2, and 6, while for radicals 4 and 5 C12, C13, and C14–C19 correspond to C10', C9', and C2'–C7'.

be generated in solution and under inert atmosphere.

X-ray Crystallography. Final atomic coordinates of radicals 2-6 are listed in Table II. The large peaks in final difference Fourier syntheses for the structure of radical 2 around Cl atoms lead to a poor R factor. Attempts to obtain better intensities from crystals of this compound have not been successful. Several crystallizations were performed in different solvents and conditions, producing crystals in P1 and $P2_1/c$ space groups, which give rise to similar results. Some data of the structure of the 1:1 benzene clathrate of perchlorotriphenylmethyl radical (1·C₆H₆) are included as a reference for comparing geometric conformations.⁵

The perspective views, with atom numbering, of the structures of radicals 1-6 are given in Figure 1 and Figure S1-S5 of the supplementary material (see paragraph at end of paper regarding supplementary material). In radicals 1-5, the C1, C2, C8, and C14 atoms lie in a plane (reference plane) with rmsd lower than 1%. These are therefore pure p radicals, the C1 hybridization being sp². In radical 6, those atoms lie in a plane with rmsd of 8.3%, the C1 atom lying 0.2 Å away from the C2, C8, C14 plane. This out-of-plane position is too large to be assigned to an accident of crystal packing (as has been reported for some triarylamines)⁷ but indicates a partial sp³ hybridization of C1.

The general conformation of these radicals is conditioned by the great volume of the chlorine atoms in the ortho positions, which induce a torsion of the phenyl rings around their bond with the C1 atom, adopting a propellerlike conformation. This fact is clearly reflected by the dihedral angle values (Table III), which are defined as the angles between the least-squares mean planes for each phenyl ring and the reference plane. In radicals 1-5 (with six ortho chlorines each), the π dihedral angles are very similar in value for two of the rings, while it is different for the third, therefore disturbing a symmetric propeller-shape structure. In radical 6 (with one ortho hydrogen and five ortho chlorines) the three dihedral angles are very different; in particular, the ring with one ortho hydrogen C_6HCl_4 - (37.7°) is the most planar one. The inner phenyl angles with C2 (or C8, or C14) as the vertex are significantly lower than 120° (minimum value 114°); this fact could be due to the steric strength produced by the ortho chlorine atoms. Accordingly, the highest value $(119^\circ)^8$ is that of the C_6HCl_4 - of radical 6, where one of the ortho chlorines is missing. In brief, the general structure of these radicals is similar to that of trimesitylborane, perchlorotriphenylamine, and perchlorotri-



Figure 2. Space-filling representation of the structure of radical 4.

phenyl methide, as had been predicted by Mislow.⁷

The C_{ar}-Cl and C_{ar}-C_{ar} mean bond lengths for radicals **2-6** are 1.72 (1) and 1.39 (2) Å, respectively, which are normal values [1.70 (1) and 1.394 (5) Å].^{9a-c} The Cl-C_{ar} bond distances (from 1.441 to 1.512 Å) show a partial double bond character [between 1.373 (4) and 1.53 (1) Å].^{9c} The comparison of the three Cl-C_{ar} bond lengths for each structure shows that the shortest one always corresponds to the ring with the least dihedral π angle, as could be expected from a larger spin delocalization into the most coplanar ring. For the structure of radical 6, the distance Cl-C2 (1.466 Å) is significantly shorter than Cl-C8 (1.512) and Cl-C14 (1.499), thus increasing its double bond character; however, in spite of its out-of-plane deformation, it is still in the range of the other Cl-C_{ar} bond lengths. This result would give rise to a large spin delocalization in the ring bearing the ortho hydrogen, and therefore a large hcc. Unfortunately (see Electron Spin Resonance Spectra. (2) Solid-State Spectra), no ESR hyperfine splitting is observed for crystal or powdered samples of radical 6.

The distances between neighboring ortho chlorines in radicals 1–5 range from 3.55 to 4.01 Å,¹⁰ depending on the π dihedral angles of the rings. Since these distances are close to the sum of the van der Waals radii of two chlorine atoms (3.5 Å),^{9d} we can confirm for the first time the steric shielding of the trivalent carbon atoms in these radicals. A space-filling representation of such shielding in radical 4 is shown in Figure 2. On the other hand, the distances between C1 and ortho chlorine atoms in pure p radicals 1–5 are independent of the π dihedral angles, being the mean value 3.03 (3) Å. This very low rmsd value (~1%) is remarkable since in the studied series radicals with and without meta chlorines are included, and therefore it can be concluded that the so-called buttressing effect of the chlorines in meta positions has a very small, or even negligible importance.

Different molecular packings are observed in these radicals, the most interesting one is that of radical 6, where the molecules are aligned through their three phenyl rings along the A or B axis, or in a direction close to the C axis (Figure S6), forming three series of continuous parallel benzenic strips. The interaction sites between their phenyl groups are of different type for each one and also present different contact distances. The closest one (3.64 Å) is that between the pentachlorophenyl groups (Ar, C8–C13) parallel to the XZ plane, the interacting sites being two para carbons and two meta chlorines through a crossed interaction pattern (Figure 3).¹¹ The contact distances in the other strips are higher than 8 Å.

Magnetic Susceptibilities. The specific magnetic susceptibilities (χ) of radicals $1 \cdot C_6 H_6$ and 3-7 were measured in the 77–298 K temperature range; those of radicals 1 and 2 have already been reported.^{1.6} The inverse of the specific paramagnetic susceptibilities

⁽⁷⁾ Hayes, K.; Nagumo, M.; Blount, J. F.; Mislow, K. J. Am. Chem. Soc. 1980, 102, 2773, and references cited therein.

⁽⁸⁾ The phenyl bond angle with C2 as vertex in radical 2 has a similar value, but its high final *R*-factor makes this value not reliable.

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distances in the range 3.51-4.37 Å. (11) Van der Waals sum of aromatic carbon and chlorine radii is 3.65 Å. Ref 9d.



Figure 3. Projection of the crystal structure of radical 6 on the XZ plane. Dashed atoms show the closest interaction.



Figure 4. Temperature (kelvin) dependence of $1/\chi_p$ (emu⁻¹·g; × 10⁻⁶) for radical 1·C₆H₆. The dashed line is the extrapolation for low temperatures of the Curie–Weiss behavior.

 $(\chi_p = \chi - \chi_d)$ were plotted against temperature, using as specific diamagnetic susceptibility (χ_d) the calculated values derived from a revised Pascal systematics.¹² Straight lines can be fitted for all radicals in the whole temperature range. These lines, when extrapolated, pass close to the origin for radicals 1·C₆H₆, **2**, **3** and 7; however, for radicals **4**-**6**, $1/\chi_p$ cancels out at negative temperatures. Figure 4 shows the plot for radical 6. Both effective Bohr magnetons (μ_{eff}) and spin numbers (*n*) can be calculated from the slope of the lines by using the the Curie-Weiss law, $1/\chi_p = 3kM_w(T - \theta)/N_{av}\mu_{eff}^2\beta^2$, where $\mu_{eff}^2 = g_s^2S(S + 1) \simeq n(n + 2)$. The values obtained (Table IV) are, as expected, in good agreement with the theoretical ones $(\mu_{eff} = 1.73; n = 1)$ for completely disassociated radicals.

The nonnegligible, negative Weiss constants obtained for radicals 4-6 (Table IV) indicate that their molecules feel the antiferromagnetic molecular field created by their neighbors. This behavior had not been previously observed in other radicals of the PTM series.^{1,6,12} According to McConnell's theory on intermolecular magnetic interactions,¹³ the tendency toward antiparallel spin coupling in solid free radicals occurs when the product of the spin densities at the interacting sites on different molecules is positive, since the exchange integral between parallel organic







Figure 5. X-Band ESR spectra at room temperature for microcrystalline samples of (a) radical 4 (radicals 1, 5, and 6 present similar spectra); (b) radical 2 (radicals 3 and 7 show similar spectra).

radicals at distances of the van der Waals contacts is negative. For radical 6 the strongest interaction is the crossed one between para carbons and meta chlorines of two neighboring molecules (dashed atoms in Figure 3) (see X-Ray Crystallography). Since the product of their spin densities is always positive,¹⁴ and the distances are in the range of the van der Waals contact, the antiferromagnetism of this radical can be well explained by the crystal structure, in terms of McConnell's theory.

Electron Spin Resonance Spectra. (1) Theoretical Calculations. The semiempirical all-valence-electron INDO SCF-MO method developed by Pople and co-workers¹⁵ is known to be particularly useful in the calculation of isotropic nuclear hyperfine coupling constants of radicals formed by first-row atoms. Consequently, it seemed of interest to examine whether the INDO method is capable of predicting the spin-density distribution of polychlorinated triphenylmethyl radicals in a satisfactory manner. To this end the ¹H, ¹³C and ³⁵Cl isotropic hcc for radicals 1–6 were calculated from the corresponding valence s-orbital unpaired-electron populations computed from INDO spin-unrestricted Hartree-Fock (UHF)¹⁶ wave functions. The Benson-Hudson¹⁷ INDO parametrization, which includes chlorine, was employed. The calculations were performed with the experimental X-ray geometries, by using the computer code INDO-ESR.¹⁸

As it is well-known, the UHF wave functions are not an eigenfunction of the operator S^2 and do not represent a pure spin state. However, annihilation of contaminating quartet states produces a better approximation to the doublet-state wave function.¹⁹ A spin-annihilation routine was introduced in the program, but comparison of the calculated hcc values with those experimentally observed indicated that, in general, the preannihilation unpaired-electron populations give a more reasonable magnitude of the hcc values than the corresponding postannihilation unpaired-electron populations. The result agrees with previous findings of Beveridge and Dobosh for radicals containing first-row atoms.²⁰ Therefore, only the hcc calculated directly from unpaired-electron populations based on the UHF INDO wave functions without spin annihilation are here reported (Table V). Since the X-ray structures do not conform exactly with the expected molecular symmetry, the hcc values of Table V correspond to the average value of those calculated for all equivalent atoms.

(2) Solid-State Spectra. X-Band ESR spectra of powdered microcrystalline samples of radicals $1 \cdot C_6 H_6$ -7 were run at room temperature. While the spectra of radicals 2, 3, and 7 looked apparently to be symmetrical, "axial-type" spectra were obtained

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⁽¹⁴⁾ The INDO calculated total spin densities at the interacting atoms C11 and C112 are $+6.331 \times 10^{-2}$ and $+8.7 \times 10^{-4}$, respectively.

⁽¹⁵⁾ Pople, J. A.; Beveridge, D. L.; Dobosh, P. A. J. Chem. Phys. 1967, 47, 2016.

TABLE II: Fractional Atomic Coordinates (×10⁴) with Their Esd's and Equivalent Temperature Factor for Radicals 2-6

TADLE II:	riactional Atom	ic coordinates (A	NIO / WILL THEN	Lou 5 anu 1	Aquivalent 1 el	inperature ractor	TOT KAUKAIS 2-		
	X/A	<u>Y/B</u>	Z/C	BEQ		X/A	<u> </u>	Z/C	BEQ
				Radi	cal 2				
Cl3	6978 (7)	~2591 (4)	6988 (4)	6.70	C4	4381 (22)	-1978 (14)	6419 (13)	4.10
CI4	4470 (9)	-2/20(5)	5/// (5)	/.99	CS	3133 (27)	-1424 (16)	6443 (17)	7.04
	1397(8)	-158(6) -47(4)	6938 (S) 8204 (S)	8.80 6.93		2987(23) 4034(23)	-811(15) -763(14)	0939 (13) 7565 (15)	5.18
	7489 (8)	-36(4)	7051 (4)	6 38	C8	7109 (22)	-487(13)	8440 (13)	5 44
C110	9170 (7)	1599 (4)	7606 (4)	6.55	C9	7670 (19)	126(12)	7967 (11)	2.89
Cl11	9866 (10)	1842 (6)	9216 (6)	10.13	Č10	8482 (22)	868 (13)	8195 (11)	4.15
C112	8360 (9)	670 (5)	10276 (5)	7.53	C11	8759 (21)	976 (13)	8916 (11)	4.44
C113	6454 (8)	-909 (4)	9762 (4)	6.25	C12	8114 (22)	446 (12)	9416 (12)	4.67
Cl15	9770 (6)	-1718 (4)	8345 (4)	4.84	C13	7356 (24)	-293 (13)	9163 (13)	5.50
C116	10680 (7)	-3296 (5)	9312 (4)	6.12	C14	6836 (20)	-2101 (12)	8547 (13)	4.36
C117	8210 (9)	-4429 (5)	9953 (5)	8.64	C15	8371 (23)	-2342 (12)	8712 (13)	4.36
CI18	4847 (8)	-4109(5)	9508 (5)	7.24	C16	8772 (24)	-3058(14)	9117 (15)	5.10
Cl	5890 (0) 6423 (24)	-2474(3) -1310(12)	0040 (J) 9137 (15)	1.02	C18	6242 (23)	-3377(13)	9373(14) 9168(13)	4.00
C^2	5293 (21)	-1347(12)	7560 (12)	3.62	C19	5819(18)	-2702(11)	8775 (11)	3 20
C3	5428 (23)	-1946(13)	7019 (11)	3.66	H5	2236 (27)	-1482(16)	6035 (17)	5.53
	()	.,		Dad	anl 1		,		
Cl3	4587 (1)	1333 (1)	1073 (1)	4.14	C6	8521 (4)	1650 (3)	3516 (3)	3.87
Cl4	6255 (2)	2927 (1)	1216 (1)	7.11	C7	7818 (4)	914 (3)	3465 (3)	3.44
C16	10019 (1)	1818 (1)	4463 (1)	5.41	C8	6705 (4)	-823 (2)	2643 (3)	3.06
C17	8417 (1)	197 (1)	4395 (1)	5.46	C9	7514 (4)	-931 (3)	2106 (3)	3.63
C19	7665 (1)	-149 (1)	1355 (1)	4.96	C10	8133 (4)	-1694 (3)	2116 (4)	4.20
C110	9077 (2)	-1837 (1)	1426 (1)	6.56	C11	7998 (5)	-2358 (3)	2654 (4)	4.56
Cl12	7120 (2)	-3093 (1)	3922 (1)	5.97	C12	7239 (5)	-2254 (3)	3214 (3)	4.15
CIIS	2819(1)	-1382(1)	4018 (1)	4.44	C13	0013 (4) 4530 (4)	-1304(3)	3220(3)	3.32 2 QA
C115	4320(1) 1346(1)	-1165 (1)	743(1)	7.03	C14	3706 (4)	-566(3)	1550(3)	3 4 3
Cl18	1895 (1)	690 (1)	3456(1)	6.51	C16	2355 (4)	-620(3)	1337(3)	4.45
C119	4933 (1)	813 (1)	3984 (1)	4.42	C17	1799 (5)	-231(3)	1924 (4)	4.77
CI	5957 (4)	-47 (2)	2582 (3)	2.94	C18	2607 (5)	215 (3)	2723 (3)	4.27
C2	6595 (4)	773 (2)	2695 (3)	2.96	C19	3949 (4)	279 (3)	2946 (3)	3.44
C3	6088 (4)	1429 (3)	2024 (3)	3.23	H5	8628 (0)	2814 (0)	2849 (0)	6.32
C4	6822 (4)	2146 (3)	2079 (3)	4.29		8470 (0)	2949 (0)	2645 (0)	6.32
CJ	8055 (4)	2259 ()	2021 (4)	4.05	1117	752 (0)	280 (0)	1755 (0)	0.52
CIR	-2205 (1)	7471 (1)	1577 (1)	Radi	$\operatorname{cal} 4$	-2238 (4)	5735 (4)	603 (3)	3.15
C13 C14	-2393(1) -3601(1)	$\frac{7471}{6063}$ (1)	52 (1)	5.04	C5	-1726(4)	4806 (4)	368(3)	3.15
C15	-2423(1)	4004 (1)	-484(1)	4.97	Č6	-630(4)	4526 (4)	823 (3)	3.11
C16	16 (1)	3396 (1)	510 (1)	4.74	C7	-71 (3)	5176 (4)	1503 (3)	2.72
C17	1302 (1)	4852 (1)	2018 (1)	4.03	C8	0 (0)	8117 (5)	2500 (0)	2.70
C19	948 (1)	8072 (1)	1372 (1)	3.94	C9	381 (4)	8792 (4)	1991 (3)	3.24
CIII	0 (0)	12176 (2)	2500 (0)	11.19	C10	380 (5)	10034 (4)	1976 (3)	4.39
	-573 (3)	6/88 (5)	2500(0) 1761(3)	2.07		(0) (0) = 727 (22)	10520 (0)	2500 (0)	4.90
C2 C3	-1679(4)	6392 (4)	1282 (3)	3.04	1110	121 (22)	10557 (25)	1542 (10)	5.70
				Padi	cal 5				
Cl	0 (0)	683 (2)	2500 (0)	3.25	Cll	0 (0)	-3076 (2)	2500 (0)	4.24
C2	-182 (2)	1346 (2)	1729 (1)	3.37	C13	1515 (1)	5 (1)	1337 (0)	5.21
C3	455 (2)	1115 (2)	1151 (1)	3.70	C15	-551 (1)	3592 (1)	-554 (0)	7.28
C4	345 (2)	1778 (2)	450 (1)	4.38	C17	-1889 (1)	2641 (1)	2147 (0)	5.40
C5	-428 (2)	2721 (2)	309 (1)	4.63	Cl9	2070 (1)	-586(1)	3746 (0)	5.25
C6	-1100(2)	2985 (2)	838(1)	4.51		0(0)	-4602(1)	2500(0)	0./3
C/	-9/1(2)	2307(2)	2500 (0)	3.77	П0 Н4	798 (20)	1559 (20)	732 (14) 83 (14)	3.95
	879 (2)	-1273(2)	3057(1)	3.50	H10	1485(20)	-2845(20)	3448(14)	3.95
C10	888 (2)	-2492(2)	3062 (1)	4.03	1110	1,60 (20)	20 /0 (20)		0170
				Radi	cal 6				
C14	3934 (3)	-3174 (3)	-494 (2)	9.04	C4	4157 (6)	-3936 (8)	396 (5)	4.93
C15	3427 (2)	-5749 (3)	-563 (2)	8.00	C5	3940 (6)	-5080 (9)	346 (5)	4.89
C16	3906 (2)	-7114 (2)	1023 (2)	7.36	C6	4153 (6)	-5686 (7)	1067 (6)	4.65
C17	4851 (2)	-5913 (2)	2665 (1)	5.93	C7	4559 (5)	-5134 (7)	1797 (5)	3.78
Cl9	3066 (1)	-3552 (2)	2132 (1)	4.97	C8	4789 (5)	-3410(6)	3244 (5)	3.37
CI10	2450 (2)	-3030 (2) -3534 (2)	3524 (2) 5282 (2)	6.06 7 57	C10	3812 (3) 3583 (6)	-3300 (0) -3546 (7)	3733 (5)	5.71 4.16
CH12	5870 (2)	-3398 (3)	5651 (1)	7.08	C11	4197 (7)	-3503 (8)	4511 (5)	4.70
C113	6523 (2)	-3369 (2)	4274 (1)	5.77	C12	5098 (6)	-3436 (8)	4672 (5)	4.70
Cl15	4293 (2)	-995 (2)	2567 (2)	6.31	C13	5392 (5)	-3398 (7)	4040 (5)	3.85
Cl16	5419 (2)	1111 (2)	2583 (2)	7.50	C14	5675 (5)	-2297(7)	2575 (5)	3.40
CI17	7200 (2)	851 (2) 1582 (2)	2493 (2) 2468 (2)	1.71	C15	JJ04 (J) 5856 (K)	-1200 (7)	2380 (3) 2567 (6)	3.93 4.66
C110	6964 (2)	-3714(2)	2511 (2)	5.32	C17	6671 (6)	-342 (8)	2529 (6)	4.81
CI	5155 (6)	-3350 (7)	2592 (5)	4.39	C18	7016 (6)	-1432 (8)	2512 (5)	4.37
C2	4746 (5)	-3960 (7)	1826 (5)	3.39	C19	6517 (6)	-2370 (7)	2520 (5)	3.73
C3	4555 (6)	-3375 (8)	1113 (5)	4.24	H3	4638 (35)	-2375 (48)	1058 (32)	1.40

TABLE III: π Dihedral Angles (Degrees) between the Phenyl Groups (Ar) and the Reference Plane

	radical								
Ar	I⋅C ₆ H ₆	2	3	4	5	6			
 Ar (C2-C7)	46.3	50.6	48.3	49.6	48.1	37.7			
Ar (C8-C13) ^a	53.4	43.7	49.8	55.9	47.1	49.5			
Ar $(C14-C19)^{b}$	53.8	49.3	53.3	49.6	48.1	62.3			

^a For radicals 4 and 5, Ar corresponds to C atom numbering C8, C9, C10, C11, C9' and C10'. ^b For radicals 4 and 5, Ar corresponds to C atom numbering C2'-C7'.

TABLE IV: Magnetic Properties of Radicals 1.C6H6-7

radical	$\chi_d \times 10^6$, emu g ⁻¹	θ, Κ	μ_{eff} , Bohr magneton	spin number, <i>n</i>
1.C6H6	-0.532	-1.9	1.78	1.05
2 ^a	-0.517	-4.8	1.76	1.03
3	-0.525	+1.9	1.73	1.00
4	-0.521	-10.4	1.76	1.03
5	-0.541	-10.1	1.74	1.01
6	-0.517	-12.0	1.71	0.97
7	-0.521	-3.3	1.69	0.95
"Ref 6.				

for radicals $1 \cdot C_6 H_6$, 4, 5, and 6 (Figure 5). The g_{\parallel} , g_{\perp} , and average g values are presented in Table VI, the latter calculated either directly from the spectra (radicals 2, 3, and 7) or with the anisotropic values (radicals $1 \cdot C_6 H_6$, 4, 5, and 6). These solid-state g_{av} values are in good agreement with those obtained in isotropic solutions. For all of the axial-type spectra here reported, g_{\parallel} has higher values than g_{\perp} .²¹ The spectra were also run at higher gains in order to detect ¹³C hyperfine splittings, but these were not observed in any case. Two types of mechanisms, electron spinelectron spin and electron spin-nuclear spin dipolar interactions, contribute to line broadening and could therefore be responsible for no observation of the ¹³C satellites. Between these mechanisms, electron spin-electron spin interactions do not seem to be the more important contribution, since the satellites are still not observed, even at high gains, for very diluted solid solutions of the radicals in 1,2,3,4-tetrachlorobenzene. Hence, no ESR confirmation of the slight sp^3 hybridization attributed to radical 6 in the solid state (see above) can be achieved.

(3) Isotropic Spectra. X-Band ESR spectra were run at different temperatures (from 163 to 298 K) in CFCl₃. The data for radicals 1-9 are shown in Table VI. The g value for radical PTM (1) is very close to that of unsubstituted triphenylmethyl radical (g = 2.0027).²² Significant g shifts from this value are observed for radicals 3 (negative) and 5 (positive); these shifts can be explained by considering negative contributions for meta chlorines and positive for para chlorines, as had already been observed for p-chloro- and m-chlorotriphenylmethyl radicals (g = 2.0030 and 2.0025, respectively).²³

The spectra of radicals 1-9 show the lines corresponding to couplings with hydrogen atoms and pairs of ¹³C satellites (α and aromatic), while chlorine splittings are not observed. The three para hydrogens of radical 3 have identical hcc values, which coincide with that observed for the proton of radical 2 (¹H_{para} hcc $\simeq 1.96$ G), both being independent of temperature in the interval 163-298 K. Furthermore, the α and aromatic ¹³C hcc values of both radicals 2 and 3 have the same value as PTM (1) (Table VI) and are also temperature independent. All these results indicate that, in solution, radicals 1-3 have conformations with similar ring spin densities and that these conformations are locked, having energy requirements for interconversion (through a two-ring

flip mechanism)⁷ much too high to be observed on the ESR time scale, even at 298 K. The same conclusion can be drawn for the pair of radicals 4 and 5 with meta hydrogens (${}^{1}H_{meta}$ hcc = 1.24 G). These high-energy barriers agree with specific studies on closely related propeller-type molecules, which already predicted high conformational stabilities for strained Ar₃Z compounds, whose geometries are governed almost exclusively by their bulky substituents in ortho positions, and confirm as minor the buttressing effects of meta chlorines and the electronic effects of chlorine polysubstitution.⁷ When the proton hcc values of radicals 2 or 3 and 4 or 5 are compared with those of the corresponding protons in unsubstituted triphenylmethyl (${}^{1}H_{para}$ hcc = 2.85; ${}^{1}H_{meta}$ hcc = 1.14 G)²² it is observed that while those of radicals with para hydrogens are fairly lower, those of radicals with meta hydrogens are similar, as could be expected from the increased twisting of the phenyl rings, giving rise to a much more important decrease of the hcc values for the para hydrogen (through spinpolarization mechanism) than for the meta hydrogens (phenyl hyperconjugation vs. spin-polarization mechanisms).^{18,24}

The ortho ¹H hcc of radical 6 (Table VI) is constant up to 203 K but decreases above this temperature. In radical 7 the two ortho hydrogens are magnetically nonequivalent in the whole temperature range studied but show a tendency to converge on increasing temperature. These results suggest that (a) the conformations of both radicals are not locked on the ESR time scale, as could be inferred from its lower steric hindrance (only five or four ortho chlorines for radical 6 or 7, respectively) and (b) the preferred conformation of radical 7 in solution has two C₆HCl₄- rings with different π dihedral angles. In radical 8 (Table VI) no nonequivalence of its three ortho hydrogens is observed at room temperature, as expected from its even lower steric hindrance of only three ortho chlorines. However, the experimental conditions are quite different and further work on this subject must be undertaken.

The α ¹³C hcc of radicals **6–8** with at least one ortho hydrogen are slightly lower than those of radicals **1–5**, which is in qualitative agreement with the preferred conformations of the former radicals with lower π dihedral angles. In radicals **1–5** the values of the observed and calculated ¹³C hcc for the α and aromatic carbons are, within the experimental errors and inherent approximations of the INDO method, in excellent and good agreement, respectively (Tables V and VI).²⁵ Therefore, it is concluded that the INDO method is reliable in predicting spin-density distributions in this type of radicals. The deviation observed in radical **6** is a result of its slight pyramidal geometry (in the solid state) on which the calculations are based, while the observed values are those of isotropic solution, where a change of geometry can take place.

A point worth noticing is that the calculated spin-density distribution for radicals 1-6 supports the first tentative assignation of the aromatic ¹³C splittings done by Falle et al.²⁶ Our calculations show that the smaller ¹³C couplings observed in the ESR spectra of these radicals correspond to ortho and bridgehead carbon atoms rather than to ortho and para carbons. This assignation is at variance with an earlier interpretation²⁷ and, furthermore, confirms the hyperconjugative mechanism suggested by Falle to explain the large ortho ¹³C splittings as compared with the para ¹³C ones. Thus, the larger 2s orbital unpaired-electron populations on the ortho carbon atoms is caused by direct overlap of this atomic orbital with the $2p_z$ orbital of the α carbon. The small differences between the observed and calculated aromatic ¹³C hcc values could arise from the ambiguous assignation given to bridgehead and ortho carbon atoms, based on the relative proportion of these atoms in the molecule and the amplitude of

⁽²¹⁾ Organic radicals usually have higher g_{\perp} than g_{\parallel} values, and as far as the authors know, only tris(4-bromotetrafluorophenyl)methyl radical has these values reversed, as reported by Gerasimova, T. M.; Barkhash, V. A.; Vorozhtsov, M. M. J. Gen. Chem. USSR (Engl. Transl.) **1968**, 38, 510.

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⁽²⁵⁾ The calculated values of the ¹H hcc are not reliable because of the larger esd's of their positions (Table II) as compared to those of other nuclei with higher electron densities (C and Cl).

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TABLE V: INDU Calculated hcc values (Gauss) for Kadicals
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								bridgehead-			
radical	ortho- ¹ H	meta-1H	$para^{-1}H$	ortho- ³⁵ Cl	meta-35Cl	para- ³⁵ Cl	α- ¹³ C	¹³ C	ortho-13C	meta-13C	para-13C
1				-0.55 (3) -0.55 (7) -0.46 (9) -0.46 (13) -0.55 (15) -0.41 (19)	+0.64 (4) +0.53 (6) +0.52 (10) +0.44 (12) +0.56 (16) +0.65 (18)	-0.17 (5) -0.12 (11) -0.12 (17)	+30.72 (1)	-12.35 (2) -10.24 (8) -10.88 (14)	+12.52 (3) +13.47 (7) +10.94 (9) +10.47 (13) +10.89 (15) +12.05 (19)	-4.38 (4) -4.32 (6) -2.30 (10) -2.51 (12) -2.61 (16) -2.39 (18)	+5.37 (5) +2.81 (11) +3.15 (17)
2			-2.03 (5)	-0.50 (3) -0.74 (7) -0.40 (9) -0.37 (13) -0.64 (15) -0.46 (19)	+0.57 (4) +0.55 (6) +0.74 (10) +0.45 (12) +0.48 (16) +0.33 (18)	-0.09 (11) -0.14 (17)	+33.98 (1)	-10.86 (2) -11.04 (8) -11.12 (14)	+14.94 (3) +10.52 (7) +11.51 (9) +11.06 (13) +8.27 (15) +11.99 (19)	-3.65 (4) -4.22 (6) -2.79 (10) -2.94 (12) -3.75 (16) -3.69 (18)	+4.02 (5) +3.38 (11) +5.63 (17)
3			-1.94 (5) -1.83 (11) -1.46 (17)	-0.49 (3) -0.59 (7) -0.45 (9) -0.49 (13) -0.46 (15) -0.50 (19)	+0.53 (4) +0.60 (6) +0.61 (10) +0.61 (12) +0.62 (16) +0.57 (18)		+31.18 (1)	-10.95 (2) -11.15 (8) -10.30 (14)	+11.36 (3) +10.84 (7) +11.76 (9) +10.79 (13) +10.78 (15) +10.92 (19)	-3.25 (4) -3.35 (6) -3.00 (10) -3.21 (12) -2.40 (16) -2.41 (18)	+3.76 (5) +3.58 (11) +2.87 (17)
4		+2.33 (10)		-0.47 (3) -0.50 (7) -0.52 (9)	+0.65 (4) +0.54 (6)	-0.11 (5) -0.16 (11)	+30.77 (1)	-11.44 (2) -10.47 (8)	+12.04 (3) +11.53 (7) +11.16 (9)	-3.27 (4) -3.42 (6) -2.11 (10)	+4.26 (5) +2.59 (11)
5		+1.90 (4) +1.74 (6) +1.98 (10)		-0.50 (3) -0.47 (7) -0.51 (9)		-0.18 (5) -0.25 (11)	+29.29 (1)	-10.77 (2) -11.29 (8)	+11.46 (3) +10.46 (7) +11.68 (9)	-2.70 (4) -2.56 (6) -3.01 (10)	+3.67 (5) +4.20 (11)
6	-4.59 (3)			-0.51 (7) -0.36 (9) -0.49 (13) -0.41 (15) -0.53 (19)	+0.78 (4) +0.30 (6) +0.48 (10) +0.32 (12) +0.59 (16) +0.38 (18)	-0.12 (5) -0.11 (11) -0.08 (17)	+51.18 (1)	-10.10 (2) -9.38 (8) -8.46 (14)	+9.72 (3) +9.77 (7) +9.74 (9) +9.19 (13) +10.60 (15) +8.95 (19)	-4.16 (4) -4.71 (6) -2.28 (10) -2.74 (12) -1.04 (16) -1.55 (18)	+5.58 (5) +2.94 (11) +1.71 (17)

"The atom numberings (in parentheses) correspond to those of Figure 1.

TABLE VI: ESR Data of Radicals 1-9

						isotropic solu	tion spectr	a ^b	
	solid-state spectra ^a			no. of	$\Delta H_{\rm M}$ line	hcc values, G ^c			
radical	g⊥	81	gav	g_{iso}	lines	width, G	ΊΗ	α - ¹³ C ^d	aromatic ¹³ C
1	2.0014	2.0048	2.0026 ^e	2.0028	1	0.628		30.0	13.1, 10.75
2			2.0026	2.0025	2	0.624	1.93	30.0	13.1, 10.6
3			2.0025	2.0021	4	0.355	1.95	30.5	13.0, 10.6
4	2.0015	2.0048	2.0027 ^e	2.0029	3	0.700	1.24	30.0	12.9, 10.4
5	2.0023	2.0051	2.0032e	2.0034	7	0.689	1.24	30.0	12.9, 10.5
6	2.0019	2.0042	2.0027°	2.0028	2	0.803	2.99	28.5	12.8, 10.4
7			2.0030	2.0029	3	1.090	2.21 2.96	27.3 ^f	12.5, 10.5
88				2.0027	4	0.987	2.22	27.6	12.1, 8.3
9s				2.0020	9	0.824	1.40 3.80 4.20		

^aAt room temperature. ^bIn CFCl₃ at 163 K unless otherwise indicated. ^cComputer simulated. ^dAt 203 K. ^eCalculated from $g_{av} = (g_{\perp} + 2g/_{\parallel})/3$. ^fAt 253 K. ^gIn THF, at room temperature (see Experimental Section).

the overlapped lines.¹ This ambiguity can only be resolved by determining the sign of the hcc values; further experiments will be undertaken.

It must be noticed that the observed ESR line widths of the radicals 1-7 do not show any correlation with the number of chlorine atoms and that the spectra cannot be simulated with the INDO-calculated Cl hcc values.²⁸ A sharpening of the lines is observed on decreasing the temperature (T) and/or increasing the viscosity of the solvent (η) (Figure 6). This temperature dependence can hardly be attributed to the electron spin-electron

spin exchange (decrease of the radical-radical collisions on lowering the temperature), since line widths do not vary significantly with concentration (from 10^{-4} to 10^{-7} M); it must be assigned therefore to other mechanism(s). Sinclair and Kivelson²³ have pointed out that the most important process for the relaxation of nuclear spin states of halogen atoms can be governed by the interaction between their quadrupole nuclear moments and local electric fields on Brownian motion of the molecules, where the relaxation time (T_N) is then related to the molecular tumbling correlation time (τ_C) by the equation³⁰ $1/T_N = k\tau_C$, where $\tau_C =$ $4\pi\eta r^3/3kT$ (r = molecular radius).

Because of the large effective molecular radii of the radicals here studied, a large molecular tumbling correlation time is expected, and therefore when temperature is low and viscosity is high, the relaxation time of the chlorine nuclear spin states (T_N) can become much smaller than the Cl hcc (a_{Cl}) , i.e., $a_{Cl}T_N \ll 1$. In these cases the line widths are approximately $a_{Cl}^2T_N$ and are proportional to T/η as is indeed observed for radicals 1-7 at low T/η values, where this form of relaxation would be dominant. The

⁽²⁸⁾ Simulations were carried out by using the minimum line widths for the chlorine lines that gave unresolved spectra. In all cases the simulated line widths were over 5 times the experimental values.

⁽²⁹⁾ Viscosities of CFCl₃ down to 213 K were taken from Gallant, R. W. *Hydrocarbon Process.* **1968**, 47, 135. Viscosities below 213 K were extrapolated by using the Arrhenius correlation, $\eta = Ae^{B/T}$, where $A = 1.64661 \times 10^{-2}$ and B = 946.69. Viscosities of decalin and ethylbenzene were taken from Riddick, J. A.; Bunger, W. B., Eds. *Organic Solvents*; Wiley: New York, **1970**; p 30.

TABLE VII: Electronic Absorption Maxima and Extinction Coefficients of Radicals 1-8 and Their Corresponding Anions

	band A		band B		ba	nd C	band D		carbanions ^c	
no.	λ, nm	$\epsilon \times 10^{-3}$	λ , nm	$\epsilon \times 10^{-3}$	λ, nm	$\epsilon \times 10^{-3}$	λ, nm	$\epsilon \times 10^{-3}$	λ, nm	$\epsilon \times 10^{-3}$
1	220	73	283 (287)	5.5	382 (392)	37	510, 562 (511, 567)	1.1, 1.2		
2	220	83	280 (280 sh)	6.2	381 (384)	31	503, 556 (505 sh, 557)	1.1, 0.9	510	30
3	217	79	285 (285 sh)	5.1	372 (376)	30	487, 545 (475 sh, 547)	0.9, 0.7	504	34
4	218	87	270 (sh) (274 sh)	6.2	380 (387)	41	502, 552 (500 sh, 552)	1.0, 1.0	516	30
5	220	76	259 (263)	7.7	368 (371)	41	492, 537 (496, 545)	0.7, 0.8	500	36
6	218	97	278 (sh) (280)	4.8	375 (383)	32	475, 520, 560 (525 sh, 560)	0.6, 0.6, 0.8	494	28
7 8	215	100	270 (sh)	6.8	368	41	520, 554	0.5, 0.6	491 496	29 unstable

^a Values in parentheses are those collected in solid solution (KBr pellets). ^b In C_6H_{12} . ^c In THF.



Figure 6. Temperature/viscosity $(T/\eta \text{ in } K \text{ cP}^{-1})$ dependence of peakto-peak line widths $(\Delta H_{pp} \text{ in } G)$ for radical 1 in decalin (O), ethylbenzene (+), and CFCl₃ (*).²⁹

electron would then see only an average of the nuclear spin states, and therefore no chlorine hyperfine splittings must be observed. In brief, at least at low temperatures, the experimental line widths do not seem to be a consequence of the unresolved chlorine splittings, as had been previously attributed,^{1,26} but of nuclear quadrupole relaxation.

While the behavior of the aromatic ${}^{13}C$ satellite lines vs. the temperature is the same as the main line (i.e., they sharpen on decreasing T and increasing η), that of the ${}^{13}C$ satellites is just the opposite (i.e., on decreasing T and increasing η , a remarkable line broadening is observed). This is slightly more effective for the low-field line and gives rise to extremely broad, or even unobservable, lines at temperatures below 203 K. It is well-known that for slow molecular tumbling rates^{30,31} the most important contributions to the line widths are $\Delta H_{pp} = A + BM_I + CM_I^2$, where M_I is the total nuclear spin quantum number. The first term, A, includes the effects already discussed for the main lines, corresponding to species with ${}^{12}C$ in the α -position. The other terms contribute only to the lines corresponding to species with nonzero nuclear moments (i.e., ${}^{13}C$) and are caused by a modulation of the dipolar hyperfine interaction through molecular tumbling. The second term is responsible of the slight asymmetry

observed in the α ¹³C satellites. The facts that the low-field line has a slightly larger line width than the high-field one and that $g_{\parallel} > g_{\perp}$ (see solid-state ESR spectra) indicate that the α ¹³C hcc are positive,³¹ in agreement with the theoretical calculations (Table VI). The partial overlap of the aromatic ¹³C lines (bridgehead and ortho) and the main line makes difficult the observation of the selective broadening of these satellites. The coefficient *C* of the third term is proportional to the square of the π spin density on the interacting atom. Taking into account the spin-density distribution of these highly twisted radicals, this term is the largest contribution in α ¹³C line broadening, while it is of minor importance in the aromatic ¹³C satellites, as is indeed observed.

UV-Vis Spectra. Radicals 3–7 display the four bands of the chlorinated triphenylmethyl radicals previously reported;^{1,6} data are shown in Table VII. A bathochromic shift can be observed for band D in direct correlation with chlorine ring substitution. Precision spectral measurements on the radicals in dilute solutions ($\simeq 10^{-4}$ M), in air, and at room temperature for 1 week have failed to detect any alteration. In order to detect electronic changes in the radicals from solid state to solution, their visible spectra were obtained in KBr pellets (Table VII). No significant modifications of either the general shape or the position of the maxima were observed.

The visible spectra of the corresponding carbanions (generated quantitatively from the suitable polychlorotriphenylmethanes with tetrabutylammonium hydroxide in THF) present a single broad band centered a round 505 nm (Table VII). The presence of Me₂SO in the THF solutions has no effect either on the location of the absorption maxima or on the extinction coefficients of any of the studied carbanions, indicating that in THF these exist predominantly as separate ion pairs or as free ions. Therefore, the tetrabutylammonium counterion has no influence on the position of the absorption maxima, as has already been described for perchlorotriphenyl methide.^{2a} No correlation between the chlorine ring substitution and the position of absorption band has been observed, in contrast with the above-mentioned effect in the radicals. All the carbanions reported in Table VII are completely stable in solution in air, with the exception of that corresponding to radical 8, which decomposes rapidly.

Experimental Section

General Methods. The IR, UV-vis, ¹H NMR, and ESR spectra were recorded with Perkin-Elmer 457, Beckman Acta M VI, Bruker WP 80 SY, and Varian E109E spectrometers, respectively. The magnetic susceptibilities were measured in helium with a Varian 4-in. magnet with constant-force caps, and a Cahn RG electrobalance. The X-ray measurements were performed with the data-collection instrument ENRAF NONIUS CAD4-F with radiation Mo K_{α} ($\lambda = 0.71073$ Å) (monochromated in the incident beam). The INDO calculations were obtained with a DEC VAX-11/750 computer. The ESR simulations were carried out by using a modified version of the software pack of the Varian

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TABLE VIII: Experimental Data for X-ray Diffraction Study of Radicals 2-6

radical	2	3	4	5	6
formula	C ₁₉ HCl ₁₄	$C_{19}H_{3}Cl_{12}$	$C_{19}H_2Cl_{13}$	C ₁₉ H ₆ Cl ₉	C ₁₉ HCl ₁₄
molecular weight	725.3	656.4	690.9	553.1	725.3
space group	$P2_1/c$	$P2_1/a$	C2/c	C2/c	$P2_1/a$
systematic absences	(h0l): l = 2n + 1	(h0l): h = 2n + 1	(hkl): h + k = 2n + 1	(hkl): h + k = 2n + 1	(h0l): h = 2n + 1
	(0k0): k = 2n + 1	(0k0): k = 2n + 1	(h01): l = 2n + 1	(h0l): l = 2n + 1	(0k0): k = 2n + 1
a, Å	8.918 (4)	10.979 (1)	12.967 (2)	11.698 (2)	16.153 (3)
b, Å	15.253 (5)	15.993 (3)	11.128 (2)	11.360 (3)	11.716 (2)
<i>c</i> , Å	18.951 (8)	14.813 (2)	17.947 (4)	16.879 (2)	18.071 (4)
α , deg	90.0	90.0	90.0	90.0	90.0
β , deg	93.58 (4)	112.23 (1)	111.00 (1)	105.95 (1)	112.94 (2)
γ , deg	90.0	90.0	90.0	90.0	90.0
V, Å ³	2572.8 (6)	2407.7 (5)	2417.7 (5)	2156.6 (4)	3149.3 (6)
Ζ	4	4	4	4	4
F(000)	1.412	1.284	1.348	1.092	1.812
δ calcd, g/cm ³	1.87	1.81	1.90	1.70	1.53
crystal size, mm	$0.15 \times 0.20 \times 0.25$	$0.19 \times 0.32 \times 0.28$	$0.22 \times 0.20 \times 0.35$	$0.18 \times 0.18 \times 0.30$	$0.36 \times 0.23 \times 0.32$
μ (Mo K _{α}), cm ⁻¹	15.2	14.0	15.1	11.8	12.4
orientn reflns, no.; range (2θ)	25; 7–17°	25; 6-16°	25; 10–21°	25; 6–21°	25; 6-12°
scan method	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$
data collectn range, 2θ , deg	2-50.0	2-50.0	2-50.0	2-50.0	2-50.0
reflections measured $(h:k:l)$	10-10; 15-15; 0-19	13–13; 0–19; 0–17	15-15; 0-13; 0.21	13-13; 0-13; 0-20	0-19; 0-13; 21-21
no. of unique data, total	1.720	3.048	1.367	1.679	2.431
with $I > n_{\sigma}(I)$	n = 3.0	n = 2.5	n = 2.5	n = 2.0	n = 2.5
no. of parameters refined	303	281	151	138	302
R^a	0.120	0.036	0.044	0.031	0.051
$R^{\mathfrak{b}}\omega$	0.123	0.042	0.045	0.036	0.054
$\omega = 1/(\sigma^2(F) + mF^2)$	m = 0.001777	m = 0.000402	m = 0.000693	m = 0.001776	m = 0.000590
largest shift/esd, final cycle	0.28	0.17	0.21	0.18	0.32
largest peak, e Å ⁻³	0.72	0.24	0.30	0.20	0.40
-					

E-935 Data Acquisition System.

The handling of radicals in solution was performed in the dark. For the registration of the ESR spectra, very diluted ($\simeq 10^{-5}$ M) solutions of the radicals in the ESR tube were carefully degassed by the freeze-pump-thaw technique.

Preparation of Triarylmethanes. Bis(pentachlorophenyl)-(2,3,5,6-tetrachlorophenyl)methane, tris(2,3,5,6-tetrachlorophenyl)methane, bis(pentachlorophenyl)(2,4,6-trichlorophenyl)methane, tris(2,4,6-trichlorophenyl)methane, bis(pentachlorophenyl)(2,3,4,5-tetrachlorophenyl)methane, and phenylbis(pentachlorophenyl)methane were prepared according to the method already described elsewhere.⁴ The nonpreviously reported methanes 10-12 were prepared by the same method and are described in the supplementary material.

Isolation of Triarylmethyl Radicals. General Procedure. A slight excess of tetrabutylammonium hydroxide (40% in water)(0.65 mmol) was added, under argon and in the dark, to a solution of the corresponding polychlorotriarylmethane (0.5 mmol) in purified THF, and the resulting mixture was stirred at room temperature (4 h). Then, chloranil (0.7 mmol) was added and the stirring was continued (30 min). Elimination of the solvent gave a residue which was passed through silica gel (CCl_4) to give bis(pentachlorophenyl)(2,3,5,6-tetrachlorophenyl)methyl (2)tris(2,3,5,6-tetrachlorophenyl)methyl (3), bis(pentachlorophenyl)(2,4,6-trichlorophenyl)methyl (4), tris(2,4,6-trichlorophenyl)methyl (5), bis(pentachlorophenyl)(2,3,4,5-tetrachlorophenyl)methyl (6), and (pentachlorophenyl)bis(2,3,4,5-tetrachlorophenyl)methyl (7) radicals. Yields and physical properties of these radicals are given as supplementary material.

Detection of Nonisolable Radicals. The nonisolable radicals were generated from the parent methanes in ESR tubes with degassed THF solution by means of tetrabutylammonium hydroxide and oxidation of the resulting carbanion with iodine. Stable (ESR) red solutions of tris(2,3,4,5-tetrachlorophenyl)methyl (8) and (phenyl)bis(pentachlorophenyl)methyl (9) radicals were obtained, which rapidly decayed when air was introduced in the sample tube.

X-ray Crystallography. Suitable red crystals of radicals 2-6 were glued at the end of glass fibers to be mounted on the diffractometer. Crystal data and a summary of data collection are given in Table VIII. Data were gathered by diffractometer routine procedures and data reduction was performed by using a local version of the CRYSTAN³² system. The structure amplitudes were obtained after usual Lorentz and polarization reductions.

Structures of radicals 3, 5, and 6 were solved by straightforward application of MULTAN 11/84³³ and completed by means of weighted F_0 Fourier Syntheses. Structure of radicals 2 and 4 were determined by an automated Patterson Search procedure ROT-SEARCH³⁴ with the structure of radical 1 as the input search model.

The refinement of these five structures was carried out by using a full-matrix least-squares procedure SHELX-7635 and, in first step, with unit weights and anisotropic thermal parameters for non-H atoms and by minimizing the $\sum \omega \Delta^2 / \sum \omega F_0^2$ function. The H atoms were introduced in calculated positions and refined with global isotropic temperature factors. Adequate symmetry constraints on parameters were considered in molecules with crystallographic binary axes. The scattering factors were taken from ref 36. The Xanadu program³⁷ is employed for geometrical calculations and the Pluto program³⁸ for drawings.

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Supplementary Material Available: Lists of bond lengths, bond

angles, and final anisotropic thermal parameters of radicals 2-6; stereoscopic views of molecular packing of radical 6; perspective views of radicals $1 \cdot C_6 H_6$, 2, 4, 5 and 6 with numbering schemes; and complete synthetic procedures and physical properties of precursors and radicals not given in the main text (20 pages). Ordering information is given on any current masthead page.

Theoretical Studies of Transition-Metal Hydrides. 2. CaH⁺ through ZnH^{+†}

J. Bruce Schilling, William A. Goddard III,* and J. L. Beauchamp

Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125 (Received: May 21, 1987)

We present consistent ab initio calculations (generalized valence bond plus configuration interaction) of the spectroscopic parameters for the ground and low-lying electronic states of the diatomic transition-metal hydrides CaH⁺ through ZnH⁺. We examine, in detail, the competing factors affecting metal hydride bonding: (1) the relative energies of the metal low-lying electronic states; (2) the intrinsic bond strength of H to various size 4s, 3d, or hybridized metal orbitals; and (3) the loss of high-spin metal exchange energy on bonding.

Introduction

In the past few years, an ever increasing number of experiments have been carried out to determine the bond dissociation energies of the first-row transition-metal hydride cations. The various techniques include high-pressure proton transfer,¹ ion cyclotron resonance,² and ion beam mass spectrometry.³ Recent investigations by Elkind and Armentrout⁴ using "guided" ion beam methods have produced the most accurate, consistent, and complete set of M⁺-H bond energies. However, in some cases there remain significant inconsistencies.

Additional experiments have been carried out to study the gas-phase activation, at transition-metal centers (using atomic metal ions), of alkanes, alkenes, and cycloalkanes.⁵ Most of the proposed mechanisms for the observed reactions involve insertion of the metal ion into either C-C or C-H bonds of the neutral species. The reaction intermediates and sometimes the products thus involve metal systems with metal-ligand σ bonds. Studies have also been carried out on the reactions of the metal hydride ions for the first-row metals of groups 8-10.6

In order to help understand the reactions of the metal hydrides and of the bare metal ions, we have carried out theoretical studies of the metal hydride bonding in the case of CaH^+ through ZnH^+ , with the emphasis on bond dissociation energies and spectroscopic properties.

The ground states, geometries, vibrational frequencies, and bond dissociation energies have been summarized previously.⁷ In this paper, we will examine the competing factors affecting metal hydride bonding in some detail. A detailed description of the calculational methods (including how the level of electronic correlation in the wave function affects the calculated bond dissociation energies) is also presented. Some low-lying electronic states of the metal hydride ions are also described.

Results and Discussion

Calculated total energies for MH^+ (at R_e), M^+ , and H are presented in Table I and the resultant MH⁺ bond dissociation energies in Table II. Table III summarizes the configurations, bond lengths, vibrational frequencies, and excitation energies for various ground- and excited-state species. A major point of this paper will be to explain the dramatic variations of the bond energies and excitation energies in terms of the atomic states and bond character.

Low-Lying Electronic States. The simplest way to understand the bonding in the first-row metal hydride cations MH⁺ is to start

TABLE I: Total Energies for Ground-State MH⁺ (R_e), M⁺, and H

		total energy, ^a hartrees					
species	state	GVB-PP	DCCI-GEOM	DCCI			
CaH+	$1\Sigma^+$	-676.35376	-676.367 60	-676.367 60			
Ca+	^{2}S	-675.79379	-675.793 79	-675.79379			
ScH ⁺	$^{2}\Delta^{\pm}$	-759.23792	-759.24271	-759.254 53			
Sc ⁺	³ D	-758.66317	-758.66317	-758.66365			
TiH ⁺	${}^{3}\Phi^{\pm}$	-847.80648	-847.823 24	-847.82788			
Ti ⁺	4F	-847.238 03	-847.238 09	-847.23867			
VH ⁺	$^{4}\Delta^{\pm}$	-942.158 93	-942.177 86	-942.18614			
V+	⁵ D	-941.60584	-941.60584	-941.613 38			
CrH ⁺	${}^{5}\Sigma^{+}$	-1042.48981	-1042.51595	-1042.527 62			
Cr ⁺	۴S	-1041.97641	-1041.976 41	-1041.985 50			
MnH ⁺	${}^{6}\Sigma^{+}$	-1148.906 83	-1148.927 28	-1148.93267			
Mn ⁺	^{7}S	-1148.366 28	-1148.366 28	-1148.36685			
FeH ⁺	${}^{5}\Delta^{\pm}$	-1261.372 04	-1261.39378	-1261.404 62			
Fe ⁺	۴D	-1260.823 09	-1260.82415	-1260.82664			
CoH ⁺	${}^{4}\Phi^{\pm}$	-1380.21703	-1380.240 28	-1380.256 58			
Co ^{+b}	۶F	-1379.66373	-1379.665 59	-1379.66836			
NiH ⁺	$^{3}\Delta^{\pm}$	-1505.54170	-1505.56404	-1505.59710			
Ni ^{+b}	⁴F	-1504.98306	-1504.98413	-1504.99697			
CuH+	$^{2}\Sigma^{+}$	-1637.491 55	-1637.51731	-1637.58045			
Cu ^{+b}	³ D	-1636.923 28	-1636.924 27	-1636.940 55			
ZnH ⁺	${}^{1}\Sigma^{+}$	-1776.12985	-1776.143 22	-1776.14797			
Zn+	^{2}S	-1775.556 52	-1775.55678	-1775.56091			
Н	^{2}S	-0.499 28	-0.499 28	-0.499 28			

^a For MH⁺ the total energies are for the calculation levels shown while the M⁺ and H total energies are for the calculation levels to which these MH⁺ molecules dissociate (see Calculational Details). ^b For these metals, MH⁺ dissociates to an excited state of M⁺ as shown.

with the $4s^{1}3d^{n-1}$ configuration of M⁺ and to spin pair the 4s orbital of M^+ with the 1s orbital of H. The n-1 electrons in d orbitals

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